ADSORPTION OF THIOPHENES AND BENZENES
ON A COBALT–MOLYBDENUM CATALYST

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Adsorptivity on alumina and a cobalt–molybdenum catalyst was studied in homologic series of thiophenes, benzenes, cyclohexanes, and n-alkanes by a pulse chromatographic technique using helium as carrier gas at 350°C. Adsorptivities in homologic series of benzenes and thiophenes do not differ from one another and the logarithm of the retention volume depends linearly on the boiling point of the reactant. The nature of the interaction with the surface in relation to hydrodesulphurization of thiophenes and hydrogenation of benzenes is discussed as well as similarity of both reactions. Relative adsorption coefficients of thiophenes were compared with reactivities of thiophenes during hydrodesulphurization.

Stabilities of individual sulphur compounds during hydrodesulphurization differ from each other[1,2]. A deeper understanding of the relation between the reactivity and structure of a sulphur compound is inseparable from the knowledge of the reaction mechanism. So for example, without knowing it is difficult to say whether the increased stability of higher sulphur compounds, which was observed during an industrial hydrodesulphurization[3-5], is caused by the surface reaction or by transport phenonema. In this respect we have investigated the competitive reactivity in the homologic series of alkylthiophenes[6].

In this work we have aimed our efforts at finding the effect of the structure of the reactant on the assumed first reaction step, *i.e.* on the equilibrium adsorption of thiophenes. Starting from the hypothesis which states that the first step in hydrodesulphurization of thiophene is hydrogenation of its nucleus[7-9] analogous to hydrogenation of benzenes[6], we have also investigated the adsorption in the homologic series of benzenes.

The chromatographic technique employed is generally known. In works bearing on our problem, *e.g.* adsorption of alkanes and benzenes on alumina impregnated with salts[10] at 250°C has been studied in a similar manner as well as adsorption of basic compounds in the homologic series (benzene, toluene, cyclohexane, hexane, thiophene) on a cobalt–molybdenum catalyst at 150 − 300°C (ref.[11]). For our purposes we selected a still higher temperature of 350°C, which is already sufficient for practical hydrodesulphurization, and followed the behaviour of a greater number of members of the homologic series.

EXPERIMENTAL

Materials used. The catalyst (Co—Mo—Al_2O_3, mesh size $0.4-0.5$ mm) and thiophenes were the same as in the preceding work[6]. Alumina: CHEROX-33-00, mesh size $0.4-0.5$ mm. Remaining compounds were commercial products whose purity was determined chromatographically. Before entering the apparatus, helium passed through a Cu_2O column at 200°C and hydrogen through a column with a deoxidating palladium catalyst and a molecular sieve.

Apparatus. A stainless-steel column (length 2.5 or 1.5 m, I.D. 4 mm) packed with the catalyst was thermostated with a ± 0.5°C accuracy in an electric furnace. The maximal temperature gradient in the furnace was 5°C at 350°C. A metal evaporator heated to $350-400$°C and a linear piston feeder, which enabled a continuous feed of liquids, were in the line before the column. Substances were injected in pulses through the septum between the evaporator and the column. The column was followed with a katharometer heated to $200-240$°C. The apparatus was tested with the column packed with glass beads; up to the volume of the liquid sample of 10 μl, all substances yielded sharp symmetrical peaks with the same retention volume, larger pulses led to a deformation of peaks of highly boiling substances. Pulses which passed through the column could be trapped in a condenser at ~ -78°C and analyzed.

