

Professor's Malinowski last notes

The last months of Professor's Malinowski life were especially difficult for him. The periods of weakness when he could not leave his bed or his armchair alternated with the clear days, enabling him to take a stroll along the streets in the neighborhood and a lively contact with the nearest family. Despite his physical weakness he resumed his intellectual activities and came back to the problem which had attracted his interest in a couple of preceding years: the specific catalytic and physicochemical properties of alkaline earth metal oxides. In particular he was fascinated by the results described in the eighties and the nineties in the papers published by F. Freund in Germany and USA and saw vast perspectives for catalysis and geochemistry in the further development of the research in this field.

Freund had shown that when the proper conditions of sufficiently high temperature are fulfilled magnesium oxide can incorporate carbon dioxide and water, thus forming a number of crystal lattice defects such as vacancies, interstitial carbon atoms and even interstitial hydrogen atoms. On heating at temperatures 500–1000 K the gradual emission of gases from such samples occurs.

Mass analysis indicated the presence of not only H₂O and CO₂ but also of hydrogen, oxygen and even certain amount of different hydrocarbons. The latter are the products of the interactions of the lattice defects forming upon the incorporation of CO₂ and H₂O. The former supply carbon and the latter hydrogen for the formation of hydrocarbons.

Yet soon it was confirmed that other alkaline earth metal oxides such as SrO or BaO and also some silicates give similar effects. Professor Malinowski understood well the importance of all these investigations for the studies of the Earth's inner structure and some processes in tectonically active regions. He discussed the problem with his friends from the Institute of Geophysics of the Polish Academy of Sciences. The result of their collaboration was Malinowski's paper "Physical and Chemical Properties Related to Defect Structure of Oxides and Silicates Doped with Water and Carbon Dioxide" containing the critical review of the papers on defect structure of MgO published in the literature. It appeared as a chapter in the book "Earthquake Thermodynamics and Phase Transformations in the Earth's Interior" (Academic Press 2001) and was the last paper published during his life. Thanks to the courtesy of the Academic Press, the editors of the present issue can publish it again in the "Polish Journal of Chemistry", which is accessible to the polish chemical community.

As it was already said, in the last months of his life Prof. Malinowski returned continually to this problem studying recent literature. He was also preparing a kind of expertise indicating how interesting and important is developing this line of investigation and aimed to stimulate the research in Poland in a program the guide-lines, of which were sketched in his last note. The whole of his elaborate work needs some editorial preparation and I hope it will be published in the future. Here we present the English translation of the last chapter "Summary and Conclusions", the outline of the program. It is both very valuable proposal for scientific discussions and research, but also a testimony of Professor's Malinowski scientific passion and invention persisting to the last days of his life. I trust it will be at the same time a reminiscence of his unforgettable personality, a text read with emotion by his friends and students.

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Summary and Conclusions

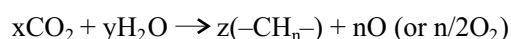
This elaboration intended to find the answer whether the formation of hydrocarbons (in the Earth's crust) directly from CO₂ and H₂O as the sources of carbon and hydrogen is possible. When discussing this problem as the point of departure we should look for raw materials containing carbon and hydrogen present in sufficient amounts enabling the formation of mineral oil. It has been here assumed that such conditions are only fulfilled by carbon dioxide as the source of carbon and water as the source of hydrogen. Consequently the question arises whether these two compounds can react with the formation of hydrocarbons. In the light of the present review the answer is positive. It indicates that at the conditions of high pressure and temperature at which – as it is now assumed – mineral oil had been forming, and at the presence of different minerals, the formation of hydrocarbons of carbon dioxide and water was essentially possible. This conclusion is based on the results of laboratory experiments carried out in recent years (1978–1984) indicating that such reactions may occur at the presence of alkali earth metal oxides. Until now in literature magnesium oxide has been investigated extensively (8 papers) in this respect. Two papers were published concerning calcium oxide there were. Also strontium oxide has been mentioned a few times.

These oxides play the role of catalysts in the reactions between water and carbon dioxide or carbonates. Their products are saturated and non-saturated hydrocarbons of different chain length and structure; aromatic hydrocarbons of different number of rings are also forming as well as certain amount of elemental hydrogen and oxygen. At the pressure of 1 atm. some of these reactions occur already at 200°C, the others at 600–800°C.

