QUANTUM CHEMICAL MODEL OF THE ADSORPTION OF THIOPHENES DURING HYDRODESULPHURIZATION

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In relation to the problem of the mechanism of the catalytic hydrodesulphurization of cyclic sulphur compounds, three types of interactions between thiophene and ten of its alkyl derivatives with an electron acceptor centre are discussed from the point of view of their electron structure as determined by the CNDO/2 and HMO methods. It was found that during the hydrodesulphurization the adsorption on the catalyst is effected rather through the sulphur atom than through the interaction between the surface centre of the catalyst and the whole π-electron system of the aromatic ring.

The main stress in existing studies of the hydrodesulphurization mechanism of thiophene is being laid on the kinetic scheme of the reaction and on correlations between properties of the catalyst and its activity[1-6]. Simultaneously the interaction between thiophene and the catalyst is described rather schematically. Two basic orientations of thiophene towards the surface are usually distinguished. In the first one, thiophene behaves like an aromatic hydrocarbon; the plane of the ring is parallel to the surface, which leads to the interaction through the π-electron system or its parts. Thus the adsorption of benzene during hydrogenation proceeds in this manner[7,8] and, if we extrapolate this similarity also to further stages of the hydrodesulphurization, we may expect the hydrogenation of the thiophene nucleus. In the second orientation, the plane of the ring is perpendicular to the surface. This position is favourable for the manifestation of sulphidic properties of thiophene and the interaction with the catalyst is accomplished through the free electron pair of sulphur. If the sulphidic and diene character of thiophene is decisive also in subsequent reaction steps, sulphur can split off from the ring without its saturation. During most different molecular interactions thiophene behaves like benzene, namely as an electron donor. In all hydrodesulphurization models the catalyst is visualized as an electron acceptor[9,10], whereas the conception of the substantial role of electron donor centres of the catalyst is encountered only exceptionally[11].

In our work we attempted to analyze some conceptions of the adsorption of thiophene or, possibly, of its further changes during the hydrodesulphurization from the point of view of its electron structure as determined by quantum chemistry methods and from the point of view of its chemical properties. We investigated different types of the interaction between thiophene and the electron acceptor catalytic centre which was approximated by proton. Although this simplification is a drastic one, for a basic analysis it might prove useful.

METHODS

Our quantum chemical calculations were performed on two approximation levels — by the CNDO/2 and HMO methods. A computer program[12] for the CNDO/2 method was employed to obtain results for thiophene and a series of its alkyl derivatives (3-methyl, 3-tert-butyl, 2-methyl, 2-ethyl, 2-propyl, 2-isobutyl, 2-tert-butyl, 2,5-dimethyl, 2,5-diethyl, and 2,5-dipropyl) and further for three models of the adsorption of thiophene on the electron acceptor catalytic centre represented by proton. Another calculation was also performed for the butadiene molecule with a special geometry. In all calculations only s- and p-orbitals of sulphur were considered. Here we started from results of other authors[13−16] who found that the inclusion of the d-orbitals improves the agreement with experiment only within a certain limit but that this agreement is basically satisfactory even if they are neglected. Our calculations are based on the geometry of thiophene as determined by microwave spectrometry[17]. A standard geometry[18] was used for alkyl groups in alkyl thiophenes. The geometry of the models of the adsorption of thiophene is obvious from Fig. 1. The geometry of butadiene was taken identical with that of thiophene ring in which the sulphur atom was replaced by two hydrogen atoms located in the direction of the original C—S bonds.

Calculations were performed also by the HMO method[19] for thiophene, butadiene and A′, B′, C′ adsorption models which are analogous to the A, B, C models employed in our CNDO/2 calculations. Within the HMO method the acceptor centre was approximated by:

model A′

$$\alpha_A = \alpha + 0.618\beta \qquad (1)$$

$$\beta_{AS} = h\beta ; \quad h = 0.0 - 1.8 \qquad (2)$$

model B′

$$\alpha_S = \alpha + k\beta ; \quad k = 1.0 - 2.0 \qquad (3)$$

$$\beta_{CS} = 0.7\beta \qquad (4)$$

model C′

$$\alpha_A = \alpha + 0.618\beta \qquad (5)$$

$$\beta_{AS} = \beta_{AC} = h\beta ; \quad h = 0.00 - 0.36 . \qquad (6)$$

Several different characteristics were used for the interpretation of the calculations. In the CNDO/2 method it was the bond index and bonding saturation of the atomic orbital according to Wiberg[20]. These two quantities are defined by the relations