Working procedure. The catalyst was reduced by hydrogen at 400°C for 2 h, sulphurized, and stabilized by a continuous feed of a mixture of alkylthiophenes and benzenes with hydrogen at 400°C for 8 h. Hydrogen was replaced by helium (mostly at 50 ml/min), temperature reduced to 350°C, and the measurement started after ~ 10 h. Alumina was preheated before the experiments in hydrogen at 400°C for 2 h. Retention times t_r were read off at peak maximums. The column pressure drop was not higher than 50 kPa. As long as some dealkylation occurred, the record contained two to four only partially separated or deformed peaks. Basically, this does not prevent one from making use of the method[12]. By freezing out several identical pulses, a sample was obtained which was further subjected to chromatographic analysis (2-m×4-mm column, $0.2-0.3$ mm Rysorb BLK with 10% dinonylphthalate). The extent of the dealkylation was varied by changing the amount of the catalyst and by the carrier gas flow rate. It was verified by comparing records from the adsorption apparatus and from the analysis of frozen-out pulses that a definite peak actually corresponds with the unmodified injected substance. Dehydrogenation of cyclohexanes could be neglected. In the employed range $0.1-20.0$ μl of liquid sample ($0.1-5.0$ μl for low boiling and $1-20$ μl for highly boiling liquids), the retention time depended on the magnitude of the pulse n. The overall effect was the same as if the adsorption temperature of one adsorbate were changed (e.g.[13]). The t_r-n dependence for low boiling liquids was flat and it became steeper with increasing boiling temperature of the liquid. The t_r-n curves of individual adsorbates had similar shapes and never crossed one another. They were always extrapolated to the zero amount of the sample. The ageing of the packing, which leads to a decrease in t_r, was periodically tested by several adsorbates with different boiling points and retention times were recalculated to the initial state. Adsorption capacities aK were calculated from relation (1), in which K is the equilibrium adsorption constant, a is the activity of the unoccupied surface, Δt_r is the difference between retention times of the substance and nitrogen, F is the molar rate of flow of the carrier gas, W is the weight of the catalyst, and P is the mean pressure in the column (e.g.[13]):

$$aK = \Delta t_r F / WP \, . \qquad (1)$$

RESULTS

In experiments with alumina practically no decrease in the adsorption capacity was observed during the measurement. The extent of dealkylation was negligible even for the highest alkylthiophenes. A typical record for a mixture of alkylthiophenes is on Fig. 1. Adsorption capacities in hydrogen and helium were identical. The results are plotted in Table I and plotted against boiling points of substances T_b on Fig. 2.

Experiments on the cobalt–molybdenum catalyst were complicated by a decrease in the adsorption capacity during the measurement and by a higher extent of dealkylation. Both these effects decrease the accuracy of measurements but they cannot affect basic facts derived from the experiments and discussed in the following text. Ratios of adsorption capacities for individual substances were verified by experiments with mixtures of substances at different ages of the packing. During one series of experiments, *i.e.* after about three weeks, the adsorption capacity dropped to approximately one half. This change of the adsorption capacity is probably in no relation to the change of the sulphur content in the catalyst. It is due only to the injection of pulses of both sulphur and non-sulphur compounds, and the ageing of the catalyst proceeds more rapidly during experiments with highly molecular substances.
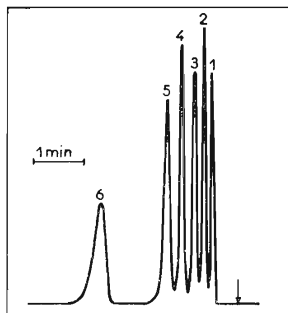

FIG. 1

Separation of Alkylthiophenes on Alumina

Carrier gas He 48 ml/min, pressure drop on the column 50 kPa, 350°C, 5 µl of the mixture, 2·5 m × 4 mm column, 22 g Al_2O_3. 1 Thiophene, 2 2-methylthiophene, 3 2-ethylthiophene, 4 2-propylthiophene, 5 2-isobutylthiophene, 6 2,5-dipropylthiophene.

FIG. 2

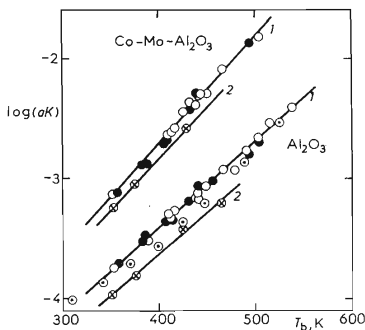The Dependence of Adsorption Capacities on the Boiling Point of Substances

Carrier gas He, 350°C, ⊙ Alkanes, 1 ○ benzenes, ● thiophenes, 2 ⊗ cyclohexanes.

