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The Desulfurization of Polynuclear Aromatic Sulfur Compounds with a Raney Nickel

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The mechanism of the desulfurization of the polynuclear thiophene compounds with a Raney nickel was studied in ethanol at atmospheric pressure and from 0 to 78.3 °C. The desulfurization rate was initially fast but reached zero in about 30 minutes. The major products were biphenyl in the desulfurization of dibenzothiophene (**1**), 1-phenylnaphthalene in the desulfurization of benzo[*b*]naphtho[1,2-*d*]thiophene (**2**), and 2-phenylnaphthalene in the reaction of benzo[*b*]naphtho[2,3-*d*]thiophene (**3**) and benzo[*b*]naphtho[2,1-*d*]thiophene (**4**). The desulfurization extent for the four compounds decreased in this sequence: **3**>**1**>**2**>**4**. The extent of the desulfurization of the polynuclear thiophene compound was not related to the reaction indices, Fr(E), Fr(N), and Fr(R), of the sulfur atom of the compounds, which were calculated by using a simple Hückel theory; rather, it was related to both the free valence and the π-electron density. Therefore, the polynuclear thiophene compounds were considered to adsorb on a Raney nickel through the free-electron pair of the sulfur atom; consequently, the adsorption led to the C–S bond scission.

The hydrodesulfurization of heavy petroleum feedstocks and coal-derived liquids requires the conversion of high-molecular-weight compounds like dibenzothiophene and benzonaphthothiophenes.[1,2] There are several studies in the literature which deal with the mechanism of the hydrodesulfurization of polynuclear thiophene compounds on cobalt or nickel molybdenum catalysts at high pressures and high temperatures.[3–5] However, there are only a few studies which relate the chemical reactivity of polynuclear thiophene compounds to their electronic structure,[6] although the adsorption and hydrodesulfurization of simple sulfur compounds, e.g., thiophene, have been studied recently using Hückel theory.[7,8]

There is competition between the different processes (hydrogenation and desulfurization) during the reaction. The hydrodesulfurization occurs through the extrusion of a sulfur atom to give the corresponding hydrocarbon, with some hydrogenation of the aromatic ring occurring either prior to or following the removal of the sulfur. It is difficult to understand the relationship between desulfurization and the electronic properties of the compounds under reaction conditions. However, a Raney nickel extrudes a sulfur atom from the molecule to form hydrocarbons without hydrogenation at a low temperature in a solvent. In the present investigation, the desulfurization studies are performed in a batch reactor over a Raney nickel. The sulfur compounds used here are dibenzothiophene, benzo[*b*]naphtho[1,2-*d*]thiophene, benzo[*b*]naphtho[2,3-*d*]thiophene, and benzo[*b*]naphtho[2,1-*d*]thiophene (Fig. 1). The dependence of the desulfurization extent on the electronic structure of the compounds was considered using simple Hückel molecular orbital calculations. The mechanism of the adsorption and desulfurization of benzonaphthothiophenes and dibenzothiophene is also discussed.

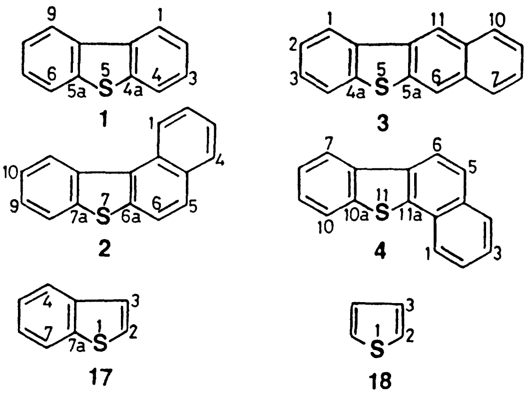

Fig. 1. Various thiophene compounds.

