Prediction of microbial metabolism of petroleum ethylmethylmercaptane in the environment

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Abstract: *The amount of sulphur in crude oils plays an important role in determining their prices. Sulfur compounds are the most abundant non-hydrocarbon constituents in petroleum. The aim of this work is to predict the possible microbial metabolism of petroleum ethylmethylmercaptane by a software of (Q)SAR Application Toolbox. The ethylmethylmercaptane was metabolically activated in the microorganisms and their protein and DNA binding was estimated. Predicted microbial pathway was observed. Predicted metabolites have different mechanisms of protein binding.*

Key words: *ethylmethylmercaptane, microbial metabolism, environment*

INTRODUCTION

Sulfur, after carbon and hydrogen, is often the most abundant element in fossil organic materials, whereas in biological tissues and their degradation products oxygen and nitrogen usually are more abundant than sulfur. In rare cases, the sulfur content on a weight basis even exceeds the hydrogen content. Nevertheless, sulfur in petroleum appears to be non essential, i.e., it is not a necessary component for the formation of petroleum and related bitumens because some of these materials contain only trace amounts.

The chemistry of sulfur in fossil fuels and related materials is of interest for two major reasons: 1) For its behavior during processing and in applications: It can cause problems in processing and has deleterious effects on the environment in many applications, and 2) For its geochemical significance, i.e., for understanding processes which determine its abundance, distribution, and chemical combination (forms) during both the formation and alteration of fossil organic materials in geologic environments [8].

The sulphur content is in the range 0.5-3.0 % in most crudes, but is up to 8 % in the vacuum residue of heavy crude oils [11]. However, the incorporation of sulphur into crude oil has not been clearly understood until now, although many hypoyheses have been proposed. All are collectively termed organic sulphur compounds. These hypotheses are based on biosynthesis and formation during early diagenesis [3].

Most of the sulphur present in crude oils is organically bound sulphur while elemental sulphur and hydrogen sulphide usually represent a very minor portion of the total sulphur [8]. Some sulphur may be derived from amino acids in the original contributing organic matter in sediments [9]. However, most primarily sulphur in oils originates from early diagenetic reactions between the deposited organic matter and aqueous sulphide species such as hydrogen sulphide or polysulfides [4].

Sulfides are produced by sulphate-reducing bacteria, such as *Desulfovibrio*, primarily in highly reducing to anoxic marine sediments. Two sinks compete for sulphide in sediments: metals and organic matter. High- and low-sulfur crude oils are derived from high- and low-sulfur kerogens, respectively [5]. In addition, biodegradation can lead to an increase in the sulphur content in oils by the preferential removal of saturated hydrocarbons [3].

Sulfur compounds in crude oils are distributed over a wide range of molecular structures: aliphatic thiols mono- and disulfides are sometimes present [10, 13], but a large amount of sulphur occurs in aromatic structures, especially as alkylated thiophene benzologues [1].

Sea water contains a wide range of micro-organisms that can partially or completely degrade oil to water soluble compounds and eventually to carbon dioxide and water. There are many types of micro-organisms that tend to degrade a particular group of compounds in crude oil [3].

The aim of this work is to predict the possible microbial metabolism of petroleum ethylmethylmercaptane by a software of (Q)SAR Application Toolbox. The ethylmethylmercaptane was metabolically activated in the microorganisms and their protein and DNA binding was estimated. Predicted microbial pathway was observed. Predicted metabolites have different mechanisms of protein binding.

MATERIALS AND METHODS

Compound. The ethylmethylmercaptane [12] was investigated which is presented in Table 1.

OECD (Q)SAR Application Toolbox. The software used for prediction of the microbial metabolism (biodegradation) of petroleum ethylmethylmercaptane is the OECD (Q)SAR Application Toolbox. The Toolbox is a software application intended to be used by governments, chemical industry and other stakeholders in filling gaps in (eco) toxicity data needed for assessing the hazards of chemicals. The Toolbox incorporates information and tools from various sources into a logical workflow [7].

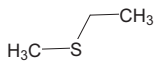
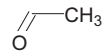
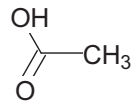
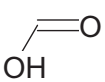
Degradation pathways used by microorganism to obtain carbon and energy from 200 chemicals are stored in a special file format that allows easy computer access to catabolic information. The collection includes the catabolism of C1-compounds, aliphatic hydrocarbons, alicyclic rings, furans, halogenated hydrocarbons, aromatic hydrocarbons and haloaromatics, amines, sulfonates, nitrates, nitro-derivatives, nitriles, and compounds containing more than one functional group. Most of pathways are related to aerobic conditions. Different sources including monographs, scientific articles and public web sites such as the UM-BBD [2] were used to compile the database.

The original CATABOL simulator of microbial metabolism is implemented in the OECD (Q)SAR Application Toolbox [6]. Single pathway catabolism is simulated using the abiotic and enzyme-mediated reactions via the hierarchically ordered principal molecular transformations extracted from documented metabolic pathway database. The hierarchy of the transformations is used to control the propagation of the catabolic maps of the chemicals. The simulation starts with the search for match between the parent molecule and the source fragment associated with the transformation having the highest hierarchy. If the match is not found search is performed with the next transformation, etc. When the match is identified, the transformation products are generated. The procedure is repeated for the newly formed products. Predictability (probability that the metabolite is observed, given that the metabolite is predicted) evaluated on the bases of documented catabolism for 200 chemicals stored in the database of “Observed microbial catabolism” is 83%.

RESULTS AND DISCUSSION

In this work will be researched the possible metabolites (observed and predicted) for the petroleum ethylmethylmercaptane. For this aim we will use the OECD (Q)SAR Application Toolbox system. Predictions are based on biotransformation rules that, in turn, are derived from reactions found in the UM-BBD and the scientific literature. The UM-PPS most accurately predicts compounds that are similar to compounds with known biodegradation mechanisms, for microbes under aerobic conditions and when the compounds are the sole source of energy, carbon, nitrogen or other essential elements for these microbes. Results in the OECD (Q)SAR Application Toolbox system are presented in Table 1

Table 1. Observed and predicted microbial metabolism of the petroleum ethylmethylmercaptane

CAS number	Name of compound	Observed Microbial metabolism	Predicted Microbial metabolism
624-89-5	(Methylthio)-ethane 	No metabolite	5 metabolites;  1) No DNA binding; Protein binding – Schiff base formation; 2)  No DNA binding; No Protein binding;  3) No DNA binding; Protein binding – Disulfide formation;  4) No DNA binding; Protein binding – Schiff base formation;  5) No DNA binding; No Protein binding;

CONCLUSIONS

Degradation by the action of microorganisms is one of the major processes that determines the fate of organic chemicals in the environment. Quantitative Structure-Activity Relationships (QSAR) methods can be applied to biodegradation. Such relationships, often referred to as Quantitative Structure-Biodegradability Relationships (QSBRs), relate the molecular structure of an organic chemical to its biodegradability and consequently aid in the prediction of environmental fate. The ethylmethylmercaptane was metabolically activated in the microorganisms and their protein and DNA binding was estimated. Predicted microbial pathway was observed. Some of predicted metabolites have different mechanisms of protein binding – Schiff base formation and disulfide formation.

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This paper has been reviewed