TABLE I

Relative Adsorption Capacities[a] on Al_2O_3 and $Co-Mo-Al_2O_3$

Adsorbate	Al_2O_3	$Co-Mo-Al_2O_3$
Benzene	1.00^b	1.00^c
Toluene	1.65	1.70
o-Xylene	2.96	3.50
m-Xylene	2.52	3.20
p-Xylene	2.61	3.20
1,2,3-Trimethylbenzene	4.70	6.60
1,2,4-Trimethylbenzene	4.13	6.40
1,3,5-Trimethylbenzene	3.70	5.20
1,2,4,5-Tetramethylbenzene	6.52	10.8
Pentamethylbenzene	12.0	19.6
Hexamethylbenzene	21.7	—
Propylbenzene	—	5.70
Isopropylbenzene	—	4.78
Tert-butylbenzene	3.70	6.64
Naphthalene	9.57	—
2-Methylnaphthalene	16.3	—
Tetraline	6.31	—
Thiophene	1.09	1.00
2-Methylthiophene	1.65	1.60
3-Methylthiophene	1.74	—
2-Ethylthiophene	2.39	2.83
2-Propylthiophene	3.61	5.40
2-Isobutylthiophene	4.78	—
2,5-Dimethylthiophene	2.39	2.50
2,5-Diethylthiophene	5.13	—
2,5-Dipropylthiophene	11.0	—
Tert-butylthiophene[d]	—	6.87
Benzothiophene	8.70	18.5
Cyclohexane	0.65	0.78
Methylcyclohexane	0.87	1.17
Isopropylcyclohexane	2.17	3.47
cis-Decalin	3.37	—
Pentane	0.54	—
Hexane	0.76	—
Heptane	1.09	—
Octane	1.52	—
Nonane	2.39	—
Decane	3.37	—
Dodecane	7.39	—
Tetradecane	15.7	—

^{a} 350°C, carrier gas helium; ^{b} the absolute value was $aK = 1.80 . 10^{-4}$ mol/g MPa; ^{c} the absolute value was $aK = 7.41 . 10^{-4}$ mol/g MPa; ^{d} a mixture of 30% 3- and 70% 2-isomer, no separation was observed.

Apparently it can be connected with the deposition of carbon on the catalyst, whole intensity is considerable at the employed conditions[14]. The blocked part of the surface might be partially replaced by the surface of the deposited carbon so that the total surface remains approximately constant (during one series of measurements it dropped by about 10%), but the adsorption capacity of carbon is probably lower. The adsorption capacity can be partially recovered by heating in hydrogen. The dealkylation of thiophenes was somewhat more rapid than that of benzenes. It proceeds in a stepwise manner, *e.g.* for 2-propylthiophene not only thiophene was found at the column outlet, but also 2-methyl- and 2-ethylthiophene. Dealkylation of 2-tert-butyl- and 3-tert-butylthiophene was negligible. For 2-isobutylthiophene, 2,5-diethyl-thiophene, and 2,5-dipropylthiophene the extent of dealkylation was so large that no direct data could be obtained and relative adsorption coefficients, which were employed in further work, were estimated by interpolation. Benzothiophene was quite stable in this respect. Results obtained from the cobalt–molybdenum catalyst are also given in Table I and on Fig. 2.

DISCUSSION

The behaviour of hydrocarbons on alumina, which is illustrated on Fig. 2, is quite similar to that described by Brookman and Sawyer[10] for alumina impregnated with salts at 250°C (NaCl, Na_2SO_4, Na_2MoO_4 etc.). They observed that the dependence of $\log(aK)$ on the boiling point T_b was in the case of unbranched alkanes slightly curved. The extent of adsorption for cyclic alkanes was lower than for n-alkanes, most probably due to different geometric configurations and flexibilities of these molecules. Aromatic hydrocarbons were adsorbed to a higher extent than saturated ones, which the authors ascribed to a π-interaction between the nucleus and the surface. The $\log(aK)$ *vs* T_b dependence was linear for methylbenzenes, for higher alkyls than methyl a certain steric hindrance of the π-interaction became apparent.

