HYDRODESULPHURIZATION OF ALKYLTHIOPHENES ON A COBALT-MOLYBDENUM CATALYST

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Hydrodesulphurization of twelve alkylthiophenes was studied by the method of competitive reactions at atmospheric pressure and 300—450°C. The reactivity increases with increasing molecular weight and the steric effect of substituent in positions 2 and 3 is similar. Spectra of tetracyanoethylene complexes of the alkylthiophenes were measured and relations to the trend in the reactivities were investigated. Evidences for the decisive role of hydrogenation of the aromatic ring in the hydrodesulphurization reaction have been collected.

Even though the catalytic hydrodesulphurization, which is employed in large scale by industry, has been studied for many times, opinions of its mechanism differ considerably[1,2]. Because the thiophene nucleus forms the basic structural unit of less reactive sulphur compounds in petroleum[3], the hydrogenolysis of thiophene has been often selected as the model reaction. Data have been published on products isolated from the reaction mixture[4-9], on the reaction kinetics with effects of products and other substances[4,7,9-14] included, on the exchange reaction between the thiophene hydrogen and deuterium[15], on the mathematical modelling of the reaction[16], *etc.*, all that on different, but most often cobalt–molybdenum catalysts.

As a continuation of studies of reactant structure — reactivity relations performed in our laboratory (*e.g.*[17-19]), we have investigated the hydrodesulphurization of twelve alkylthiophenes by the competitive method. A comparison of several alkylthiophenes in a non-competitive arrangement was made by Desikan and Amberg[5] and Obolentsev and coworkers[20]. We have chosen the method of competitive reactions as it is simple and its results are directly applicable for studying hydrogenolyses of mixtures of sulphur compounds which proceed during industrial hydrodesulphurizations.

EXPERIMENTAL

Catalysts and substances used. A cobalt–molybdenum catalyst crashed to the particle size of 0·25 to 0·5 mm, a product of Chemical Plants of the Czechoslovak-Soviet Friendship in Záluží (Co—Mo/Al_2O_3, 36 00), was employed. Thiophene, 2-methyl-, 3-methyl-, 2-ethyl-, and 2,5-dimethylthiophenes products of Fluka, were rectified before use. 2-Propylthiophene (b.p. 158°C) and 2-isobutylthiophene (b.p. 167°C) were prepared by acylation of thiophene by the corresponding anhydride[21] followed by reduction of the resulting acyl derivative by hydrazine[22]. 2,5-Dipropyl-

thiophene (b.p. 95°C/15 Torr) and 2,5-diethylthiophene (b.p. 182°C) were prepared by the same procedure from the corresponding 2-alkyl derivative. All the products were rectified and their purity checked by gas chromatography. 2,3,4-Trimethylthiophene was prepared from the tribromo derivative[23] and purified by simple distillation. Measured NMR spectra of the substances prepared confirmed their purity and the position of substituents on the nucleus. Of a mixture of 2- and 3-tert-butylthiophenes prepared by alkylating thiophene by tert-butyl chloride[24], the rectified fraction boiling at 161—2°C was employed in the experiments (ref.[24] 2-tert-butylthiophene b.p. 165°C, 3-tert-butylthiophene b.p. 172°C); according to its NMR spectrum, it was a mixture of 30% 3-tert-butylthiophene and 70% 2-tert-butylthiophene.

Apparatus and analysis of products. The hydrodesulphurization was being performed at atmospheric pressure in a glass flow reactor described in an earlier work from our laboratory[25]. Liquid products were frozen out (CO_2–ethanol or liquid N_2) and the residual gas analyzed by a chromatograph connected to the line after the condenser (katharometer, column 4 mm × × 1 m, Porapak Q 0·15—0·18 mm, 150°C, 50 ml/min H_2). Products from the condenser were analyzed on a chromatograph with flame-ionization detection, column 4 mm × 2·5 m, 10% Apiezon L on Chromosorb P 0·5—0·25 mm, temperature 80—150°C, carrier gas N_2 50—70 ml/min; the conditions were varied according to the composition of the reaction mixture.

