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Hydrodesulfurization of Thiophenic Compounds: The Reaction Mechanism

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It has often been assumed that catalytic hydrodesulfurization of thiophene and related compounds proceeds via a one-point "end-on" adsorption involving bonding of the sulfur atom with Mo ions at an anion vacancy on the catalyst surface. This interpretation is inadequate, failing to account for hydrogen–deuterium exchange results, the reactivities of benzothiophene and dibenzothiophene, and the small steric effects of methyl substituents on the adsorption and reaction of compounds in the thiophene, benzothiophene, and dibenzothiophene families of homologs. An alternative mechanism, presented here, involves a multipoint adsorption of the reactant, with a C═C bond interacting with a Mo cation, and the S atom of the reactant interacting with a S ion on the surface. The new mechanism accounts for the observed deuterium exchange and hydrodesulfurization reactions and is consistent with the observed steric effects.

INTRODUCTION

Catalytic hydrodesulfurization is a subject of intensive research, most of it centered on the physical characterization of the industrially applied sulfide catalysts. Our objective is to evaluate the literature of hydrodesulfurization of thiophenic compounds, focusing on the neglected subject of the nature of the organic surface intermediates and mechanisms of the catalytic reactions. The following paragraphs include a review of the commonly assumed "one-point" model of the adsorption of thiophenic compounds and a proposed alternative, a "multipoint" adsorption, which more successfully accounts for the available data.

The most widely discussed mechanism proposed for the hydrodesulfurization of thiophenic compounds (Fig. 1) has been deduced from studies of the reaction of thiophene itself catalyzed by sulfidic Co–Mo/Al_2O_3 and related solids (*1–8*). An initial step is assumed to be an end-on adsorption, whereby only the sulfur atom of the reactant experiences chemical interactions with the catalytic sites, assumed to be anion vacancies at the surface. Since the remainder of the thiophenic ring is assumed to stand upright from the sulfur bonded to the surface, the mechanism has been referred to as the "one-point" mechanism (*8*).

This interpretation was derived largely from catalytic kinetics and product distribution data of Amberg and co-workers (*6, 7*), who detected butadiene among the products of thiophene hydrodesulfurization at low pressures (<1 atm). Desikan and Amberg (*7*) interpreted the formation of butadiene as an indication that hydrogenation of the thiophene ring need not precede hydrogenolysis of the sulfur–carbon bond. Kieran and Kemball (*9*), however, observed butadiene as a product of the reaction of hydrogen with tetrahydrothiophene catalyzed by MoS_2, indicating that hydrogenation could precede C–S bond breaking in hydrodesulfurization. Kolboe (*10*) observed that the amount of butadiene formed in hydrodesulfurization of tetrahydrothiophene exceeded that arising from hydrodesulfurization of thiophene and sug-

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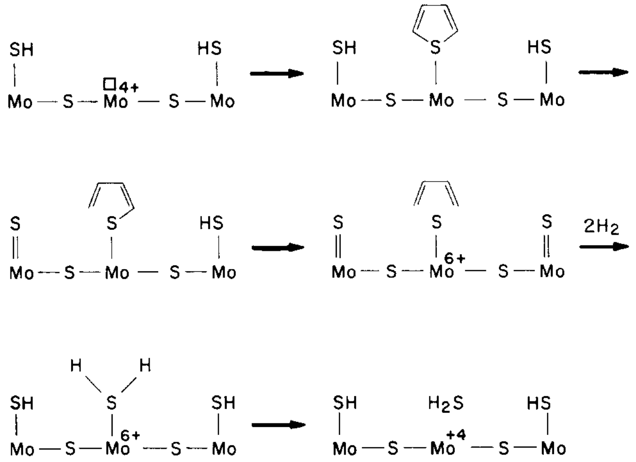


FIG. 1. The suggested one-point mechanism of thiophene hydrodesulfurization on sulfided Co–Mo/Al_2O_3 and related catalysts.

gested that the reaction of thiophene did not occur by a hydrodesulfurization, but instead by a dehydrosulfurization route, whereby H_2S was removed by β-elimination (illustrated in Fig. 2) to produce an initial diacetylene product. Infrared evidence has been presented purporting to indicate an acetylenic intermediate (*11*). Deuterium tracer experiments by Mikovsky *et al.* (*12*) have also provided support for the Kolboe mechanism.