Experimental

Raney Nickel. The procedure was similar to that used in the preparation of W-7 Raney nickel described by Adkins et al.[9] A solution of 100 g of sodium hydroxide in 500 ml of H_2O at 50 °C was carefully added to 100 g of the Raney nickel alloy (41% Ni; Koso Chemical Co.). The addition was completed in approximately four and a half hours. The residue was washed by decantation with water and then by stirring with three successive portions of ethanol. The procedure was repeated three times using equal amounts of diethyl ether. The Raney nickel was used after it had then been stored in diethyl ether at 0 °C for more than one month.

Reactants. Dibenzothiophene (1): Compound **1** was synthesized according to the method of Gilman and Jacoby.[10] Mp 100.5—101 °C (lit, 99 °C[10])); Found: C, 78.29; H, 4.40; S, 17.31%. (Calcd: C, 78.22; H, 4.38; S, 17.40%).

Benzo[*b*]naphtho[1,2-*d*]thiophene (2): **2** was synthesized by dehydrogenating 5,6-dihydrobenzo[*b*]naphtho[1,2-*d*]-

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thiophene (**8**) in the presence of a Pd-C catalyst by the method of Campaigne and Osborn.[11] Compound **8** was obtained by the cyclization of 2-phenylthio-1-tetralone (**9**) in the presence of phosphorus pentaoxide. Compound **9** was prepared by reacting thiophenol with 2-bromo-1-tetralone. Mp 100.5—102 °C (lit, 102—102.5 °C,[10] 101.5—102 °C[11]); Found: C, 82.17; H 4.39% (Calcd: C, 82.01; H, 4.30%).

Benzo[*b*]naphtho[2,3-*d*]thiophene (3): **3** was synthesized in five stages from **1** and succinic anhydride as the starting compounds. Using 4-(dibenzothiophen-2-yl)-4-oxobutanoic acid, prepared by the Friedel Craft's reaction from the two starting compounds,[10] 4-(dibenzothiophen-2-yl)butanoic acid (**10**) was synthesized by the Huang-Minlon modification of the Wolff-Kishner reduction.[11] 9,10-dihydrobenzo[*b*]naphtho[2,3-*d*]thiophen-7(8*H*)one (**11**) was synthesized by the cyclization of **10**.[12] Compound **3** was prepared by the dehydrogenation of the tetrahydrobenzo[*b*]naphtho[2,3-*d*]thiophene (**12**) with amorphous selenium. Compound **12** was synthesized by the reduction of **11** using the Wolff-Kishner procedure by the method of Campaigne and Osborn.[11] Mp 158.5—160 °C (lit, 160.5—161 °C,[11] 159—160 °C[13]).

Benzo[*b*]naphtho[2,1-*d*]thiophene (4): **4** was synthesized by a three stage reaction using 2-bromocyclohexanone (**13**) and 1-naphthalenethiol (**14**) as the starting compounds, while 2-(1-naphtylthio)cyclohexanone (**15**) was prepared by condensing **13** and **14**, which had been synthesized according to the method of Rabindran and Tilak.[12] Compound **4** was synthesized by the dehydrogenation of 7,8,9,10-tetrahydrobenzo[*b*]naphtho[2,1-*d*]thiophene (**16**) using amorphous selenium powder.[12] **16** was prepared by heating a mixture of **15** and phosphorus pentaoxide.[9] Mp 184—185 °C (lit, 182—184 °C,[11] 184—185 °C,[12] 186—187 °C[13]).

Apparatus and Procedure. Ten ml of abs. ethanol was placed in a pear-shaped flask equipped with a thermometer, a Dimroth condenser, and an electric stirrer. The Raney nickel (ca. 0.2 g) was weighted into the flask. An amount of the sample (0.2—1.47 mmol) was added to a certain solvent with the Raney nickel. The flask was then immediately placed in a glycerol bath at room temperature. After the solution had quickly been raised to the desired temperature, the stirrer was started and the initiation time was recorded. After the reaction, the flask was removed from the glycerol bath and cooled to room temperature. The catalyst was removed by filtration and washed with ethanol. The reaction mixture was then concentrated by evaporation to remove the solvent.