Procedure. 2—5 g of the catalyst were being reduced in the reactor at 400°C for one hour and then thiophene was injected at feed $F = 0{\cdot}040$ mol/h and the partial pressure of thiophene $p = 0{\cdot}1$ atm. After hydrogen sulphide had achieved its steady state concentration at the reactor exit, *i.e.* after approximately 30 min, the catalyst became ready for the measurements. Mixtures of two alkylthiophenes and an internal standard, *i.e.* methylcyclohexane, isopropylcyclohexane or decaline, prepared with respect to possibilities of the chromatographic analysis, were injected during the competitive experiments. The molar ratio of the internal standard and the sum of both thiophenes in the mixture was equal approximately to 1 : 1. Corrections to an observed 3% dehydrogenation of methylcyclohexane was taken into account in our calculations. It has been verified for several pairs of alkylthiophenes that the results do not depend on the internal standard used. The degrees of conversion were calculated from changes in the ratios of alkylthiophenes and the internal standard. As we had no access to pure tert-butylthiophene isomers, their reactivity was evaluated from experiments with a mixture of 3-tert-butyl-, 2-tert-butyl-, 2,5-dimethylthiophene and isopropylcyclohexane. A higher reactivity of 2-tert-butylthiophene has been confirmed qualitatively for the feed of a mixture of 2-tert-butylthiophene and 3-tert-butylthiophene.

Spectrophotometrical measurements. Spectra of the complexes were measured by a Specord spectrophotometer (Zeiss, Jena) in a 5 cm cell. A 10^{-3}M solution of tetracyanoethylene in CH_2Cl_2 and a saturated solution in isooctane were employed. Tetracyanoethylene (Lachema) was subjected to two crystallizations from chlorobenzene and two sublimations.

RESULTS AND DISCUSSION

Selectivity to hydrogen sulphide and to a hydrocarbon with the same number of carbon atoms as the original alkylthiophene achieved at least 90% during preliminary experiments with pure substances as well as during competitive experiments. The extent of dealkylation and isomerization of original alkylthiophenes and cracking of products were therefore negligible.

The competitive experiments were evaluated without knowing the kinetic equation by an earlier described procedure[26]. Several pairs of conversions (Fig. 1) were ob-

tained for the pairs 2,5-dimethylthiophene/thiophene and 2-methylthiophene/thiophene at 400°C and different molar ratios of the thiophenes in feed α. The conversion of one reactant depends only on the conversion of the second one and not on α. (Expected independence[26] of the sum of partial pressures of both thiophenes Σp has been verified many times during our experiments in the range of 0·02 – 0·1 atm). The experimental dependence between the conversions thus conforms to the relation

$$x_i = 1 - (1 - x_j)^{R_{i/j}}, \qquad (1)$$

where x_i, x_j are the conversions of the reactants and $R_{i/j}$ is relative reactivity; this relation can be deduced[26] on the assumption that the partial pressure of thiophene in the numerator of the kinetic equation appears in its first power. This result is in accordance with the published kinetics of the reaction[10]. For further pairs of alkylthiophenes, 1 – 3 pairs of conversions have been obtained from the range of 20 to 70% at 400°C, $\alpha = 1$ and $\Sigma p = 0{\cdot}05$ atm. These have been used for evaluating the relative reactivities according to relation (*1*) (Table I).

The temperature dependence of the relative reactivity has been tested for the pairs 3-methylthiophene/thiophene and 2-isobutylthiophene/2,5-dipropylthiophene. The

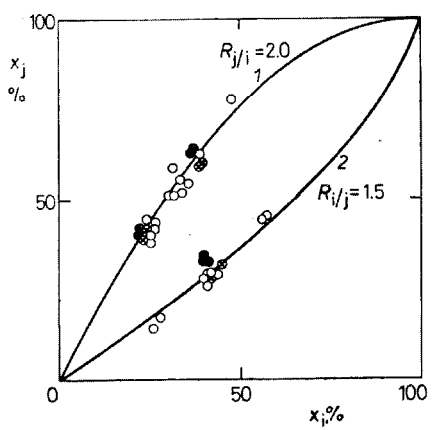

FIG. 1

Competitive Experiments with Mixtures of 2-Methylthiophene and 2,5-Dimethylthiophene with Thiophene at 400°C

1 i Thiophene, j 2,5-dimethylthiophene; *2* i 2-methylthiophene, j thiophene; ○ $\alpha = 1$, ● $\alpha = 3$, ⊗ $\alpha = 0{\cdot}3$, the curves are calculated with given values of R.