$$W_{AB} = \sum_\mu \sum_\nu P_{\mu\nu}^2 ; \quad \mu \in A , \quad \nu \in B \qquad (7)$$

$$V_\mu = \sum_{\mu \neq \nu} P_{\mu\nu}^2 \left(= P_{\mu\mu}(2 - P_{\mu\mu}) \text{ for a closed shell}\right) \qquad (8)$$

$P_{\mu\nu}$'s are matrix density elements and A, B two different atoms. In the HMO methods it was the bond order defined in the familiar way[21]. Other employed quantities may be defined simulta-

neously for both methods. In the first place it is the electron density ϱ_μ of an orbital which is the element of the MO base

$$\varrho_\mu = 2 \sum_i^{occ} c_{i\mu}^2 , \tag{9}$$

where $c_{i\mu}$ is the expansion coefficient of the μ-th base orbital in the i-th MO.

Further we employed an index constructed on the basis of a perturbation expression for the energy of interaction between the empty acceptor level and occupied donor levels[22]:

$$E = 2 \sum_i^{occ} \left(\sum_\mu \sum_\nu c_{i\mu} c_{LUMO\nu} \, \beta_{\mu\nu} \right)^2 / (\varepsilon_i - \varepsilon_{LUMO}) , \tag{10}$$

where c's are expansion coefficients of MO, β's resonance integrals between MO base orbitals of the acceptor and the donor, and ε's energies of MO. For the special case of the A, B, C models, Eq. (10) may be simplified by considering only dominant terms in the second summation. As a result we obtain the following indices, which are proportional to the interaction energy:

$$I_A = \sum_i^{occ} \left[q c_{ip}^2 + (1 - q) \, c_{is}^2 \right] / (\varepsilon_i - \varepsilon_A) , \tag{11}$$

$$I_B = \sum_i^{occ} c_{ih}^2 / (\varepsilon_i - \varepsilon_A) , \tag{12}$$

$$I_C = \sum_i^{occ} \left(\sum_j^{p_z} c_{ij} \right)^2 / (\varepsilon_i - \varepsilon_A) , \tag{13}$$

where c_{ip}, c_{is}, c_{ih}, c_{ij} are subsequently expansion coefficients of p_z and s sulphur atomic orbitals, of a χ_h hybrid orbital representing the free electron pair of sulphur, and of p_z-orbitals of all five atoms constituting the thiophene ring; ε_A is the energy of the acceptor level; parameter q enables to express different mutual ratios of resonance integrals between the acceptor orbital and p_z and s sulphur atomic orbitals. The hybrid orbital χ_h was constructed from s, p_x and p_y sulphur orbitals and from other two orbitals which were oriented in the direction of the S—C bonds, and satisfied the conditions of orthonormality and of the conservation of symmetry in the system. Eq. (13) was obtained from the assumption of the equality of all five resonance integrals between the acceptor orbital and p_z atomic orbitals of the ring.

RESULTS AND DISCUSSION

In present works dealing with hydrodesulphurization, the adsorption by means of sulphur is most often assumed[2,3], but the geometry of the arising complex is not specified. A question appears whether the active centre of the catalyst lies in the plane of the thiophene ring or outside it. Differences in the geometry may here namely lead to substantial changes in the selection of orbitals which can interact with respect to symmetry conditions.

In the construction of our models we started from the assumption that the active surface centre is formed by the coordinationally unsaturated molybdenum ion, which is located in a crystal field of octahedral symmetry[2,3,23]. At these conditions the lowest unoccupied level of the surface acceptor centre may be, besides the $5s$ orbital, also the $4d_{z^2}$ or $4d_{x^2-y^2}$ orbital (axis z is oriented in the direction of the arising surface bond, *i.e.* perpendicularly to the catalyst surface). Both the symmetry and directional properties of the $4d_{x^2-y^2}$ orbital are unsuitable. Therefore it may be expected that in the active interaction with a thiophene molecule preferably the $5s$ or $4d_{z^2}$ orbitals will be involved as both of them exhibit a σ-symmetry in the direction of the bond with the adsorbate. The same symmetry is displayed by the proton orbital, which served in our computations as an approximation of the electron acceptor surface centre of the catalyst.