Analysis. The reaction products were analyzed by the use of conventional gas chromatography (Column packing: Apiezon Greese 20% Chromosorb W or Silicone OV-17 5% Uniport HP), using acenaphthene as the internal standard. The reaction products were identified by comparing the retention times with those obtained for known samples. No H_2S was observed during the reaction. Hydrogen sulfide was not trapped as zinc sulfide when an aqueous solution of zinc acetate was used for trapping. The extent of desulfurization, R, (mmol/g-Raney nickel), was calculated by the use of the following equation: $R=(A_0-A)/W$. A_0 is the initial number of moles of the reactant, while A is the number of moles of the reactant which have not reacted. W is the weight of the Raney nickel.

The simple Hückel theory (NEC microcomputer, Model PC-9801VM2) was used to calculate the π-electron density of a sulfur atom in addition to such other reaction indices as the π-bond order, free valence, and Fr(E), Fr(N), and Fr(R) introduced from the highest occupied, lowest unfilled, and singly occupied orbital (HOMO, LUMO, and SOMO) coefficients. In addition, benzothiophene (**17**) and thiophene (**18**) were studied in order to compare their behavior with that of the above compounds.

Results

Desulfurization of Dibenzothiophene. The extent of the desulfurization of dibenzothiophene with the Raney nickel in the ethanol solvent is shown in Fig. 2. Biphenyl was the principal product, with other compounds being formed only in trace amounts. The rate of desulfurization was fast initially, but reached zero in each case following a reaction time of about 30 minutes. This observation suggested that the activity of the Raney nickel was extremely high initially and that it then gradually diminished with the reaction. Therefore, for the time being, we shall assume that the desulfurization activity of the Raney nickel can be estimated by means of the initial rate of the desulfurization, v_0, at the starting time. The initial rates are 2.1, 1.5, 1.2, and 0.23 mmol/g-cat·h at 78.3, 48.8, 20.0, and 0 °C respectively.

A plot of log v_0 vs. $1/T$ gives an activation energy of 18.4 kJ mol^{-1} for the desulfurization of dibenzothiophene. This result is in good agreement with those obtained by Bartsch and Tanilian,[14] who studied the hydrodesulfurization of benzothiophene and dibenzothiophene, in dodecane as a solvent, over a sulfided $CoMo/Al_2O_3$ catalyst under atmospheric pressure and at 300—400 °C. These authors reported activation energies of 20.5 (for benzothiophene) and 22.5 kJ mol^{-1} (for dibenzothiophene). Moreover, a value of 15.5 kJ mol^{-1} was observed by Satterfield and Robert[15] for the

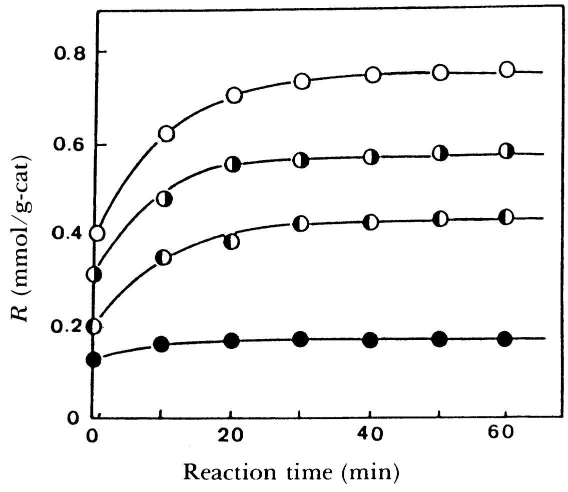

Fig. 2. The extent of desulfurization of dibenzothiophene with the Raney nickel in the ethanol solvent. The initial amount of the sample was 0.294 mmol and the catalyst weight was 0.2 g, ○: 78.3; ◑: 48.8; ◐: 20.0; ●: 0 °C.

hydrodesulfurization of thiophene over a sulfided $CoMo/Al_2O_3$ catalyst at 234—265 °C and at atmospheric pressure using a continuous-flow, stirred-tank reactor. On the other hand, in a previous gas phase study carried out in a fixed-bed microreactor,[16)] an activation energy of 102 kJ mol^{-1} for the hydrodesulfurization of dibenzothiophene over a sulfided $NiMo/Al_2O_3$ catalyst was obtained. This is significantly higher than the 18.4 kJ mol^{-1} reported in the present study, which was performed in ethanol at low temperatures. These different results appear to be attributable to differences in the diffusion limitation for reactions carried out in the gas phase as opposed to the liquid phase.