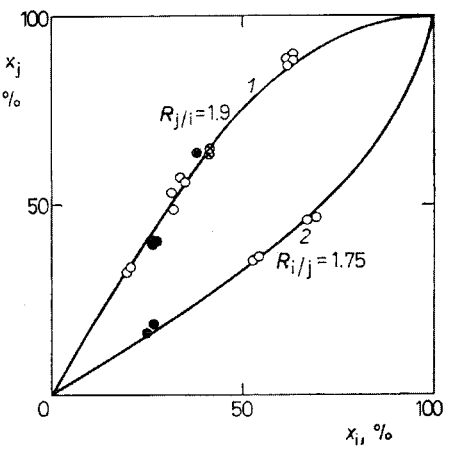

FIG. 2

Competitive Experiments with Mixtures 3-Methylthiophene + Thiophene and 2-Isobutylthiophene + 2,5-Dipropylthiophene at Different Temperatures

1 i Thiophene, j 3-methylthiophene; *2* i 2-isobutylthiophene, j 2,5-dipropylthiophene. ● 300°C, ○ 400°C, ⊗ 450°C.

TABLE I

Relative Reactivities of Thiophenes

Reactants		$R_{i/j}$
2-Methylthiophene	thiophene	$1{\cdot}5_0$
3-Methylthiophene	thiophene	$1{\cdot}9_0$
2,5-Dimethylthiophene	thiophene	$2{\cdot}0_0$
2-Ethylthiophene	thiophene	$2{\cdot}2_0$
2-Propylthiophene	2,5-dimethylthiophene	$1{\cdot}5_3$
2-Isobutylthiphene	2,5-dimethylthiophene	$1{\cdot}9_3$
2-Tert-butylthiophene	2,5-dimethylthiophene	$1{\cdot}1_0$
3-Tert-butylthiophene	2,5-dimethylthiophene	$0{\cdot}8_0$
2,3,4-Trimethylthiophene	2,5-dimethylthiophene	$1{\cdot}3_5$
2,5-Diethylthiophene	2-isobutylthiophene	$1{\cdot}0_0$
2,5-Dipropylthiophene	2-isobutylthiophene	$1{\cdot}7_5$
2,5-Diethylthiophene	2-propylthiophene	$1{\cdot}4_5$
2-Propylthiophene	2-ethylthiophene	$1{\cdot}3_5$

TABLE II

Relative Reactivities of Alkylthiophenes and Thiophene

Reactant	R	Reactant	R
Thiophene	1·0	2-Tert-butylthiophene	2·2
2-Methylthiophene	1·5	3-Tert-butylthiophene	1·6
3-Methylthiophene	1·9	2,5-Dimethylthiophene	2·0
2-Ethylthiophene	2·2	2,5-Diethylthiophene	4·2
2-Propylthiophene	3·1	2,5-Dipropylthiophene	6·8
2-Isobutylthiophene	3·9	2,3,4,-Trimethylthiophene	2·7

results on Fig. 2 show that the relative reactivities are independent of temperature from 300°C to 450°C within experimental error. This interesting result cannot be interpreted unambiguously as $R_{i/j}$ is the ratio of either the rate constants or products of adsorption and rate constants[26]; it might be a consequence of constant activation energies and heats of adsorption or of compensations of temperature changes of the adsorption and rate constants.

Relative reactivities are mutually recalculable quantities[27]. The values in Table I make it possible to calculate some of $R_{i/j}$ in two independent ways and make oneself

sure that the data are consistent; the agreement among $R_{i/j}$ calculated by the different ways was always good. Relative reactivities of alkylthiophenes with respect to thiophene were evaluated from reactivities in Table I and they are given in Table II.

The order of reactivity of reactants in a competitive arrangement need not generally agree with results from isolated experiments. Different trends in adsorption and rate constants may lead to quite opposite orders. This has been observed *e.g.* during hydrogenation of alkylbenzenes on a cobalt–molybdenum catalyst[28]. Therefore we have not been surprised by disagreement between the trend in Table II and other authors' results of experiments with separate thiophenes on a cobalt–molybdenum catalyst. So *e.g.* Desikan and Amberg[5] have found out that 3-methylthiophene reacts in the range 280–360°C more rapidly than 2-methylthiophene and that the reactivity of thiophene at 225°C lies between the both methylderivatives. Obolentsev and coworkers[20] have observed a small difference, more probably a decrease with increase in the molecular weight, in the series 2-octyl-, 2,5-dibutyl-, 2,5-diethylthiophene at 375°C. Givens and Venuto[29] have established a retardation of hydrodesulphurization in the series benzothiophene, 2-methylbenzothiophene, 3-methylbenzothiophene. In our case, the reactivity increases considerably with increasing molecular weight with the exception of tert-butyl derivatives. Simultaneously, the reactivity does not depend too much on the position of the substituents.