Three models were constructed (Fig. 1) in which the proton interacted efficiently with each of the ring atoms (model C) or with the sulphur atom only (models A and B). In contrast to model A, no direct interaction with π-orbitals of the ring appears in model B (zero overlap of orbitals caused by a different symmetry). In the actual reaction that adsorption type will be preferred, which induces hydrodesulphurization promoting changes in the adsorbate molecule and which is simultaneously energetically favourable. In our calculations we limited ourselves to the first of the above conditions since, for a reliable evaluation of the stability of the adsorbent–adsorbate complex, it would be necessary to employ a much more accurate catalyst
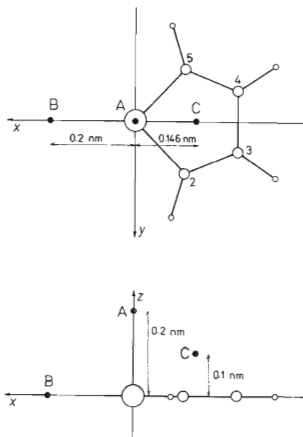

FIG. 1

Models used for the Adsorption of Thiophene

Positions labelled A, B and C correspond to the location of proton in models A, B and C, resp.

model, which exceeds available technical possibilities. Nevertheless, as regards the two models of the sulphur adsorption, some conclusions in this respect may be drawn from the electron structure of thiophene itself.

Calculations by the CNDO/2 method for this molecule showed that a considerable electron density is localized in the p_z-orbital of the sulphur atom and that, consequently, this orbital possesses strong features of an nonbonding orbital with a free electron pair. Differences between properties of p_z-orbitals of sulphur and p_z-orbitals of the remaining atoms in the ring can be clearly illustrated on the value of the bonding saturation which is equal to zero for an orbital not participating in the bond (occupied by two electrons or unoccupied) or reaches unity for a fully bonding-saturated orbital (occupied by one electron). The value of this quantity for the p_z-orbital of sulphur in thiophene is 0·42 whereas for p_z-orbitals of carbon atoms it is 1·00. In this respect it is interesting to examine the bonding saturation of the hybrid orbital χ_h, which represents the true free electron pair of sulphur and for which the corresponding value drops to 0·11.

If the orbital of the electron acceptor (with a σ-symmetry) lies in the plane of the ring (model B), due to symmetry reasons it can interact with a free electron pair only. If this orbital lies outside of the plane (model A), it may interact both with the "free pair" of the p_z-orbital and again with the free pair of the χ_h orbital or, more accurately, with its s-component which prevails (the χ_h orbital is within 93% of the s-type due to a small C—S—C bonding angle). With regard to the adsorbent–adsorbate complex corresponding to model A it may be then assumed that it is energetically more favourable than the structure corresponding to model B. This conclusion is in accordance with calculations performed for protonated thiophene by Clark[14].

Further calculations were made for thiophene adsorbed according to one of the three aforementioned models. We employed a somewaht unusual combination of the two methods since calculations by the CNDO/2 method were performed always for only one configuration of the given type. To eliminate the possibility of an erroneous conclusion as an artifact of the chosen geometry, we performed a supplementary calculation by the HMO method for a subsequently increasing strength of interaction in each of the models. Conclusions following from both kinds of computations were always identical.

The aromaticity of thiophene consists in the energetical stabilization accompanying the interaction of two components of the thiophene ring, i.e. of the p_z-orbital of sulphur and the π-electron system of butadiene[16], and it is brought about by a redistribution of electron densities in the participating orbitals. This fact is illustrated in Table I, which reports electron densities of butadiene π-orbitals in thiophene and in models A, B and C. The aromaticity of a system is measured by deviations between the reported values and those valid for butadiene itself, i.e. four for bonding and zero for antibonding π-orbitals. The same quantities obtained by the HMO method are

collected in Fig. 2. For a better illustration Fig. 3 and Table II further contain bonding orders, respectively changes of the bonding index of selected bonds. The following conclusions may be drawn from the reported values and from the comparison of the individual models and thiophene: the adsorption of type C weakens all bonds of the ring and this weakening is least pronounced for the S—C bonds. The distribution of the electron density in butadiene orbitals differs from that in butadiene; the occupation of antibonding orbitals is identical with that in thiophene. This type of adsorption therefore disturbs neither the aromaticity of the ring nor the strength of the sulphur bond in this ring to a more significant extent. From the point of view of the promotion of the hydrodesulphurization reaction, this model appears to be ineffective.