The Initial Rate vs. the Extent of Desulfurization at 60 min. The Raney nickel initially exhibited a very high activity with dibenzothiophene, even though the reaction occurred before the reaction temperature reached the desired temperature. It is difficult to measure accurately the high initial rate of dibenzothiophene in the solvent of hydrocarbons, and there is a poor reproducibility in estimating the values of the desulfurization of benzonaphthothiophenes in small amounts. The Raney nickel gradually became less active during the reaction, though the extent of desulfurization was constant 60 min after the reaction had started. The extent of desulfurization at 60 min showed the total activity of the Raney nickel over the reaction time. Figure 3 shows that the extent of desulfurization at 60 min was proportional to the initial rate of desulfurization. Therefore, the extent of desulfurization at 60 min will be applied to further measurements of the desulfurization of dibenzothiophene and benzonaphthothiophenes with the Raney nickel.

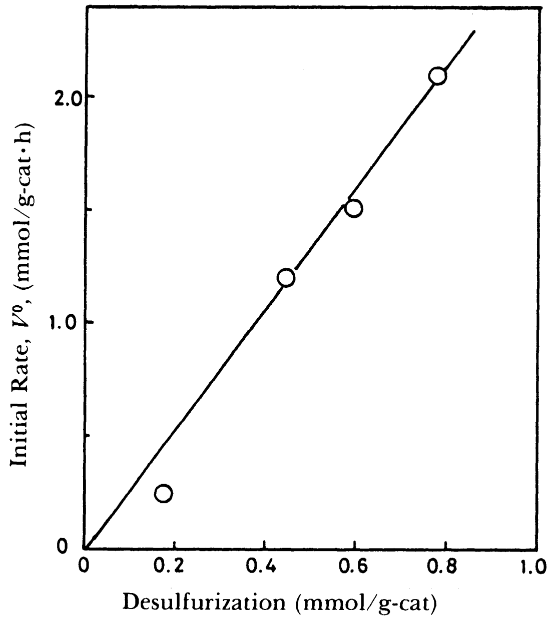

Fig. 3. The extent of desulfurization of dibenzothiophene at 60 min was proportional to the initial rate of desulfurization at 78.3 °C.

Effects of Solvents on the Desulfurization of Dibenzothiophene. The effects of the solvents on the desulfurization of dibenzothiophene by the Raney nickel at 78.3 °C for 60 min are shown in Table 1. The solvents exhibited a strong effect on the desulfurization activity of the Raney nickel. A high extent of desulfurization was observed when nonpolar solvents such as benzene or xylenes were used as solvents. This observation suggests that the nonpolar solvent blocks the Raney-nickel surface to a smaller extent than do other solvents. On the other hand, protic solvents, such as acetic acid and formic acid, depress the desulfurization. The extent of the desulfurization of dibenzothiophene in the presence of formic acid, acetic acid, and ethanol decreases with a decrease in the *Y* values of formic acid (*Y* value, +2.05), acetic acid (−1.64), and ethanol (−2.03). Since the *Y* value represents the ability of ionization of a solvent to the Raney nickel,[17)] the protic solvents appear to decrease the activity of the Raney nickel because of the ionization of the nickel atom of the Raney nickel. Furthermore, formic acid poisons the surface of the Raney nickel by its carbonyl group.