Reaction mechanisms which have been so far proposed differ from one another mainly in two points (for a review see *e.g.*[1]). The first one is the adsorption of thiophene; an S-atom bond, two-point adsorption on neighbouring carbons or a multi-

TABLE III

Position of Absorption Maxima of Alkylthiophene Complexes of Tetracyanoethylene ($\tilde{\nu}$, cm^{-1})

Donor	Dichloromethane			Isooctane		
	$\tilde{\nu}_{II}$	$\tilde{\nu}_{I}$	$\Delta\tilde{\nu}$	$\tilde{\nu}_{II}$	$\tilde{\nu}_{I}$	$\Delta\tilde{\nu}$
Thiophene	26 100	22 300	3 800	—	—	—
3-Methylthiophene	24 400	20 900	3 500	24 390	20 920	3 470
2,3,4-Trimethylthiophene	21 400	18 000	3 400	—	—	—
2-Methylthiophene	24 740	20 210	4 530	25 500	21 000	4 500
2-Ethylthiophene	24 640	20 030	4 610	25 400	20 600	4 430
2-Propylthiophene	24 530	19 950	4 580	—	—	—
2-Isobutylthiophene	24 510	19 900	4 610	—	—	—
Tert-butylthiophene[a]	24 500	20 000	—	—	—	—
2,5-Dimethylthiophene	23 900	18 080	5 820	24 630	18 730	5 900
2,5-Diethylthiophene	23 740	17 790	5 950	24 430	18 400	6 030
2,5-Dipropylthiophene	23 600	17 600	6 000	24 200	18 260	5 940

[a] Mixture of 2- and 3-isomer.

nuclear adsorption have been assumed. The second point is removal of sulphur from the molecule; it has been assumed that it is eliminated either without any hydrogenation or after hydrogenation of the ring.

Conceptions of the elimination of hydrogen sulphide from thiophene with resulting diacetylene[30] are in contradiction with the observation[5] stating that 3-methylthiophene yields isopentanes and isopentenes. The absence of tetrahydrothiophene in the products cannot disprove unambiguously the assumption that the hydrogenation of the ring is the first reaction step. Its reaction on the surface may proceed more quickly than its desorption. It is interesting to note that it had been found among the products only in experiments at increased pressure[6,31]. On the contrary, a hydrogenolysis of the C—S bond in a single step without the preceding hydrogenation of the ring seems to be improbable with respect to aromaticity of the nucleus. The C—S bond order is comparable to that of C—C bonds in thiophene[32,33] and its cancellation must include both the disturbance of aromaticity of the nucleus and interruption of the σ bond. For examination of adsorption of thiophene it is interesting to note that the π orbitals of the nucleus and not the n orbital of sulphur are energetically richest orbitals in thiophene[34]. This need not be of course of decisive importance but despite this it rather supports conceptions according to which thiophene is bonded to the catalyst through a π-system, similarly as it has been assumed for hydrogenation of alkylbenzenes[35].

According to its derivation[26] the relative reactivity is a parameter composed only of constants of kinetic equations. It is confirmed by the experimentally observed independence of this parameter on kinetic variables and by the possibility of its recalculation for different pairs of alkylthiophenes. Due to lack of knowledge of a precise kinetic scheme its composite kinetic constants cannot be determined unambiguously, however, in all cases it is related to decisive steps of the reaction and its logarithm is proportional to the change in the free energy. In our attempts to interpret

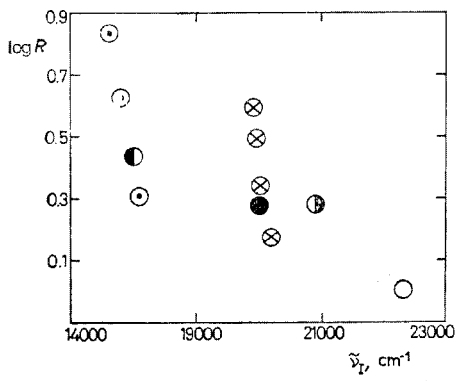

FIG. 3

Relative Reactivity of Alkylthiophenes with Respect to Thiophene *versus* Position of the Energetically Lower Band