The adsorption of type B brings about a considerable decrease in the electron density of butadiene antibonding orbitals and, consequently, a decrease in the aromaticity of the ring. Interesting changes are here observed in strengths of the bonds since C_2—C_3 and C_4—C_5 bonds are strengthened whereas S—C_2 and S—C_5 (more) and

TABLE I

Electron Densities for Two Bonding and Two Antibonding Butadienic π-Molecular Orbitals in Thiophene and in Models A, B and C

Orbitals	Thiophene	Model		
		A	B	C
π	3·9940	3·9776	3·9942	3·7090
π^*	0·1854	0·1043	0·1448	0·1888

TABLE II

Relative Weakening of Wiberg Bond Indices in Models A, B and C (Related to thiophene; per cent)
The parentheses contain the share of π-orbitals.

Bond	Model		
	A	B	C
S—C_2; S—C_5	−11·0 (−5·3)	−14·5 (−2·7)	−5·3 (−1·8)
C_2—C_3; C_4—C_5	2·2 (1·9)	1·4 (0·8)	−7·8 (−6·3)
C_3—C_4	−3·1 (−2·7)	−2·7 (−0·5)	−8·4 (−6·2)

C_3—C_4 (less significantly) bonds are weakened. The adsorption of type B thus supports the fragmentation of the ring to sulphur and butadiene, which is favourable for the further reaction course. Similar but much stronger changes are produced by the adsorption of type A. The weaker response of the electron structure of the ring during the adsorption of type B is brought about by the fact that the electron acceptor interacts with π-orbitals of the ring only indirectly. There is no overlap between these two types of orbitals; only static mixing of the orbitals appears as a result of the interaction with the acceptor electric field[24]. For the adsorption of type A, the overlap between electron acceptor and π-orbitals of the ring is different from zero and the static mixing is supplemented by dynamical mixing caused by direct interaction of the orbitals[24].

Further we also investigated a group of alkyl thiophenes. In this series of calculations we interpreted experimental equilibrium adsorption constant[25] in terms of theoretical quantities. Applicability of results of these calculations to correlations of experimental data is demonstrated on Fig. 4, in which quantities with a close physical correspondence are plotted against one another. These quantities are the position of the charge-transfer band[26] and the computed energy of highest occupied MO's. The correlation may be denoted as satisfactory.
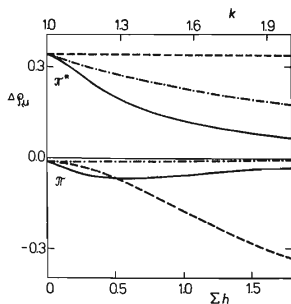

FIG. 2

Relative Electron Densities (related to butadiene) for Two Bonding and Two Non-bonding Butadienic π-Orbitals in Models A′ (full line) and C′ (dashed line) in Dependence on the Sum of Parameters h or, in Model B′ (dotted and dashed lines), in Dependence on Parameter k
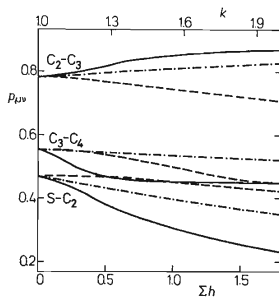
FIG. 3

π-Bond Orders in Model A′ (full line) and C′ (dashed line) in Dependence on the Sum of Parameters h or, in Model B′ (dotted and dashed lines), in Dependence on Parameter k