A comparison with our results shows that the difference between absolute values of adsorption capacities corresponds roughly with the difference between temperatures of the measurements, *e.g.* for benzene on impregnated alumina at 250°C it was $\sim25 . 10^{-4}$ mol/g MPa (ref.[10]) whereas on our alumina it was $\sim2 . 10^{-4}$ mol/g MPa at 350°C (Table I). The behaviour in the homologic series is similar in both cases, however, we observed generally smaller differences between individual structural types and lower slopes of the straight lines $\log(aK) - T_b$, *i.e.* about 0·007 on Fig. 2 and 0·010 in ref.[10]. This can be obviously related to the higher temperature of our measurements. The steric hindrance of the π-interaction due to higher alkyls was also lower, but still evident, *i.e.* for instance in the case of tert-butylbenzenes $(aK)_{rel} = 3·7$ and 1,2,4-trimethylbenzene $(aK)_{rel} = 4·13$ even though their boiling points are identical, $T_b = 441$ K, or for 1,2,4,5-tetramethylbenzene $(aK)_{rel} = 6·5$ and $T_b = 467$ K, and, in contrast to this, for tetraline $(aK)_{rel} = 6·3$ and $T_b = 479$ K. (These

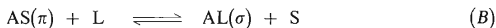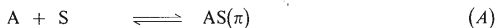results were confirmed by experiments during which both substances of the pair were injected simultaneously.)

Moreover, our results show that the behaviour of thiophenes and aromatic hydrocarbons is similar. Analogous alkylderivatives in both homologic series posses boiling points which are extremely close to one another and they cannot be separated by chromatography on Al_2O_3 or $CoO-MoO_3-Al_2O_3$. However, in the series of thiophenes there is a possibility of an interaction between the catalyst and the free electron pair of sulphur; it should be most favourable if the plane of the ring is perpendicular to the surface. On the other hand, the interaction through the π-system will be maximal for a parallel orientation of the molecule and the surface, similarly as in the case of benzens. As long as the orientation of thiophenes towards the surface is the same as that of benzenes, contributions from alkyl groups are similar in both series and the interaction of the free electron pair on sulphur becomes weak. The perpendicular orientation between the thiophene ring and the surface results in a strong interaction with the free pair of sulphur and the interaction of the surface with methyl in position 3 is practically excluded: this should also lead to a steric hindrance of the sulphur interaction by alkyl groups in position 2. The effect of the substitution should then differ from the benzene series, which was not observed. Apparently the interaction of the free electron pair with the surface is not significant. This is in agreement with a similar behaviour of naphthalene and benzothiophene.

On the cobalt–molybdenum catalyst the situation is much the same as on alumina, only the adsorption capacity of the not too frequently employed catalyst is by an order higher. Simultaneously, their surfaces are comparable $(200-250 \text{ m}^2/\text{g})$ and differ consequently from each other qualitatively. The difference between benzenes and cyclohexanes is smaller than on alumina. Faskhutbinov and coworkers[11] described the adsorption of benzene, toluene, cyclohexane, and thiophene on a cobalt–molybdenum catalyst in helium or hydrogen at $150-300°C$. They established an order in the adsorptivities of substances which corresponds with our data on Fig. 2 and a decrease of differences between adsorptivities with increasing temperature. The adsorptivity in hydrogen was lower than in helium, but the difference also decreased with increasing temperature and at $300°C$ it amounted to only about 20%. Apparently the nature of interactions of reactants with different alumina and the cobalt–molybdenum catalyst is qualitatively identical.

