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CHROMATOGRAPHY OF HYDROCARBONS ON MOLYBDENUM SULPHIDE

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SUMMARY

The adsorption properties of molybdenum sulphide have been investigated by gas chromatography. The retention volumes per unit surface area, $V_{A,1}$, and the differential molar changes in internal energy, $\Delta\bar{U}_1$, at small (zero) sample size for C_5–C_{12} *n*-alkanes, C_6–C_{12} monoalkylbenzenes and some polymethylbenzenes have been determined. Molybdenum sulphide protected against oxidation is a non-specific adsorbent. Owing to its lamellar structure, like graphite it separates the structural and geometric isomers of hydrocarbons of different classes. Separations of an molybdenum sulphide may be performed at a lower temperature than on graphitized thermal carbon black.

INTRODUCTION

Crystals of molybdenum sulphide (MoS_2) have a hexagonal structure with a well shaped basal face (0001) filled with sulphur atoms. A unit cell of hexagonal MoS_2 has the parameters $a = 3.16$ and $c = 12{,}29$ Å (ref. 1). The lamellar structrue is made up of S–Mo–S units, the bonds being due to intermolecular forces.

The adsorption of molecules of different groups with regard to their ability to undergo specific intermolecular interactions on MoS_2 has been studied by a few workers using static methods alone[2–7]. The surface of MoS_2 is subject to rapid oxidation and is, therefore, usually chemically non-homogeneous. Hence, the adsorption of molecules capable of specific intermolecular interactions is substantially greater than that of molecules adsorbing mainly due to non-specific interactions. However, the adsorption isotherm of *n*-heptane on MoS_2 indicated geometrical homogeneity of the surface[3].

In a previous paper[8] we described methods for obtaining different samples of molybdenum sulphide and, as was shown by gas chromatography, some samples had a nearly homogeneous non-specific surface. The retention volumes of *n*-alkanes both on these adsorbents and on graphitized thermal carbon black (GTCB)[9,10] are greater than those of benzene and mono-*n*-alkylbenzenes having the same number of carbon atoms (toluene has a retention volume close to that of *n*-heptane, as in the case of GTCB[10,11]). This may indicate that adsorption on non-oxidized molybdenum sulphide takes place due to non-specific intermolecular interactions.

This paper deals with the determination of the thermodynamic characteristics of adsorption on molybdenum sulphide by gas chromatography at zero surface coverage (retention volumes, $V_{A,1}$, equal to the Henry constants, K_1, differential molar changes in internal energy, $\Delta \bar{U}_1$[10,11]) for *n*-alkanes, benzene and monoalkyl- and polymethylbenzenes. The influence of substitution in the benzene ring in polymethylbenzenes on adsorption on MoS_2, in comparison with the chain extension in isomeric mono-*n*-alkylbenzenes, has been investigated. The determination of the thermodynamic characteristics of retention on MoS_2 is of interest regarding both the study of adsorbate–adsorbent intermolecular interactions and the estimation of the possibility of employing different new adsorbents in the gas chromatographic analysis of some complex mixtures.

EXPERIMENTAL

MoS_2 samples synthesized from $Mo(CO)_6$ were used as the main adsorbent. X-ray analysis showed that the sample is MoS_2 with a hexagonal structure. Electron-microscopic studies (Fig. 1) showed that the crystals of MoS_2 are thin plates of about $2 \times 2 \times 0.1$ μm. This permits us to conclude that the surface of MoS_2 is formed mostly by basal planes. The sample was introduced into the pores of Chromosorb W (MoS_2 content 30% of the support weight). The specific surface area(*s*) of the adsorbent (MoS_2 and support) determined by the BET method from low-temperature krypton adsorption was 2 m²/g. A sample of MoS_2 obtained from ammonium paramolybdate[8] on Chromosorb W (MoS_2 content 50% of the support weight, $s = 3$ m²/g) has also been studied.