A reinterpretation by Cowley (*13*) of the earlier results suggests that the Kolboe one-point mechanism may not be the only one occurring in hydrodesulfurization. Moreover, the hydrodesulfurization of benzo[*b*]thiophene (referred to as benzothiophene) (*14*) and dibenzothiophene (*15*) cannot readily be accommodated by the Kolboe mechanism without formation of high-energy benzyne intermediates, shown in the unlikely reaction step of Fig. 2b.

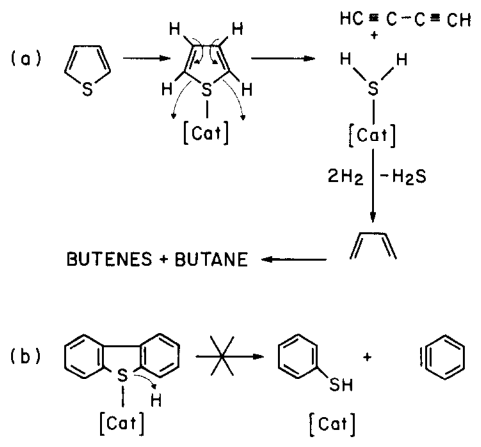
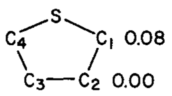


FIG. 2. The Kolboe one-point mechanism for hydrodesulfurization of thiophene and dibenzothiophene.

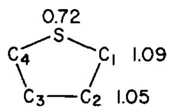
Kinetics data determined recently with dibenzothiophene and related compounds provide new evidence of the reaction mechanisms. The presence of a methyl group in a position β to the sulfur atom (as in 4-methyldibenzothiophene) could restrict access of the reactant to the active site on the catalyst surface. The steric hindrance caused by this methyl substitution in the one-point adsorption would be expected to be even more pronounced in the case of 4,6-dimethyldibenzothiophene. The experimental results obtained with sulfided Co–Mo/Al_2O_3 catalyst at about 300°C and 100 atm (*16*) show that 4,6-dimethyldibenzothiophene is about 10 times less reactive than dibenzothiophene, but only about 2 times less reactive than the 4-methyldibenzothiophene. Conversions determined at subatmospheric pressures give qualitatively the same reactivity pattern (*17*). In contrast to these results, however, the expected steric inhibition of adsorption by the one-point mechanism suggests [on the basis of abundant literature illustrating the rate effects associated with model cases of steric hindrance (*18*)] that differences of several orders of magnitude in hydrodesulfurization rate should distinguish these reactants.

Similar conclusions can be drawn from the low-pressure conversion data of Givens and Venuto (*14*) for benzothiophene and methyl-substituted benzothiophenes. They reported, for example, that 3-methylbenzothiophene is slightly less reactive than 2-methylbenzothiophene, which would be regarded as much more sterically hindered on the basis of the one-point mechanism. Similarly, Desikan and Amberg (*7*) have shown that 2-methyl- and 3-methylthiophene hydrodesulfurization reactions take place in the presence of sulfided Co–Mo/Al_2O_3 with indistinguishable apparent activation energies. And the adsorption studies of Zdražil (*19*), who used substituted thiophenes and aromatics contacting Co–Mo/Al_2O_3 in a pulse system, show that the bonding with the surface is only slightly affected by the substituent groups and is similar for thiophenic compounds and substituted benzenes having nearly the same molecular weight. All these substituent effects, taken together, strongly suggest that the one-point adsorption model is inadequate.

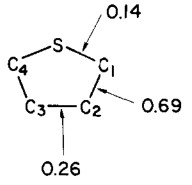
Further, we infer that the expected bonding characteristics of thiophene do not support the one-point adsorption model. Following Daudel *et al.* (*20*), we express the expected thiophene chemistry in terms of the following bonding parameters. The bond order refers to the "double bond character" of a bond or the sum of the partial bond orders contributed by each π electron; the free valence is a measure of the potential for homolytic (free radical) reactivity at each of the ring atoms; and the total charge at each atom is an expression of the potential for reactivity toward an approaching, polarizing species such as an electron-deficient reagent.



Free valence



Charge



Bond order

Apparently, the C_1–C_2 bond has the highest electron availability.

