SCIENTIFIC SESSION ON THE CHEMISTRY AND TECHNOLOGY OF ORGANIC SULFUR COMPOUNDS AND SULFUR-CONTAINING PETROLEUM OILS

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The 13th scientific session on the chemistry and technology of organic sulfur compounds and sulfur-containing petroleum oils, which was organized by the Scientific Council of the State Committee for Science and Engineering (SCSE) on the problem "The Chemistry and Technology of Organic Sulfur Compounds," was held in Dushanbe May 28-31, 1974 by the Institute of Chemistry of the Academy of Sciences of the Tadzhik SSR (AS TadzSSR) and the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR (AS LatvSSR). A total of 330 individuals from 40 cities of the country participated in the work of the session. Five plenary papers were presented, and ~250 communications and papers were discussed in the sections.

The enormous reserves of sulfur-containing petroleum oils in our country, the sulfur-containing components of coals and shales, and the waste products of the cellulose-paper industry are the richest but as yet least-used resource for the production of substances that are beneficial to the national economy.

The problems involved in the utilization of sulfur are also becoming particularly acute in connection with the further increase in the recovery and reprocessing of sulfur-containing oils, coals, and natural gas and in connection with the intensification of the degree of purification of fuel and the recovery of the refuse of industry and transportation.

The urgent problems of the chemistry and technology of organic sulfur compounds in the USSR were elucidated in a plenary paper presented by the president of the Soviet Council of the SCSE Academician S. A. Giller on the problem "The Chemistry and Technology of Organic Sulfur Compounds."

Comparative data on the percentages of individual groups of organic sulfur compounds and other nonhydrocarbon components are of interest in petroleum refining and in the utilization of organic sulfur compounds in industry. A plenary paper presented by Professor G. D. Gal'pern (A. V. Topchiev Institute of Petrochemical Synthesis, AS USSR) was devoted to these problems.

Papers presented by the Institute of Chemistry of the Bashkir Branch of the AS USSR, the Institute of Chemistry of the AS TadzSSR, the A. B. Arbuzov Institute of General and Physical Chemistry, and the All-Union Scientific-Research Institute of the Petroleum Industry and its Élektrogorsk Branch were devoted to the establishment of the structural-group composition of organic sulfur compounds of various oils (mainly by spectral methods), and their isolation, separation (by means of complexing, extraction, and chromatography), and identification. Mono-, di-, and polythiacyclanes, polyalkyl-, cycloalkyl-, benzo-, and dibenzothiophenes, and condensed naphthenothiophenes were detected in the distillates of various oils. A method for the isolation of mixtures of thiophenes and hydrocarbons from petroleum fractions that insures the absence of admixtures of any other different heteroatomic compounds was proposed by Ya. B. Chertkov and co-workers.

Data on the distribution of nitrogen in various oils and the correlation of this data with the percentage of sulfur and metals, particularly vanadium and nickel, are assuming great importance in connection with the extensive development of processes involving the catalytic reprocessing of distillates and the residual products of various oils and also in connection with the increase in the requirements for the quality of commercial petroleum products. (A. S. Éigenson and co-workers, Bashkirsk Scientific-Research Institute of the Petroleum Industry; G. N. Aleshin and co-workers, S. M. Kirov Tomsk Polytechnic Institute; N. A. Azi-

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zov and D. I. Zul'fugarly, V. I. Lenin Tadzhik University). The percentage of nickel and vanadium in oils increases symbatically with the increase in the percentage of nitrogen- and sulfur-containing heterocyclic compounds in them. This is due to the electron-donor character of these heterocycles and the tendency of vanadium and nickel to form complexes. The possibility of more nearly complete extraction of sulfur- and nitrogen-containing heterocyclic compounds from oils and their refinement products was investigated by A. P. Kulik and co-workers (F. É. Dzerzhinskii DKhTI) on the basis of a study of the properties of these complexes.

Various pyridines, quinolines, and pyrimidines were identified in the oils and their distillates (Institute of Chemistry of the Bashkir Branch of the AS USSR, the All-Union Scientific-Research Institute of the Petroleum Industry and its Élektrogorsk Branch, the Institute of Chemistry of the AS TadzSSR, etc.).

Several communications were devoted to the study of sorption on various adsorbents of sulfur-, nitrogen-, and oxygen-containing heterocyclic compounds isolated from petroleum products [Institute of Chemistry of the Academy of Sciences of the Uzbek SSR (AS UzbSSR), the Institute of Chemical Sciences of the Academy of Sciences of the Kazakh SSR (AS KazSSR), Institute of the Chemistry of Petroleum and Natural Salts of the As KazSSR, and Institute of Chemistry of the Bashkir Branch of the AS USSR].

The extraction capacity of cyclic sulfides and sulfoxides of both individual and petroleum origin with respect to precious and rare metals was also studied.

A plenary paper presented by I. M. Nasyrov and several sectional and generally circulated papers presented by the Institute of Chemistry of the Tadzhik SSR were devoted to the chemistry of thiaindane and its derivatives. Numerous preparations for the identification of petroleum sulfides were synthesized, the transformations of 1-thiaindane and its derivatives were studied, and substances with useful properties were obtained from them.