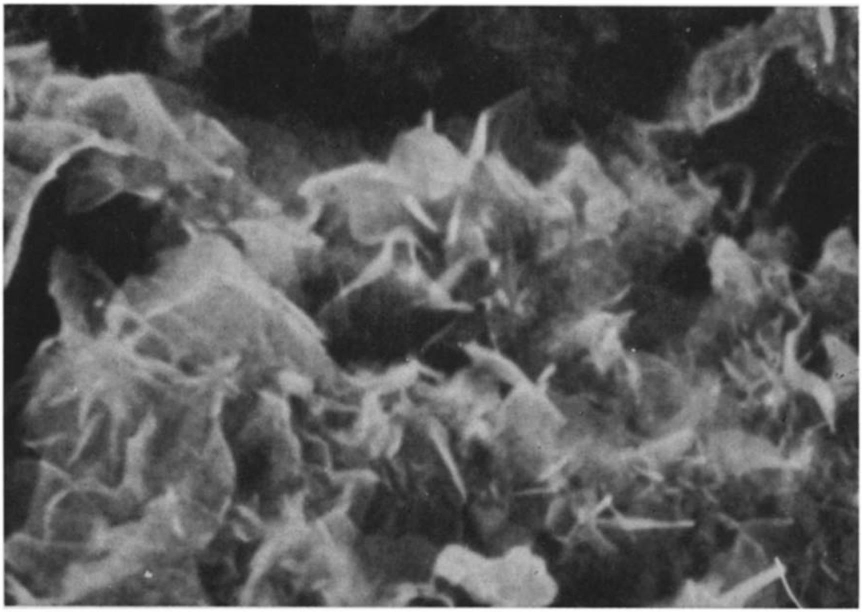


Fig. 1. Electron micrograph of the MoS_2 used.

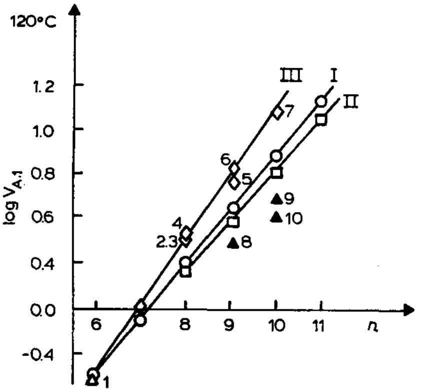
The studies on MoS_2 were carried out on Tsvet-I and Tsvet-102 chromatographs with flame-ionization detectors and pure nitrogen as the carrier gas, from which oxygen had been removed by a low-temperature chromium–nickel catalyst and water by freshlycalcined zeolite. The thermodynamic characteristics of the retention on MoS_2 were determined in the range 20–170°. The retention volumes on MoS_2 remained constant at temperatures up to 170°. However, when the column temperature was increased to 300°, even if pure helium or nitrogen was used as the carrier gas, greater $V_{A,1}$ values were obtained for diethyl ether and hydrocarbons (toluene, *n*-heptane). In this instance the peaks were asymmetric and very broad, which may be indicative of an increase in the surface non-homogeneity of the adsorbent due to the formation of oxygen complexes (from traces of oxygen in the carrier gas) and the emergence on the surface of cracks and other defects of higher adsorption energy. Therefore, reproducible thermodynamic characteristics of retention on molybdenum sulphide were obtained only at temperatures lower than 170°. However, molybdenum sulphide can be used to separate saturated hydrocarbons at temperatures up to 260° (at higher temperatures it is necessary to treat the sample with hydrogen sulphide[8]).

RESULTS AND DISCUSSION

Figs. 2–4 show plots of log $V_{A,1}$ and $-\Delta \bar{U}_1$ against carbon number (n) for different *n*-alkanes and polymethyl- and monoalkylbenzenes. The dependences for *n*-alkanes are nearly linear ($V_{A,1}$ is expressed in cm^3/m^2, *i.e.*, in μm):

$$\log V_{A,1}\ 120° = -3.18 + 0.45\,n \qquad (1)$$

$$-\Delta \bar{U}_1 = 14.3 + 4.7\,n \quad \text{kJ/mole} \qquad (2)$$



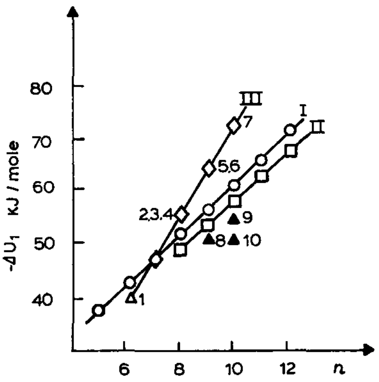


Fig. 2. Dependence of log $V_{A,1}$ on the number of carbon atoms (n) in molecules of *n*-alkanes (○, curve I), mono-*n*-alkylbenzenes (□, curve II), benzene (△, 1), polymethylbenzenes (◇, curve III), *m*-xylene (2), *p*-xylene (3), *o*-xylene (4), 1,3,5- and 1,2,4-trimethylbenzenes (5,6), 1,2,4,5-tetramethylbenzene (7) and branched monoalkylbenzenes [▲: isopropylbenzene (8), *sec.*-butylbenzene (9) and *tert.*-butylbenzene (10)].