Raney nickel contains hydrogen.[18,19,20)] The carbon-sulfur bond of dibenzothiophene is split, and biphenyl formation occurs after the hydrogen has been used up. The solvent also reacted with this hydrogen of the Raney nickel. Methyl ethyl ketone was hydrogenated by the hydrogen. Therefore, the desulfurization of dibenzothiophene on the Raney nickel was depressed by the solvents because of the decrease in the amount of hydrogen in the Raney nickel, as well as because of the poisoning effect of the solvents and because of the ionization of the nickel atom of the Raney nickel.

Reactivity of Dibenzothiophene and Benzonaphthothiophenes. The desulfurization of dibenzothiophene and benzonaphthothiophenes over a Raney nickel in the ethanol solvent was performed at 78.3 °C for a period of 60 min. The major products (biphenyl **5** in the desulfurization of **1**, 1-phenylnaphthalene (**6**) in the desulfurization of **2**, and 2-phenylnaphthalene (**7**)

Table 1. Influence of Solvents on the Desulfurization of Dibenzothiophene

Solvent	*R* mmol/g-Raney nickel
Methyl ethyl ketone	0.44
Acetic acid	0.23
Formic acid	0.07
Ethanol	0.78
Benzene	1.27
Toluene	0.76
o-Xylene	1.01
m-Xylene	0.97
p-Xylene	0.80

Reaction time, 60 min; reaction temperature, 78.3°C; solvent volume: 10 ml.

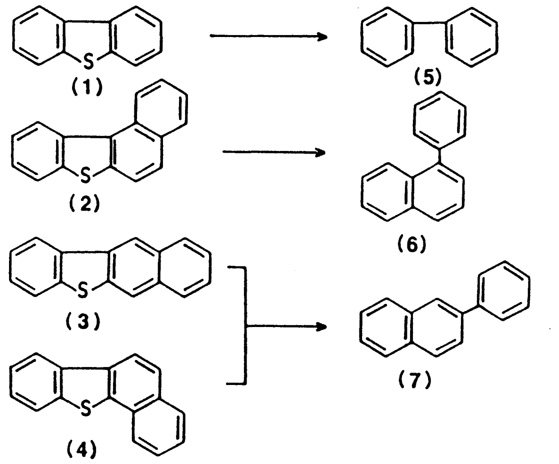

Fig. 4. The desulfurized compounds from the desulfurization of dibenzothiophene and benzonaphthothiophenes.

Table 2. The Desulfurization of the Four Compounds with a Raney Nickel at 78.3°C for 60 min

Compound	1	2	3	4
R (mmol/g-Raney nickel)	0.78	0.63	0.86	0.58

Initial mole of the sample, 0.2 mmol; weight of the Raney nickel, 0.2 g.

in the desulfurization of **3** and **4**) are shown in Fig. 4. Observation of these products shows that the reaction occurs through the extrusion of a sulfur atom to give the corresponding hydrocarbon, without any hydrogenation of the aromatic ring occurring either prior to or following the removal of sulfur. This indicates that the perpendicular adsorption of these compounds to the nickel atom is preferred during the reaction.

The results of the desulfurization of the four compounds with the Raney nickel in the ethanol solvent at 78.3 °C for 60 min are shown in Table 2. The extent of desulfurization for the four compounds decreased in this sequence: **3**>**1**>**2**>**4**. These results show that the tricyclic thiophene compound is not always more reactive than the tetracyclic compounds, since the reactivity of dibenzothiophene is lower than that of compound **3**. This last result is consistent with that obtained by Sapre et al.,[3] who found **3** more reactive than **1** on a sulfided CoMo/Al_2O_3 catalyst. This suggests that the reactivity of polynuclear thiophene compounds is not governed solely by the size of the molecule, but also by other elements which are related to the molecular structure.