One should note the communication presented by N. N. Novitskaya (Institute of Chemistry of the Bashkir Branch of the AS USSR) dealing with a method for the synthesis of thiabicyclanes on the basis of the reaction of SCl_2 with butadiene trimers and with the study of the transformations of the products to give thiabicyclotridecene, sulfolane, and thiacyclohexane derivatives and sulfoxides and sulfones of thiophene. The oxidation of thiabicyclotridecenes and the transannular reactions for the formation of sulfonium salts, which proceed with the participation of the sulfur atom and a double bond, were studied. E. N. Karaulova and others (A. V. Kopchiev Institute of Petrochemical Synthesis, AS USSR) proposed a new promising (from a synthetic point of view) method for the synthesis of polyfunctional sulfides, which is based on the amination of sulfonium salts, a reaction discovered by the authors. The results of research involving the study of compounds of the 1,2-dithiolane series (Institute of Heteroorganic Compounds of the AS USSR), and cyclic oxa- and dithianes (Ufim Petroleum Institute and Institute of Chemistry of the Bashkir Branch of AS USSR) were presented. The radiochemical synthesis of dithiane was also accomplished. [Institute of Inorganic Chemistry and Electrochemistry, Academy of Sciences of the Georgian SSR (AS GSSR)]. L. Ya. Avota and S. A. Giller (Institute of Organic Synthesis of the AS LatvSSR) reported the synthesis of, study of the mechanism of the formation of, and proof of the structure of some dipyridazodithiynediones. The results of research on the synthesis of compounds of the thiapyran series were presented by the Institute of the Chemistry of Petroleum and Natural Salts of the As KazSSR and the Institute of Chemistry of the As TadzSSR.

S. N. Baranov and co-workers (Donetsk Physical-Organic Chemistry Division, Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR (AS UkrSSR) studied the reactions of thiapyrylium salts with aromatic and heterocyclic nucleophiles. Thiapyrans and thiapyrylium salts with phosphorus-containing substituents were obtained. Hetarylideneoxazolones, which proved to be convenient starting compounds for the synthesis of amino acid derivatives and new heterocyclic systems, were obtained from thiapyrylium salts and similarly constructed heteroaromatic cations.

The chemistry of thiophene was represented extensively in the session. M. G. Voronkov and co-workers (Irkutsk Institute of Organic Chemistry, Siberian Branch of the AS USSR) accomplished the high-temperature reaction of hydrogen sulfide with halo-substituted benzenes and thiophenes and also with their derivatives to give the previously hard-to-obtain corresponding thiols, sulfides, disulfides, and sulfur-containing heterocyclic compounds. Thiophene, S,S-dioxide derivatives that have the properties of tranquilizers and central nervous system stimulators were obtained by the addition of amines to 2,3-dichlorobenzo[b]thiophene S,S-dioxide (Institute of Organic Synthesis, As LatvSSR). The photochemistry of thiophene was illuminated in detail in a paper presented by E. N. Prilezhaeva (N. D. Zelinskii Institute of Organic Chemistry of the AS USSR), which elicited great interest. A number of papers were devoted to the development of catalytic methods for the synthesis of thiophene and its homologs: the preparation of thiophene from the bu-

tane–butylene fraction and hydrogen sulfide (N. D. Zelinskii Institute or Organic Chemistry of the AS USSR and the Scientific-Research Institute of Petroleum Chemistry) and from acetylene and hydrogen sulfide (Lensovet Leningrad Technological Institute) and the synthesis of 2-methylthiophene from piperylene and hydrogen sulfide (Scientific-Research Institute of Petroleum Chemistry). The fundamental principles of the chemisorption of thiophenes and sulfur-containing compounds on catalysts and the resulting changes in the properties of both the sulfur-containing component and the solid catalyst were elucidated in a paper presented by A. V. Mashkina (Institute of Catalysis, Siberian Branch of the AS USSR).

The catalytic transformations of cyclic sulfides were discussed in communications from M. V. Lomonosov Moscow State University, the Institute of Catalysis of the Siberian Branch of the AS USSR, and N. G. Chernyshevskii Saratov State University. The A. V. Topchiev Institute of Petrochemical Synthesis of the AS USSR presented data from a study of the cationic copolymerization of propylene sulfide and trimethylene sulfide with α-methylstyrene.

A great deal of attention was directed to the synthesis and study of the properties of sulfur- and nitrogen-containing heterocycles – thiazolines, thiazines, thiazoles, benzothiazines, etc. One should note the paper presented by V. M. Fedoseeva and co-workers (M. V. Lomonosov Moscow State University), which was devoted to a study of the effect of the type of solvent and competitive reagents on the reaction rate and the composition of the products of a dihydrothiazine-thiazoline rearrangement in a number of 5-substituted 2-amino-5,6-dihydrothiazines. S. N. Baranov and co-workers obtained a number of previously unknown thiazole derivatives fused with pyrylium and thiapyrylium rings.

Technological and design developments with respect to the production of organic sulfur compounds were the subject of discussion of a special section. A method for the preparation of thiophene from coal tar crude material by extractive rectification was perfected. The technology for the extractive separation of mixtures of benzothiophene and naphthalene and for the preparation of dimorpholinyl disulfide and dithienyl sulfide was developed. A new technology for the manufacture of 4-methyl-5-(β-hydroxyethyl)thiazole – an intermediate in the synthesis of vitamin B_1 – was proposed.

Upon the whole, the session noted the timeliness of the topics, the increased level of the research, and the intensification of the role of instrumental methods of investigation. The tasks faced by the Scientific Council and all of the specialists engaged in research in the chemistry and technology of organic sulfur compounds and the study of sulfur-containing petroleum oils were defined more accurately in a resolution adopted by the session.