Fig. 3. Dependence of $\Delta \bar{U}_1$ on the number of carbon atoms (n) in molecules. Symbols as in Fig. 2.

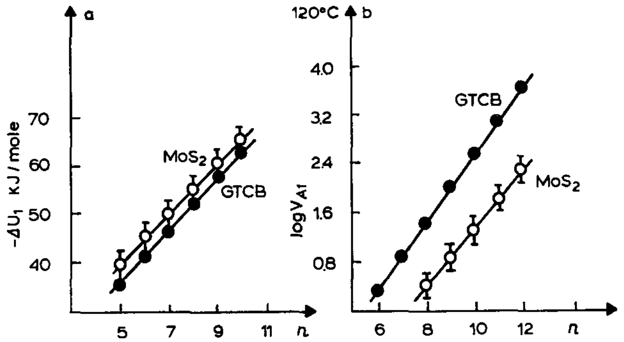


Fig. 4. (a) Dependence of $\Delta \bar{U}_1$ on the number of carbon atoms (n) in molecules of n-alkanes on MoS_2 and GTCB. (b) Dependence of $\log V_{A,1}{}^{120°}$ on the number of carbon atoms (n) in molecules of n-alkanes on MoS_2 and on GTCB. Measurement errors are indicated by vertical bars.

The increment increase in $\log V_{A,1}$ per CH_2 group for n-alkanes on GTCB (0.55) is greater than that on molybdenum sulphide[9]. This indicates a better selectivity of GTCB as regards the separation of n-alkanes.

Benzene molecules can interact specifically with the polar surface of the adsorbent[10,12]. However, in adsorption on MoS_2 (and in adsorption on GTCB[9,10,13]) the energy of benzene adsorption is smaller than that of n-hexane adsorption. This leads to the conclusion that the character of the interaction of benzene molecules with the surface of pure molybdenum sulphide is non-specific.

Likewise for GTCB[9,10,13], the increase in $V_{A,1}$ and $-\Delta \bar{U}_1$ for mono-n-alkylbenzenes (from ethylbenzene) occurs in the same manner as for n-alkanes. The following approximate equations have been obtained for mono-n-alkylbenzenes ($n \geqslant 8$) on MoS_2:

$$\log V_{A,1}{}^{120°} = -3.04 + 0.43\,n \tag{3}$$

$$-\Delta \bar{U}_1 = 11.6 + 4.7\,n \text{ kJ/mole} \tag{4}$$

As can be seen from eqns. 2 and 4 and Fig. 3, the graph representing the dependence of $-\Delta \bar{U}_1$ on n for mono-n-alkylbenzenes is parallel to but lower than that for n-alkanes; $-\Delta \bar{U}_1$ values for mono-n-alkylbenzenes are smaller by approximately 3 kJ/mole than those for the n-alkanes with the same carbon number.

Figs. 2 and 3 show that $V_{A,1}$ and $-\Delta \bar{U}_1$ for isopropylbenzene are lower than those for n-propylbenzene (as in adsorption on GTCB[9,10,13]).

Fig. 3 also shows that the lowest value of $-\Delta \bar{U}_1$ for butylbenzenes was obtained with the most branched molecule, *tert.*-butylbenzene. The value $-\Delta \bar{U}_1$ of *sec.*-butylbenzene lies between the values for *tert.*- and n-butylbenzene.