Electronic-Structure Calculations. Parameters appropriate for the thiophene molecule are given in review articles by Zahradník[21,22] and Zdražil et al.[23] In this parameterization, $\alpha(S)=\alpha(C)+\beta(CC)$, $\alpha(C_\alpha)=\alpha(C)+0.1\beta(CC)$, and $\alpha(C_\alpha S)=0.8\beta(CC)$. Duben[24] studied thiophene using the simple Hückel molecular theory. He reported that, after a few trials had been made with other parameters, the only differences noted were some small changes in the orbital coefficients. For this reason, it was decided that the parameters specified in Zahradinik's article[21] could be used. Using these parameters, the Hückel molecular orbitals of polynuclear thiophenic compounds which are not adsorbed on the catalyst surface were calculated. The π-electron density of the sulfur atom and the π-bond order of the C-S bond are shown in Table 3, while the reaction indices, Fr(E), Fr(N), and Fr(R), of the sulfur atoms are presented in Table 4. Fr(E), Fr(N), and Fr(R) represent the ease of electrophilic, nucleophilic, and radical reactions at the sulfur atom of the compounds respectively. The π-electron density of the four compounds decreased in the following order: **3**>**1**>**2**>**4**. This order is in agreement with that of the desulfurization, but not with those of the reaction indices, Fr(E), Fr(N), and Fr(R).

Table 3. π-Electron Density and π-Bond Order of the Thiophene Compounds as Determined by a Simple Hückel Molecular Orbital Theory

Compound	q_s[a)]	q_s-q_c[b)]	πBond order of C-C bond	π-Bond order of C-S bond
3	1.732	0.685	(2-3) 0.597	(4a-5) (5-5a) 0.384 0.384
1	1.722	0.677	(4-4a) 0.614	(4a-5) 0.393
2	1.706	0.645	(9-10) 0.632	(7a-7) (7-6a) 0.402 0.405
4	1.697	0.637	(5-6) 0.747	(10a-11) (11-11a) 0.400 0.420
17	1.663	0.543	(2-3) 0.755	(7a-1) (1-2) 0.421 0.472
18	1.599	0.501	(2-3) 0.794	(1-2) 0.508

a) The π-electron density of the sulfur atom in the compounds. b) The difference between the π-electron density of the sulfur atom and the highest π-electron density of the carbon atom in the compounds.

Table 4. The Reaction Indices

Compound	1	2	3	4
Fr(E)[a)]	0.372	0.660	0.110	0.315
Fr(N)[b)]	0.000	0.047	0.068	0.083
Fr(R)[c)]	0.186	0.354	0.089	0.199

a) $2(C_{\mathrm{HOMO,S}})^2$. b) $2(C_{\mathrm{LUMO,S}})^2$. c) $(C_{\mathrm{HOMO,S}})^2+(C_{\mathrm{LUMO,S}})^2$.

Discussion

Relation between Desulfurization and Electron Structure. It was shown that the extents of desulfurization of the four compounds in ethanol at 78.3 °C for 60 min were 0.86, 0.78, 0.63, and 0.58 mmol/g-Raney nickel respectively. The correlation between the π-electron density of the sulfur atom of the polynuclear thiophene compounds and the extent of desulfurization is shown in Fig. 5. These data demonstrate that the desulfurization extent is proportional to the π-electron density of the sulfur atom. It appears, there-

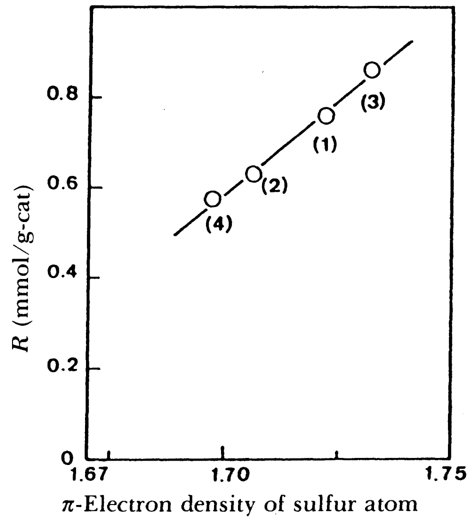

Fig. 5. Relationship between the extent of desulfurization of the polynuclear sulfur compounds and the π-electron density of their sulfur atom. The initial amount of sample was 0.2 mmol and the weight of the Raney nickel was 0.2 g.