⊗ 2-Alkylthiophenes; ⊙ 2,5-dialkylthiophenes, ○ thiophene, ◑ 3-methylthiophene, ◐ 2,3,4-trimethylthiophene, ● mixture of 2- and 3-tert-butylthiophenes.

the observed trend in the relative reactivities by comparisons with energetical characteristics of other physico-chemical processes in the alkylthiophene series, we were limited by insufficient amount of adequate data in the literature. Trying to record changes in the electron system of our set of reactants, we measured spectra of alkylthiophene complexes of tetracyanoethylene in the visible region. Spectra of these complexes of thiophene, 2- and 3-methylthiophene and 2,5-dimethylthiophene have been described and it has been shown that $\pi \rightarrow \pi^*$ transitions are involved[36,37]. All the alkylthiophenes exhibit two well distiguishable bands which overlap considerably only for thiophene, 3-methylthiophene and 2,3,4-trimethylthiophene where they had to be separated similarly as in the literature[36]. Results in Table III show that the ratio of maximal wavenumbers $\tilde{\nu}_{II}/\tilde{\nu}_{I}$ is higher for isooctane than for dichloromethane, so that on taking into account the well-known asymmetry of charge-transfer bands[38], the isooctane bands are separated better. The character of the spectrum is affected by the manner of the substitution; according to $\Delta\tilde{\nu}$, three alkylthiophene groups which differ by symmetry may be distinguished in the table. Highest values of $\Delta\tilde{\nu}$ are displayed by 2,5-substituted thiophenes analogically to the behaviour of *para*-dialkylbenzenes[38,39]. In each group the maxima shift to lower energies with increasing size of the alkyl groups. This is related to decrease in the ionization potential of the thiophenes[36,38,39] and, by our results, to increase in the relative reactivity. In contrast to the spectra, the three alkylthiophene groups are not evident from the reactivities so that no simple relation between the position of the maxima and reactivity can be found (Fig. 3). The data split into three groups and the distribution of thiophenes among them coincides with the distribution according to $\Delta\tilde{\nu}$: an approximate linear relation between log R and $\tilde{\nu}$ exists in each of the groups and the reactivity increases with decreasing wave number or ionization potential. For the interaction of the reactant with the catalyst is important not only the energy of energetically highest occupied π orbitals, which is taken into account through parameters $\tilde{\nu}_{I}$ and $\tilde{\nu}_{II}$, but, obviously, also steric factors which do not manifest themselves during ionization. These are very similar inside each of the thiophene groups, but the change among them proceeds in a stepwise manner, which explains the splitting of the data into the three groups. We have tried to obtain further information by measuring equilibrium constants of alkylthiophene complexes of tetracyanoethylene in chloroform, but we have observed a reaction between both components. The constants of four alkylthiophene complexes of iodine have been described in the literature[36]; they increase parallelly with the relative reactivity: thiophene $K = 0{\cdot}61$ mol^{-1}; 2-CH_3 0·79; 3-CH_3 0·81; 2,5-CH_3 1·19, but it is a small series for a reliable correlation of changes in the free energy. Steric effects from Table II are perhaps most useful for making conceptions of the mechanism. Substituents in positions 2 and 3 affect the reactivity similarly and the sterical screening of sulphur manifests itself not even in the case of 2,5-dipropylthiophene. The steric effect appears in tert-butylthiophenes but it is identical in positions 2 and 3; 2-tert-butylthiophene

reacts clearly even more quickly than 3-tert-butylthiophene. Steric effects thus stress the role of π electrons of the nucleus in the decisive reaction step and deny the conception of an adsorption or reaction in the vicinity of sulphur. Similar arguments have been employed in discussing the problem whether transitions in thiophene complexes of tetracyanoethylene are of the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ type[36]. Accordingly we deduce that the adsorption by the electron system of the nucleus and hydrogenation of the ring are the most important reaction steps. It could be then useful to search for analogies to hydrogenation of benzenoid aromates; actually, toluene and *m*-xylene react more quickly than benzene during competitive hydrogenation on a cobalt–molybdenum catalyst[28].

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