An important question arises whether the observed adsorption behaviour of benzenes should be actually related to hydrogenation and the behaviour of thiophenes to hydrodesulphurization. During the hydrogenation of benzenes, the existence is assumed of π- and σ-complexes of the reactant with the electron acceptor centre on the surface, i.e. with adsorbed hydrogen or a metal $(e.g.$[15,16]$)$. Many complexes of both these types with different particles or molecules have been described in the series of aromatic compounds[17]. The substitution of benzene by alkyl groups af-

fects the stability of complexes of both types in a different manner. The effect of alkyl groups is roughly additive for π-complexes; their stability increases regularly with the molecular weight and differences between positional isomers are small (*e.g.* benzenes–tetracyanoethylene[18], benzenes–HgCl$_2$[19], benzenes–HCl in toluene[20]). A quite different effect is exhibited by alkyl groups on σ-complexes; the stability does not increase regularly with the molecular weight and positional isomers differ considerably from each other, *i.e.* the positional effect of methyl groups outweighs the effect of their number (*e.g.* benzenes–HF in liquid HF, ref.[17,21]). The change of the stability due to the substitution is considerably greater than for π-type complexes (Fig. 3).

Let us assume the following scheme for the hydrogenation

$$A + S \rightleftharpoons AS(\pi) \tag{A}$$

$$AS(\pi) + L \rightleftharpoons AL(\sigma) + S \tag{B}$$

$$AL(\sigma) + \ldots \rightleftharpoons \ldots\ldots\ldots\ldots \tag{C}$$

in which A is benzene, S is a site on the surface with the ability to form the $AS(\pi)$ π-complex, and L is a site on the surface with the ability to form the $AL(\sigma)$ σ-complex. The equilibrium in steps (A) and (B) is described by the relations

$$K_1 = \frac{a(AS(\pi))}{a(A)\, a(S)} \tag{2}$$

$$K_2 = \frac{a(AL(\sigma))\, a(S)}{a(AS(\pi))\, a(L)} \tag{3}$$

in which K_i are equilibrium constants and a (i) activities. Further it is assumed that the equilibrium in step (C) of the reaction scheme need not establish during the reaction. We observed that the effect of the substitution on the adsorption capacity aK is equal to that which might be expected for K_1 (resp. for $a(S)\,K_1$) and quite different from that expected for K_2 (resp. for $a(L)\,K_2$) (Fig. 3). Consequently, either step (B) cannot proceed in the absence of hydrogen (Co—Mo—Al$_2$O$_3$) or hydrogen--activating centres (Al$_2$O$_3$), *i.e.* $aK = a(S)\,K_1$, or it proceeds extremely rapidly and in equilibrium, *i.e.* $aK = K_1[a(S) + K_2\, a(L)]$, but $a(L)\,K_2 \ll a(S)$. The same situation might be assumed also for thiophenes, *i.e.* the first two steps of the hydro-desulphurization would be analogous to steps (A) and (B) of the hydrogenation of benzenes. (The σ-complex on sulphur should be distinguished from that in which the interaction with the free electron pair of sulphur becomes effective and which has been proposed in the literature[22]).

The linear relation between $\log (aK)$ and T_b in the homologic series is a rule in gas-liquid chromatography and it is a result of the validity of Trouton's rule in the homologic series[23]. According to literature data[24], Trouton's constants of benzenes and thiophenes are practically identical. The linear dependence in the gas–catalyst system (Fig. 2) can be a result of the similar relation between adsorption quantities, i.e. $\Delta H_a / T_b = \Delta S_a = $ const., where ΔH_a and ΔS_a are the enthalpy and entropy of adsorption, resp. The slope of the straight line for the Co—Mo—Al$_2$O$_3$ catalyst on Fig. 2 yields the entropy of adsorption of about 100 J/mol (the entropy of vaporization is ~88 J/mol (ref.[24])) and enthalpies of adsorption are by 4—10 kJ/mol higher than enthalpies of vaporization, which are in the range 30—42 kJ/mol (ref.[24]).