The logarithm of the equilibrium adsorption constant[25], which is proportional to the energy of adsorption, was correlated with indices which are proportional to the decrease in the energy accompanying the interaction between thiophene and the electron acceptor (for the definition *cf.* Eqs $(11)-(13)$). Since these indices are
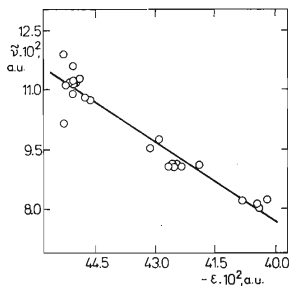

Fig. 4

Correlation of the Position of Bands in Tetracyanoethylene Charge-Transfer Spectra[26] with Energies of Two Highest Occupied MO's in the Series of Alkyl Thiophenes
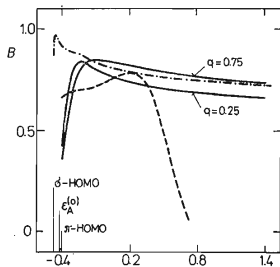

Fig. 5

Correlation Coefficient B Between the Experimental Quantity[25] (log K_{ads}) and Theoretical Indices $I_A = f(q)$ (full line), I_B (dotted and dashed lines) and I_C (dashed line) in Dependence on the Energy of the Acceptor Level

Highest occupied MO's in the series of alkyl thiophenes and the acceptor level determined from the ionization potential of Mo (ref.[27,28]) are denoted by arrows.
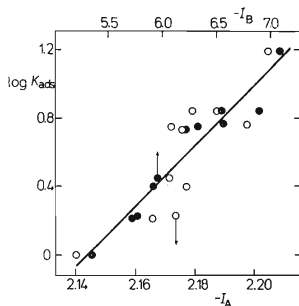

Fig. 6

Correlation of the Logarithm of the Relative Adsorption Constant[25] with the Theoretical Index of Adsorption Strength in the Series of Alkyl Thiophenes

○ Model A, $q = 0.75$, $\varepsilon_A = -0.11$ a.u., $B = 0.848$; ● model B, $\varepsilon_A = -0.45$ a.u., $B = 0.967$.

functions of the energy of the acceptor orbital, these correlations were performed for several different values of this energy. Dependences of the correlation coefficients on the acceptor energy level are plotted on Fig. 5 for each index type corresponding always to one of the interaction types A, B, or C. Before discussing the shape of the curves we must comment that this energy should be equal approximately to $\varepsilon_A^{(0)} = -0.41$ at. units, which was obtained from the ionization potential of molybdenum[27] (it is equal to the electron affinity of an Mo^+ ion) corrected by 4 eV (ref.[28]). This value corresponds to an isolated ion. For an ion on the catalyst surface this energy will be somewhat higher due to the effect of the crystal field, but it will not reach positive values.

From this point of view we may exclude model C, since in the region of the probable acceptor energy level it yields a low value of the correlation coefficient. In the region $\varepsilon_A = -0.2$ to -0.1 at. units, the indices for models A and B then give correlations of a comparable quality. Although for model B and $\varepsilon_A = -0.45$ at. units the correlation coefficient is extremely high, the physical meaning of the correlation in this region is questionable. The theoretical index is derived from the perturbation expansion which is accurate for relatively distant energy levels, but in our case we are in a close vicinity of the highest occupied σ-level and, moreover, under the highest occupied π-level. Therefore the correlation could be here only formal. Correlations between experimental quantities and theoretical indices for models A, B and for ε_A yielding maximal correlation coefficients are for illustration shown in Fig. 6.

The discussion of our results can be summarized in the following way. The most probable of the three investigated models of the adsorption of thiophene during hydrodesulphurization is model A, which is characterized by a strong promotion in the direction of the reaction course and leads to acceptable values of the correlation coefficient of the corresponding index and the experimental quantity. The adsorption of type B cannot be excluded, since it affects the adsorbed molecule in the same direction, even though to a lesser extent. In the region of the probable acceptor energy level it gives a comparable correlation coefficient. On comparing models A and B it might be assumed that the latter will be energetically less favourable. Finally, the adsorption of type C is not much probable, since it neither leads to changes promoting the reaction course nor does it yield any satisfactory correlation.