The bonding characteristics of thiophene and of its polycyclic aromatic homologs therefore indicate that the tendency of the compound to be adsorbed at an anion vacancy on the catalyst would not occur preferentially at the sulfur (say, through an available 3*p* orbital situated at right angles to the plane of the thiophene ring), but instead at the C_1–C_2 bond, if indeed a one-point mechanism were demanded. The unshared, nonbonded electron pairs on sulfur are so involved with the resonance of the thiophene nucleus that the sulfur has little residual electron availability for direct coordination by the electrophilic catalyst.

PROPOSED MULTIPOINT MECHANISM OF HYDRODESULFURIZATION OF THIOPHENE

We suggest that thiophenic molecules may be chemisorbed such that the C_1–C_2 bond is coordinated at an anion vacancy of the catalyst, with the adjacent sulfur center then interacting with a neighboring sulfur on the surface. When the thiophene ring becomes bonded via the C_1–C_2 position at the anion vacancy, the result is expected to be a change in the electron distribution of the thiophene ring, making the sulfur atom electron deficient and consequently promoting its bonding (shown as dashed lines in Fig. 3) with a sulfur atom of high electron density on the catalyst surface. These changes facilitate the subsequent concerted hydrogen atom additions to the coordinated C_1–C_2 centers and the formation of a dihydrogenated thiophene intermediate.

This suggestion, summarized in Fig. 3, brings to mind the action of the enzyme nitrogenase, a molybdenum-containing enzyme (*21*, *22*) capable of redox activity toward a wide variety of π-bonded species including molecular nitrogen, acetylenes, and aldehydes. The mechanism proposed for the reduction of acetylenes is illustrative. This reactant coordinates to the Mo^{4+} centers of the enzyme side-on in a π interaction. The coordinated acetylene, the Mo^{4+} center, and the amine ligands are juxtaposed, and the enzyme–reactant complex is ready for the coupled hydrogen- and electron-transfer process illustrated in Fig. 4. The two-site theory of the mechanism involving Mo-containing redox enzymes, advocated by Hardy *et al.* (*23*), is considered a three-point Ogston mechanism (*24*), since the acetylenic and related reactants exhibit two points of chemical bonding to the catalyst.

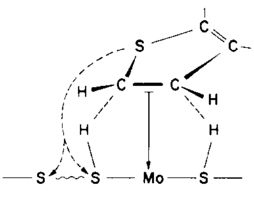


FIG. 3. Suggested structure of chemisorbed thiophene in the three-point mechanism. The dashed line indicates a weaker interaction between centers than the full line. The wavy line indicates a longer or more remote bond between centers.

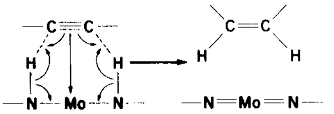
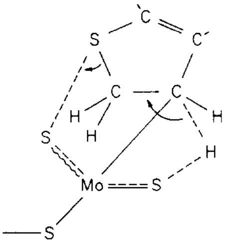
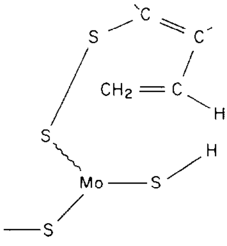


FIG. 4. A three-point mechanism suggested for the catalytic action of nitrogenase on an acetylenic reactant.

Working from the structure of Fig. 3, we now recognize several alternative pathways for product-forming steps leading from the reactant–catalyst complex. The dashed lines are intended to represent only a fractional degree of covalency in the bonds of Fig. 3. If the C_1 becomes bonded with a full covalency to a proton before a similar process occurs at C_2 (i.e., if partial hydrogenation of the C_1=C_2 double bond occurs), then, as depicted in *A*, electron delocalization from the partial covalency to the proton at C_2 can lead to rupture of the S–C_1 bond, with *A* converted to *B* (as follows):

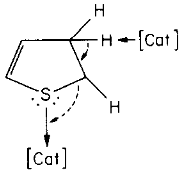


A

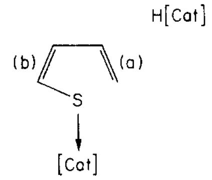


B

If the partially bonded protons in the structure of Fig. 3 become involved in covalent bonds to C_1 and C_2 by a concerted process, the resulting hydrothiophene *C* is no longer aromatic.