fore, that the desulfurization which occurs on a Raney nickel depends on the π-electron density of the sulfur atom. This, in turn, is related to the strength of the adsorption of sulfur to a surface nickel atom of the Raney nickel. Hauptmann and Wladislaw[25] have also reported that the desulfurization was responsible for the first step of the reaction, that is, the adsorption of the organic compound on the metallic surface. This interaction with the Raney nickel is accomplished through the free-electron pair of sulfur. The sulfur can then readily split off from the ring without saturation occurring.

4 might be expected to exist a steric hindrance on the desulfurization, since it has the benzene ring in the compound on the side of the sulfur atom. Table 3 shows, however, that the π-bond order of C_{11a}–S_{11} of **4** is greater than that of C_{10a}–S_{11} of **4** which is similar to that of C_{7a}–S_7 of **2** and that, therefore, **4** is more easily desulfurized than expected, even though it has a steric hindrance. Thus, the preferential fission of the C–S bond can offset the effect of steric hindrance. Therefore, the interaction of the π electrons of the sulfur atom with the Raney nickel surface is more important than the molecular size for the desulfurization of polynuclear thiophene compounds over a Raney nickel.

Desulfrization Mechanism. Eisch and his coworkers[26] have undertaken a mechanistic study of the desulfurization of dibenzothiophene by the (2,2′-bipyridyl)nickel (0) complex and reported that a radical anion of the thiophene nucleus was formed and that this subsequently underwent C–S bond cleavage into S^- and aromatic radicals. However, it is obvious that there is no correlation between the desulfurization rate and the reaction indices, Fr(E), Fr(N), and Fr(R), as is shown in Table 4. These results suggest that there is no evidence in this study for either electron transfer or nucleophilic attack. Moreover, the radical reaction is not the rate-determining step in the desulfurization of the thiophene compounds on the Raney nickel, although the mechanism of desulfurization over a Raney nickel is most generally a free-radical mechanism.[25,27,28] Therefore, the rate-determining step in this reaction is not a C–S bond breaking, but the adsorption of the sulfur compound to a nickel atom of the Raney-nickel surface, with a competitive adsorption of the solvent. This adsorption leads to the removal of the sulfur from the thiophene compound. The sulfur reacts with the nickel atom of the Raney nickel to form nickel sulfide, but not hydrogen sulfide.

In the first step, the unshared electron pair of the sulfur is attracted to a low-valent nickel atom of the Raney-nickel surface. The compound is adsorbed on the surface through the unshared electron pair of sulfur, which acts as an electron donor. The carbon-sulfur bond is, therefore, weakened, and a free radical is formed. The hydrogen present on the Raney-nickel surface[18,19,20] then reduces the radical to the corresponding hydrocarbon.

On the other hand, for the monocyclic and bicyclic thiophene compounds, the hydrogenation of the C_2–C_3 bonds of **17** and **18** appears to take place competitively with the fission of the C–S bond. The difference ($q_s - q_c$) between the π-electron density of the sulfur atom and that of the carbon atom (C_3) (the carbon atom with the highest π-electron density) is small, although the charge density index refers to the nature of the molecule before allowance is made for perturbing effects due to the approaching reactant. Furthermore, the bond order of the C_2–C_3 bonds of **17** and **18** is larger than that of the others. For this reason, these two molecules must chemisorb by a multi-point mechanism.[29] According to the multi-point mechanism, thiophene molecules are chemisorbed in such a way that the C_2–C_3 bond is coordinated to an anion vacancy at the surface, with the adjacent sulfur center interacting with a contiguous sulfur atom on the surface. The mechanism by which the tricyclic and tetracyclic thiophene compounds are desulfurized is, therefore, quite different from that of the monocyclic and bicyclic compounds, **17** and **18**.

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