In the adsorption of polymethylbenzenes on MoS_2 (from toluene), considerably greater $-\Delta \bar{U}_1$ values are observed with increase in the number of methyl groups in the ring in comparison with the isomeric mono-n-alkylbenzenes. The increase in $-\Delta \bar{U}_1$ from toluene to ethylbenzene is only 1 kJ/mole, while the average value for xylenes is 8 kJ/mole greater than that for toluene. The average $-\Delta \bar{U}_1$ values for trimethylbenzenes are also considerably greater than that for isomeric n-propylbenzene. This indicates that when adsorption on MoS_2 takes place as well as on GTCB[9,10,13,14], substitution in the ring in polymethylbenzenes is not equivalent to extension of the side-chain in isomeric mono-*n*-alkylbenzenes. This may be accounted for by the configurational effects of the structure of the molecules of alkylaromatic compounds on the MoS_2 surface similar to those studied for the adsorption of polymethyl and mono-*n*-alkyl derivatives of benzene on GTCB. The influence of differences in the electronic structure of these isomers on adsorption on MoS_2 and on GTCB[13] is probably insignificant. Thus, similar regularities in the adsorption of *n*-alkanes and alkylbenzenes are observed both on MoS_2 and on GTCB.

Fig. 4 shows that the $-\Delta\bar{U}_1$ values for the adsorption of *n*-alkanes on MoS_2 are close to those on GTCB. Let us compare only the dispersion part of the intermolecular interaction of the *n*-alkane molecules with the basal plane of molybdenum sulphide, formed by sulphur atoms, and with the basal plane of graphite. In the first instance the contribution of the dispersion intermolecular interaction energy is effected by the following factors. The greater polarizability of sulphur atoms in an analogous valence state ($\alpha_S = 5.3$ Å^3, ref. 15) compared with the carbon atoms in graphite ($\alpha_C = 0.94$ Å^3, ref. 10) should lead to an increase in the energy of dispersion intermolecular interactions with the MoS_2 basal plane. An increase in equilibrium distance and a decrease in the concentration of adsorption centres formed by sulphur atoms of greater radius than that of carbon has the opposite influence. However, the average temperature at which $-\Delta\bar{U}_1$ values on MoS_2 have been determined is considerably lower than that on GTCB, which also may result in greater $-\Delta\bar{U}_1$ values on MoS_2 because $-\Delta\bar{U}_1$ decreases with increase in temperature[10].

The most important thermodynamic characteristics of adsorption in chromatography (connected with adsorbate–adsorbent intermolecular interactions) determining the retention of molecules is Henry's constant, $K_1 = V_{A,1}$ (ref. 10). Fig. 4b shows that the $V_{A,1}$ values on MoS_2 were much smaller than those for the same *n*-alkane on GTCB owing to the influence of an entropy factor. Comparison of the basal planes of an MoS_2 crystal and of graphite (Fig. 5) shows that when adsorption on MoS_2 takes place there possibly exists a stronger retardation of translational motion than on the basal planes of graphite. Hence, judging from the thermodynamic characteristics of the retention of molecules of hydrocarbons with different electronic

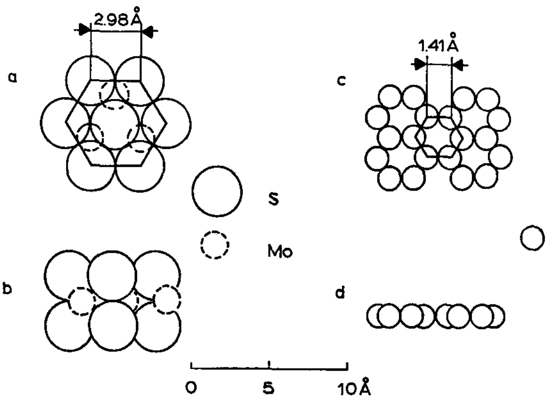


Fig. 5. Structures of MoS_2 (a,b) and graphite (c,d) layers.

configurations (molecules of A and B groups according to the Kiselev classification[10,14]), molybdenum sulphide may be classed as a non-specific adsorbent (adsorbents of type I in the same classification). In accordance with Fig. 1, this allows us to conclude that the main role in the adsorption of any hydrocarbon molecules on MoS_2 is played by non-polar basal planes (0001) formed by sulphur atoms.