C



D

Structure *C* is highly susceptible to thermal β-elimination (the pathway depicted by the dashed arrows), probably assisted by electrophilic centers on the catalyst surface, to which it is bonded via its sulfur, which has become nucleophilic upon loss of thiophenic aromaticity. The net result is the same as is realized from the pathway involving nonsimultaneous transfer of hydrogen to the chemisorbed reactant in *A*.

It is clear that the structure *D*, which is presumably strongly bonded to the catalyst, can experience chemisorption of its olefinic groups to Mo^{4+} at anion vacancies created in its vicinity by hydrogenation and desorption of H_2S, and this can again lead to rupture of its C–S bond. Ultimately, the process will lead to liberation of butadiene or, if the double bond (a) (more remote from the C–S bond) is reduced prior to reduction of the vinylic sulfide double bond (b), butene will be formed directly without butadiene.

All these mechanistic possibilities can be invoked to account for the product compositions observed in hydrodesulfurization. Thus, the predominance of biphenyl as the product in the hydrodesulfurization of dibenzothiophene and the observation that the initial rate of biphenyl formation is far greater than that of any hydrogenated biphenyls (*15*) correlate well with the preference for product formation *via* the pathway in which only the ring carbon to which the sulfur is attached becomes *covalently bonded* to hydrogen. Electron delocalization similar to the step transforming *A* into *B* occurs rapidly to restore the aromatic energy of the ring with formation of *o*-mercaptobiphenyl before a dihydro product can be realized. This picture, which assumes that thiophenes are bonded to the catalyst surface through coordination involving their π electrons, accounts for steric effects of substitution arising from planar adsorption of the ring. It eliminates the necessity of assuming orbital interaction with the surface perpendicularly to the plane of the thiophenic π orbitals as demanded by the one-point model. Thus, a 4-methyl substituent in dibenzothiophene exerts a mild steric influence inhibiting coplanar adsorption of the reactive centers because the hydrogens of a methyl group (bonded to the 4 position, which is one of the three centers involved in the coplanar adsorbate), rotating about the axis of its bond to the ring, sweeps out a sphere of revolution above and below the plane of the σ framework of the ring. The effect of the methyl substitutent is to diminish slightly the degree of coordination of these reaction centers with the catalyst. Since dibenzothiophene is a planar structure, however, a second methyl group at the 6 position would not significantly increase the difficulty of achieving an interaction with the catalyst, since it creates no greater steric separation of the ring plane from the catalyst surface.

On the other hand, methyl groups at the 3,7 and 2,8 positions, which have no proximate relationship to the three adsorbate centers, would exert little steric effect since the normal bending vibrations of the ring would readily accommodate any possible interference with coplanarity of these centers. Instead, we observe a small rate enhancement resulting from hyperconjugative electron release by the 3,7 and 2,8 methyls to the sulfur and the ring carbon to which it is linked in the reactant (*16*); increased electron density at the centers of adsorption presumably increases the catalytic reaction rate through increased ease of coordination at the anionic vacancies of the catalyst.

A model overcoming some of the shortcomings of the model of one-point (end-on) adsorption of thiophene has been proposed by Cowley (*13*). Thiophene was presumed to adsorb flat on the catalyst surface in a π complex, as suggested also by Zdražil (*19*). The π complex was presumed to be converted to a σ complex in which sulfur orbitals perpendicular to the plane of the ring become bonded to the Mo^{3+} center at the anion vacancy. The hydrodesulfurization was presumed to be completed with the reactant in this posture.

This planar modification of the one-point (end-on) mechanism is based largely on the finding that the deuterodesulfurization products of 2,5-dideuterothiophene contain major amounts of D_2S. Such results have been interpreted by Cowley as an indication that the α-deuterium exchange reaction occurs by a pathway different from that occurring in hydrodesulfurization. Cowley reasoned that the initially formed π complex, in which the ring is bound parallel to the surface, becomes equilibrated with a series of σ complexes, all of them experiencing substantial bonding between an α-carbon and an electron-deficient Mo^{3+} center. The H–D exchange reaction in thiophene, benzothiophene, and dibenzothiophene was visualized as occurring in these σ complexes. The hydrodesulfurization reaction, on the other hand, was postulated to take place in σ complexes in which the sulfur had become coordinated by σ bonding to Mo^{3+} centers. Hydrogenolysis of the C–S bond with release of butadiene was presumed to be a consequence of altering the reactivity of the sulfur through its coordination by the Mo^{3+}, with adjacent Mo^{4+} SH^- sites providing the hydrogen.