If we assume that the activity of the surface is identical for all substances, the data in Table I represent relative adsorption coefficient K and may be separated from relative reactivities R_{rel} according to the following relation (for instance ref.[25])

$$R_{rel} = K_{rel} k_{rel}, \tag{4}$$

where K_{rel} is the relative adsorption coefficient. According to the kinetic scheme, k_{rel} is either the relative rate constant of the rate-determining step or it is the relative product of rate constants of consecutive steps with identical rates (for instance ref.[26]). We may expect that the trend of k_{rel} values due to changes of the structure will be the same as in the case of rate constants obtained from kinetic data of individual substances or as for reaction rates at conditions when the surface is almost occupied and the rates are proportional to rate constants. The separation of competitive relative reactivities into adsorption and rate constants and a comparison with available literature data are made in Table II. Values of K_{rel} and k_{rel} change in the opposite
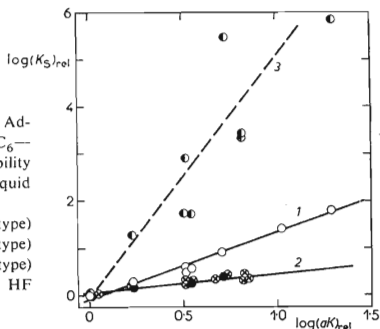

FIG. 3

The Relation between the Relative Adsorption Capacity for Alkylbenzenes (C_6—C_{11}) on Co—Mo—Al$_2$O$_3$ and Stability Constants K_s of Complexes in the Liquid Phase

1 ○ Benzenes–tetracyanoethylene (π-type) (ref.[18]); 2 ● benzenes–HgCl$_2$ (π-type) (ref.[19]), ⊗ benzenes–HCl in toluene (π-type) (ref.[20]); 3 ◐ benzenes–HF in liquid HF (σ-type) (ref.[17,21]).

direction with increasing molecular weight. The decrease in k_{rel} with increasing molecular weight is in accordance with the behaviour of rate constants described in the literature (Table II). Similarly, during the hydrogenation of benzenes an opposite trend was observed in changes of K_{rel} and k_{rel} with changes of the structure, which was accompanied by a decrease in k_{rel} with increasing molecular weight[29]. Our results are thus in agreement with the concept of the similarity between hydrogenation of benzenes and hydrodesulphurization of thiophenes.

TABLE II

Separation of the Competitive Relative Reactivity into the Adsorption and Kinetic Terms

Reactant	R_{rel} [a]	K_{rel}	k_{rel} [c]	k_{rel} [d]	r_{rel} [e]
Thiophene	1·0	1·0	1·00	1·00	1·00
2-Methylthiophene	1·5	1·6	0·94	—	—
2-Ethylthiophene	2·2	2·8	0·79	—	0·71
2-Propylthiophene	3·1	5·4	0·57	—	—
2-Isobutylthiophene	3·9	5·6[b]	0·70	—	0·52
3-Methylthiophene	1·9	1·7[b]	1·10	—	—
2-Tert-butylthiophene	2·2	6·9	0·32	—	—
3-Tert-butylthiophene	1·6	6·9	0·23	—	—
2,5-Dimethylthiophene	2·0	2·5	0·80	—	—
2,5-Diethylthiophene	4·2	5·8[b]	0·72	0·48	—
2,5-Dipropylthiophene	6·8	15·2[b]	0·45	—	—

[a] Ref.[6]. [b] Interpolated from the curve on Fig. 2. [c] Calculated from Eq. (4); values of R_{rel} taken from[6], values of K_{rel} from Table I. [d] The relative rate constant, pressure 4 MPa, Co—Mo—Al$_2$O$_3$, injection of individual substances (ref.[27]). [e] The relative rate of the hydrodesulphurization at 4 MPa on the Pt catalyst; injection of individual substances, a fully occupied surface and proportionality between the rate and the rate constant are assumed (ref.[28]).

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