It is known that non-specific adsorbents such as GTCB, the surface of which is formed by basal planes of graphite crystals, are highly selective in gas chromatography with respect to structural and geometric isomers[10,11,16]. Because of the generally planar surface of molybdenum sulphide, this non-specific adsorbent was further used for the separation of molecules with different geometrical structures and possible orientation on the basal plane at column temperatures lower than those for GTCB (according to Fig. 4). The separation of polymethylcyclohexanes is an example. Fig. 6 compares the separation of isomers of 1,2,3,5-tetramethylcyclohexane on MoS_2 and GTCB. The separation takes place due to the difference in the structures of these molecules, as the average distances of some links of the molecules from the planar surface of these isomers are different[16]. According to Figs. 3 and 4, the temperature of a column for which the separation of 1,2,3,5-tetramethylcyclohexane on MoS_2 is efficient is considerably lower than that of a column with GTCB.

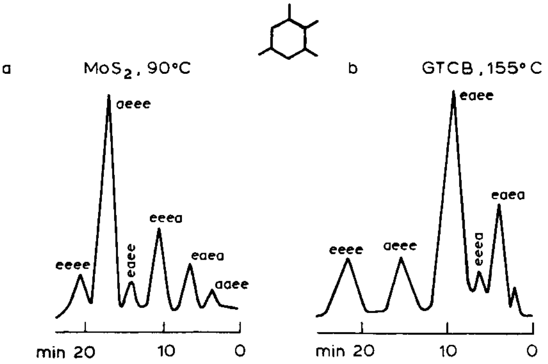
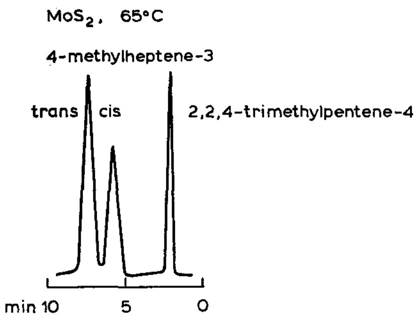


Fig. 6. Chromatograms of 1,2,3,5-tetramethylcyclohexane isomers on MoS_2 (a) and on GTCB (b). Column length, 1.2 m; I.D., 3 mm; carrier gas, He; flame-ionization detector. The isomer concentrations in (a) and (b) are different because the results on GTCB were obtained earlier with another isomer mixture[16]. The total surface areas of adsorbent, A, are: $A_{MoS_2} = 11$ m^2, $A_{GTCB} = 32$ m^2; for $V_{A,1}$, see Figs. 3 and 4.

The strong influence of the geometric structure of molecules applies in the separation of *cis* and *trans* isomers. Isomers with *cis* configurations have, as a rule, shorter retention times on MoS_2 than *trans*-isomers, as is also the case with separations on GTCB[14,16]. Fig. 7 shows the separation of *cis*- and *trans*-4-methylheptene-3[17]. The separation of naphthalene, tetralin and decalin (Fig. 8) indicates the predominant influence of geometric structure and the possible orientation of an adsorbed molecule on their retention times. The molecules of each of these compounds contain ten carbon atoms. With decalin the column with MoS_2 yields two peaks in exact correlation with the structures of *cis*- and *trans*-decalin. Tetralin is more strongly retained than decalin owing to its more planar structure. The most planar naphtha-



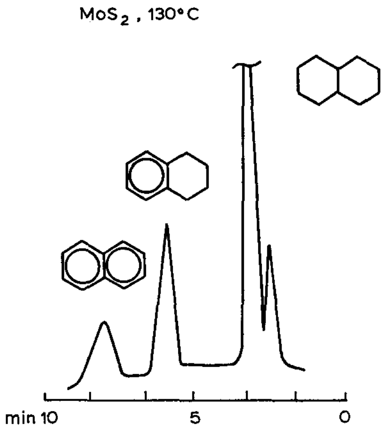


Fig. 7. Chromatogram of 2,2,4-trimethylpentene-4 and *cis*- and *trans*-4-methylheptene-3 on MoS_2. Column length, 0.9 m; I.D., 4 mm; carrier gas, He; flame-ionization detector.

Fig. 8. Chromatogram of decalin, tetralin and naphthalene on MoS_2. Column length, 1.2 m; I.D., 3 mm; carrier gas, He; flame-ionization detector.

lene molecules are the last to be eluted, although they contain fewer hydrogen atoms in the molecule.