LIST OF SYMBOLS

B	correlation coefficient
$c_{i\mu}$	coefficient of the μ-th base orbital in the i-th molecular orbital
E	interaction energy (Eq. (10))
h	parameter of the HMO method (Eqs (2) and (6))

I_A, I_B, I_C theoretical indices proportional to the energy of interaction for models A, B and C, resp. (Eqs $(11)-(13)$).

k parameter of the HMO method (Eq. (3)).

occ   summation over occupied molecular orbitals (Eqs $(9)-(13)$).

$P_{\mu\nu}$ density matrix element between the μ-th and ν-th atomic orbital

q parameter allowing to respect different rates of the resonance integrals in the index I_A (Eq. (11)).

V_μ bonding saturation of the μ-th base orbital (Eq. (8)).

W_{AB} index of the bond between atoms A and B (Eq. (7)).

α Coulomb integral in the HMO method

β resonance integral in the HMO method

ε_A, ε_i energy of the acceptor level and of the i-th molecular orbital, resp.

π symmetry classification of bonds which are antisymmetric with respect to the joining link of atoms

ϱ_μ electron density in the μ-th base orbital (Eq. (9)).

σ symmetry classification of bonds which are symmetric with respect to the joining link of atoms

χ_h hybrid orbital which is occupied by the free electron pair of sulphur

REFERENCES

1. Weisser O., Landa S.: *Sulphide Catalysts, Their Properties and Applications*, p. 210. Academia, Prague 1972.
2. Schuit G. C. A., Gates B. C.: AIChE J. *19*, 417 (1973).
3. Lipsch J. M. J., Schuit G. C. A.: J. Catal. *15*, 179 (1969).
4. Hargreaves A. E., Ross J. R. H.: Proc. Sixth Int. Congr. Catal., London 1976, paper B 33.
5. Satterfield C. N., Roberts C. W.: AIChE J. *14*, 159 (1968).
6. Kieran P., Kemball C.: J. Catal. *4*, 394 (1965).
7. Völter J., Hermann M., Heise K.: J. Catal. *12*, 307 (1968).
8. Zyuba B. I., Krichko A. A.: Neftekhimiya *10*, 813 (1970).
9. Desikan P., Amberg C. H.: Can. J. Chem. *42*, 843 (1964).
10. Satterfield Ch. N., Modell M., Mayer J. F.: AIChE J. *21*, 1100 (1975).
11. Borodin V. N.: Neftekhimiya *15*, 248 (1975).
12. Pople J. A., Beveridge D. L.: *Approximate Molecular Orbital Theory*, p. 163. McGraw-Hill, New York 1970.
13. Bielefeld M. J., Fitts D. D.: J. Amer. Chem. Soc. *88*, 4804 (1966).
14. Clark D. T.: Int. J. Sulfur Chem., Part C *7*, 11 (1972).
15. Schulte K. W., Schweig A.: Theor. Chim. Acta *33*, 19 (1974).
16. Epiotis N. D., Cherry W. R., Bernardi F., Hehre W. J.: J. Amer. Chem. Soc. *98*, 4361 (1976).
17. Bak B., Christensen D., Hansen-Nygaard L., Rastrup-Andersen J.: J. Mol. Spectrosc. *7*, 58 (1961).
18. Ref. 12, p. 110.
19. Čársky P., Pancíř J., Zahradník R.: *Molecular Orbitals in Chemistry*, p. 112. Academia, Prague 1974.
20. Wiberg K.: Tetrahedron *24*, 1083 (1968).
21. Ref. 19, p. 109.
22. Hudson R. F.: Angew. Chem. *85*, 63 (1973).
23. De Beer V. H. J., Van Sint Fiet T. H. M.; Van der Steen G. H. A. M., Zwaga A. C., Schuit G. C. A.: J. Catal. *35*, 297 (1974).

24. Imamura A., Hirano T.: Amer. Chem. Soc. *97*, 4192 (1975).
25. Zdražil M.: This Journal *42*, 1484 (1977).
26. Zdražil M.: This Journal *40*, 3491 (1975).
27. Remy H.: *Lehrbuch der Anorganischen Chemie*, Band I, p. 106. Akademische Verlagsgesell-schaft, Leipzig 1954.
28. Murell J. N., Harget A. J.: *Semi-Empirical Self-Consistent-Field Molecular Orbital Theory of Molecules*, p. 47. Wiley-Interscience, London 1972.

Translated by K. Hlavatý.