The multipoint model discussed above provides an explanation for both the observed exchange at α (preferred) and β positions and the hydrogenolysis reactions, without the necessity of assuming the intervention of two different σ complexes for the two different reactions. In the multipoint mechanism it is the π orbital on carbon at which the available electron density of the aromatic (thiophenic) system can be coordinated by the electron-deficient Mo centers of the catalyst. The very act of bonding to these centers destroys the aromaticity of the ring enough to induce a degree of electron deficiency on the ring sulfur, thereby creating the opportunity for its back-

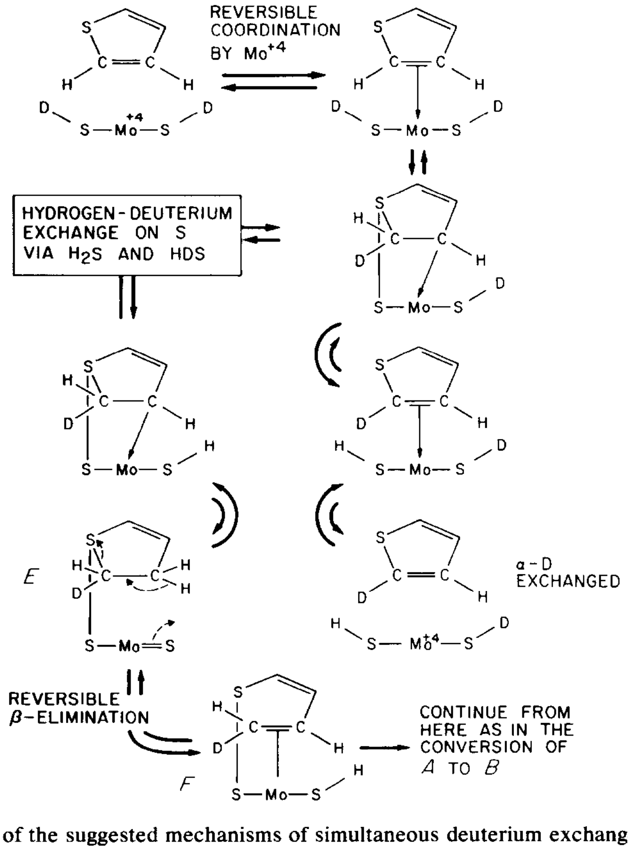


FIG. 5. Details of the suggested mechanisms of simultaneous deuterium exchange and hydrodesulfurization of thiophene adsorbed according to the multipoint model.

bonding with one of the sulfur atoms localized in the coordination sphere of the Mo center, as shown in Fig. 5.

Regarding the hydrodesulfurization of saturated sulfides such as tetrahydrothiophene, we point to the σ complex *E* in Fig. 5. Such an adsorbed intermediate can be formed with dihydrothiophene or tetrahydrothiophene through a S–S bond which steers the subsequent events, leading to formation of complex *F* and ultimate formation of butene or butadiene and H_2S. In other words, a series of steps involving β-elimination accompanied by hydrogen transfer to the catalyst is postulated on the premise of the ready formation of a S–S covalency (as in *E*) involving one of the sulfur ions near a Mo center which, in turn, is also capable of complexing with the resulting C–C π bond in forming *F*. Since the hydrothiophenes are much more nucleophilic than thiophene and readily coordinated by the sulfur, the suggested mechanism is in accord with Kolboe's observation (*10*) that the amount of butadiene produced by desulfurization of tetrahydrothiophene exceeds that arising from desulfurization of thiophene; there is no need for invoking an unprecedented dehydrosulfurization route (Fig. 2).

We recognize, however [as suggested by Cowley (*13*)], that the coordination of the sulfur atom of tetrahydrothiophene at the anion vacancy must be regarded as a competing possibility. Both the one-point mechanism, as advanced by Cowley, and the multipoint mechanism must be accepted as consistent with the available data. Experimental evidence of the surface intermediates is needed, such as might be provided by Fourier transform infrared spectroscopy and laser Raman spectroscopy.

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