Because of peculiarities in the structure of the nucleus of adamantane, many of its derivatives have high biological activity and are used in medicine[18]. However, the analysis of these substances suffers from a number of difficulties owing to their very high melting points (150–300°). Fig. 9 shows the separation of polycyclic hydrocarbons containing adamantyl nuclei in a molecule on a column with MoS_2. The order of elution of the components of the mixture is determined by their geometric structure and does not depend on either their molecular weight or their melting points. There is a 17-fold difference in the retention times of the isomers di (1,1′) (3,5,7-trimethyl) adamantyl and di (1,1′) (3-isopropyl) adamantyl. The latter molecule can make more favourable contact with the MoS_2 surface.

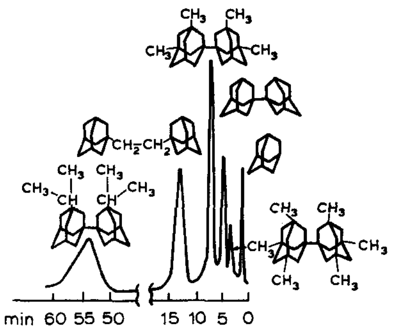


Fig. 9. Chromatogram of diadamantyl polycyclic hydrocarbons on MoS_2. Column length, 1 m; I.D., 3 mm; carrier gas, N_2; flame-ionization detector.

Molybdenum sulphide can be used for the separation not only of hydrocarbons but also of compounds containing halogens and sulphur at relatively low column temperatures.

REFERENCES

1 R. W. G. Wyckoff, *Crystal Structures*, Vol. 1, Interscience, New York, London, Sydney, 1963.
2 P. Cannon, *J. Phys. Chem.*, 64 (1960) 1285.
3 E. V. Ballou and S. Ross, *J. Phys. Chem.*, 57 (1953) 653.
4 R. R. M. Jonston and P. J. M. Moore, *J. Phys. Chem.*, 68 (1964) 3399.
5 G. J. Lopez, C. E. Barea and M. M. A. Banares, *An. Quim. Real Soc. Esp. Fis. Quim.*, 64 (1964) 699.
6 L. D. Belyakova and A. V. Kiselev, *Izv. Akad. Nauk SSRR, Otd. Khim. Nauk.*, (1966) 638.
7 G. J. Andrews, A. J. Groszek and N. Hairs, *ASLE Trans.*, 15 (1972) 184.
8 T. B. Gavrilova, A. V. Kiselev and T. M. Storozhenko, *Kolloidn. Zh.*, 38 (1976) 1070.
9 E. V. Kalaschnikova, A. V. Kiselev, R. S. Petrova, K. D. Shcherbakova and D. P. Pashkus, *Chromatographia*, 12 (1979) 799.
10 N. N. Avgul, A. V. Kiselev and D. P. Poshkus, *Adsorbtsiya Gasov i Parov na Odnorodnikh Poverkhnostyakh (Gas and Vapour Adsorption on Homogeneous Surfaces)*, Khimiya, Moscow, 1975.
11 A. V. Kiselev and D. P. Poshkus, *J. Chem. Soc.*, *Faraday Trans. II*, 72 (1976) 950.
12 L. D. Belyakova, A. M. Kalpakian and A. V. Kiselev, *Chromatographia*, 7 (1974) 14.
13 A. V. Kiselev, D. P. Poshkus and A. J. Grumadas, *J. Chem. Soc.*, *Faraday Trans. I*, 75 (1979) 1281, 1288.
14 A. V. Kiselev and Ya. I. Yashin, *Adsorptionnaya Gazovaya i Zhidkostnaya Khromatographiya (Adsorption Gas and Liquid Chromatography)*, Khimiya, Moscow, 1979.
15 B. P. Nikolsky (Editor), *Spravochnik Khimika* (Chemist's Handbook), Vol. 1, Khimiya, Leningrad, 1971.
16 W. Engewald, E. V. Kalashnikova, A. V. Kiselev, R. S. Petrova, K. D. Shcherbakova and A. L. Shilov, *J. Chromatogr.*, 152 (1978) 453.
17 A. V. Kiselev, T. B. Gavrilova and T. M. Storozhenko, *Avtorskoe Svidetelstvo*, No. 524127, Byulleten No. 39, 1976.
18 V. V. Sevostyanov, M. M. Krayushkin and A. G. Yurchenko, *Usp. Khim.*, 39 (1970) 1721.