Purpose of research

Alkanes and cycloalkanes, i.e. saturated hydrocarbons - the simple molecules composed exclusively of carbon and hydrogen atoms - have long been of interest to chemists. One of the challenging tasks of modern chemical technology is use of these light hydrocarbons (including methane, the simplest alkane, and the main component of natural gas) as raw materials for the industrial manufacturing of more complex organic molecules. The possibility of industrial synthesis of valuable products directly from natural or processed only slightly in refineries would significantly reduce production costs (eliminating the need for highly processed substrates which are not available in nature). Unfortunately, very small reactivity of the $C(sp^3)$-H bonds leads to non-catalyzed chemical reactions involving alkanes and cycloalkanes, progressing with the greatest difficulties (good illustration of this problem is the low productivity of industrial synthesis cyclohexanone directly from cyclohexane; the former is necessary in the production of nylon as well as valuable solvent extraction of citric acid). This example allows to understand the importance of the ongoing search for effective ways to activate the $C(sp^3)$-H bond in molecules of light hydrocarbons. One of the possible directions here is an oxidative pathway. The purpose of the current scientific project, which fits within current trends of research, is a reconnaissance of reactivity of three compounds of divalent silver (which are very strong oxidants) towards light aliphatic hydrocarbons - in particular methane and small ring alicyclic hydrocarbons (such as cyclohexane), as well as their derivatives. Silver(II) compound, $AgSO_4$, has recently proved to successfully activate the $C(sp^2)$-H bonds in aromatic hydrocarbons - in this project we plan to use even more aggressive oxidizers based on weakly coordinating anions, which should be able to attack saturated hydrocarbons, as well.

Research to be conducted

The reaction between compounds of the (silver(II) sulphate(VI) monohydrate $Ag(II)SO_4$ x H_2O, silver(II) fluorosulphate(VI), $Ag(II)(SO_3F)_2$ and silver(II) triflate $Ag(II)(SO_3CF_3)_2$) with organic compounds will be carried out in a mixture of liquid (hydrocarbon) and solid (silver compound) in an anhydrous and oxygen-free conditions at ambient temperature or lower. Analysis of the post-reaction mixture and identification of the products would require characterization of the liquid and solid phases by standard quantitative methods of analytical chemistry (chromatography, mass spectrometry, NMR spectroscopy, IR spectroscopy and Raman spectroscopy, X-ray diffractometry, et al.). These analytical methods allow separation of the resulting products from the post-reaction mixture and the determination of its chemical structure as well as the yield and selectivity of the reaction. An important path of research will systematic attempt of reactivity of the silver(II) compounds with a number of organic compounds for increasing the difficulty of their oxidation ability to approximate the "reactivity borderline" and determine the type of reactivity (C-C coupling, insertion of O, etc.).

Reasons for the project

Understanding the reactivity of three extremely strong oxidants towards the model alkanes and cycloalkanes systems will be important from the point of view of basic research. Successful implementation of the project will allow for the enrichment of previously used methods of oxidation in organic preparative chemistry with very strong (but not necessarily unselective!) oxidants based on silver(II) compounds. It is important that silver(I) by-products can be fairly easily regenerated using electrochemical methods and converted back into valuable starting materials, *i.e.* silver(II) compounds. The ability to effectively activate $C(sp^3)$-H bonds using silver(II) salts and providing acceptable yields and selectivity of the reactions leading to the target compounds would represent significant novelty, allowing for the development of new technologies which deliver valuable organic compounds.