

SCIENTIFIC SESSION OF THE CHEMISTRY AND TECHNOLOGY
OF ORGANIC SULFUR COMPOUNDS
AND SULFUROUS PETROLEUM OILS

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The 14th scientific session on the chemistry and technology of organic sulfur compounds and sulfurous petroleum oils was held March 15-18, 1976, in Batumi. Approximately 250 individuals participated in the activities of the session, and 139 papers, including 10 plenary papers, were discussed.

Of considerable interest for industry are the results of the isolation and study of the sulfurous and other noncarbon components of oils, among which mono-, di-, and polythiacyclanes, thiophenes, benzothiophenes, naphthobenzothiophene, and dinaphthobenzothiophene, pyridines, quinoline, etc., have been detected. Bisheterocyclic compounds containing both sulfide sulfur and a nitrogen atom have also been found in Tuimazinsk oil.

N. K. Lyapina and co-workers studied the composition of sulfur compounds from the distillates of oils of various fields by two independent schemes and made a comparative evaluation of the degree of extraction of organic sulfur compounds of various structural groups. Thiacyclanes, thiaindanes, and alkylthiophenes were found to be the most stable compounds with respect to the isolation conditions.

A. A. Polyakova and co-workers demonstrated for the first time that the high-molecular-weight sulfur compounds can be analyzed without isolation from the petroleum fractions by means of mass-defect spectrometry. In addition to the determination of the types of compounds, their molecular weight distribution is established. The use of Polyakova and co-workers of high-resolution mass spectrometry in conjunction with differential mass spectrometry enabled them to characterize the changes in the composition of sulfur compounds that occur in a three-phase fluidized bed during hydrocracking of petroleum residue from Romashkinsk oil.

High-molecular-weight compounds from petroleum, particularly asphaltenes, are the least studied and with respect to their composition, the most complex portion of oil, which, because of the limited amount of information regarding its structure and properties has not yet found qualified application. The results of the realization of a complex program for the study of high-molecular-weight compounds of petroleum in the Institute of Petroleum Chemistry of the Siberian Branch of the Academy of Sciences of the USSR (SB AS USSR) were presented in a plenary paper (A. N. Plyusnin and Yu. G. Kryazhev) and in a number of individual communications.

A considerable amount of attention is being directed to the synthesis of model sulfur compounds in the G. D. Gal'pern laboratory.

Yu. E. Nikitin and co-workers correlated the results of the synthesis and isolation of individual and petroleum sulfoxides, studied the peculiarities and principles of the extraction of mineral and organic acids and metals salts by sulfoxides, gave an explanation of the extractive capacity of sulfoxides as a function of the structure of the extracting agent molecules, pointed out methods for the preparation of individual and petroleum sulfoxides with predesignated properties, and reflected possible areas of application of petroleum sulfoxides. The Institute of Catalysis of the SB AN USSR jointly with the Scientific Research Institute of Petroleum Chemistry (SRIPC) has proposed a catalytic process for the liquid-phase air oxidation of petroleum sulfides to sulfoxides.

The chemistry of cyclic sulfides, sulfoxides, and sulfones was extensively represented in the session. A new method has been developed for the preparation of tetrahydrothiophene from tetrahydrofuran and sulfur under moderate temperature conditions (A. E. Arbuzov Institute of Organic and Physical Chemistry). N. S.

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Zefirov examined the principal conformational features of sulfur-containing compounds within the framework of effects "through the bond" and "through space" in the case of six-membered cyclic systems.

The chemistry of thiophene has undergone further development. New preparative methods for its synthesis are being worked out. Thiophene is obtained in practically quantitative yield by reaction of sodium sulfide with diacetylene, and the crude product is 99.9% pure [Irkutsk Institute of Organic Chemistry (IIOC)]. The principles of the catalytic syntheses of thiophene have been studied. The principles of the chemical behavior of compounds of the thiophene and furan series examined in a plenary paper by L. I. Belen'kii, as well as the possibilities of changing the "normal" trend of electrophilic substitution because of the reversible modification of the functional groups (particularly as a result of complexing and protonation), are not only of theoretical but also of practical interest. 2,5-Diisopropenylthiophene, on the basis of which a method for the preparation of sulfopolystyrene plastics was developed (IIOC), was synthesized from the accessible diacetylene glycol. It was shown that amino derivatives of 2-chlorobenzo[b]thiophene 1,1-dioxide [Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR (IOS AS LatvSSR)] constitute a new class of psychotropically and gangliolytically active compounds.

A new reaction of acetylene with ketoximes was found to be effective for the preparation of thienylpyrrole and the previously unknown N-vinylthienylpyrrole (IIOC).

V. P. Litvinov and co-authors studied the metallation, bromination, and formylation of selenophenothio-phenes, and the method of competitive reactions was used for the determination of the relative reactivities of thiophene, selenophene, thieno[3,2-b]thiophene, and selenopheno[3,2-b]thiophene.

V. I. Shvedov and co-authors obtained thieno[2,3-b]pyridines and studied their transformations.

New data on the mechanism of the dihydrothiazine-thiazoline rearrangement were contained in a communication by V. M. Fedoseeva and co-authors. 6-Amino-1,3,5-dithiazinium salts - a new heterocyclic system - were obtained in IIOC by reaction of divinyl sulfide with thiourea in the presence of mineral acids. The reaction of primary amines with divinyl sulfoxides leads to 1,4-tetrahydro-1,4-thiazine 1-oxides (IIOC). I. Ya. Postovskii and co-authors obtained substituted 1,3,4-thiadiazines and studied their properties.

The synthesis of new sulfur heterocycles containing boron and silicon was accomplished in the IOS AS LatvSSR, and thienyl derivatives of aminoalkylsilanes that have an effect on the central nervous system were obtained. Organylthioalkylsilatranes, 1-(thiocyanoketoalkyl)silatranes, 1-(mercaptoalkyl)silatranes, and 1-(acetylthioalkyl)silatranes were obtained in IIOC, and silatrane derivatives of isothiuronium salts were synthesized.

It should be noted that the central attention of the session was focused on the perfection of the technology for the processing of sulfur-containing raw material, the creation of new industries for organic sulfur compounds and new efficient processes for petroleum refining, the associated industrial hygiene problems, and the study of the effect of organic sulfur compounds on people, animals, and plants.