The main role as the reaction centers is played by the cationic vacancies of different types. They enable the dissociation of water into hydrogen and oxygen and carbon dioxide into atomic carbon and oxygen. Atomic carbon and hydrogen (atomic or molecular) migrate towards the surface of the CaO crystallites. Most probably reactions between carbon and hydrogen occur at the surface, thus giving a vast range of organic compounds, mainly aliphatic hydrocarbons of different chain length and aromatic hydrocarbons exhibiting different number of aromatic rings.

The detailed mechanism of the formation of hydrogen and oxygen from water at the presence of alkali earth metal oxides, exhibiting defect structure, has been proposed by Freund. It has also been shown, that at the analogous conditions carbon dioxide can dissociate into atomic oxygen and atomic carbon. Such carbon atoms exhibit high mobility at the appropriate temperatures and accumulate in the next-to-surface layer. No detailed mechanism of the surface reactions leading to the formation of hydrocarbons has been proposed.

- a) The introductory thermodynamic analysis indicates that at temperatures of several hundreds to 1000°C the following reaction may occur



- b) Such conceived reaction, in the course of which elemental oxygen and hydrocarbons are forming, may occur under condition that electrons are supplied simultaneously i.e. at the presence of some reducing agent as *e.g.* Fe or other metals.

These two points a) and b) need detailed elaboration. The present conclusions concerning the formation of hydrocarbons from CO₂ and H₂O are based mainly on the experimental results, which were presented in the main part of present review. Although the mechanism of the reactions is not fully understood, the formation of hydrocarbons is confirmed. Partially known is the composition of the mixture of products and conditions of their formation, their amount and formation rate. Basic role is played by the alkali earth metal oxides, acting as catalysts or perhaps as reagents.

Conclusions

Basing on the description of experiments and results obtained by Professor's Freund team related in my review, a number of indications and proposals concerning further studies can be formulated in both theoretical and practical aspects.

Theoretical problems

- 1) A theoretical study of thermodynamical aspects of well chosen reactions between water, carbon dioxide and carbonates, aiming to determine temperature effect on the equilibrium constants and reaction yield. Such data would give information concerning the possibility of realizing particular reactions at the laboratory conditions. A seminar concerning this topic should be organized.

- 2) A theoretical study of the possibility of the formation of earth gas and coals from inorganic material, using calcium and strontium oxides as the catalysts (other oxides should be taken into account if the appropriate investigations would be published). A seminar concerning this subject should be organized.
- 3) Further literature studies, which would answer the following questions:
 - a) are there in the literature publications concerning the effect of defect structure on physical and chemical activity of other oxides than magnesium, calcium and strontium
 - b) physical and chemical properties of the compounds other than oxides containing carbon in their crystal lattice. Is this kind of carbon also mobile?
- 4) Can the crystalline systems composed of more than one oxide (*e.g.* such as MgO-SiO₂) incorporate carbon atoms into the interstitials in a similar way as it occurs in the case of alkali earth oxides (MgO).
- 5) As it was reported in my review, magnesium oxide is the catalyst of the reaction between water and carbon dioxide, which consists in fact of the surface reaction between atomic carbon and hydrogen. This indicates that the earlier research on catalytic properties of MgO surface should be again discussed and analyzed from that point of view. Such papers are numerous. However, there are no papers in which reactions between atomic carbon and hydrogen or water were studied on the surface of magnesium oxide. Similarly no studies of the well known formation of synthesis gas from solid carbon and water vapour were undertaken at the presence of MgO. This is in fact a new and interesting problem from both scientific and technological perspectives.
- 6) One needs also some orientation and analysis from the point of view of the present report, which were the rocks and sediments accompanying – according to the present opinions – the formation of rock oil and similar products. What was their chemical composition and crystal structure? What were the reactions of the formation of such rocks? From which substrates and under which conditions? These latter questions should be answered by geologists and their interest in this field should be attracted.

Practical problems

Continuation in Poland of the further research on the possibilities of using carbon dioxide as the source of carbon in the synthesis of organic compounds. Utilization of water as the direct source of hydrogen in the formation of hydrocarbons and other organic compounds. The answer for this question – I think – will be found in the analysis of the work of Freund's team (and partially of Derouane) described above in my report and also in those theoretical studies suggested in the preceding section of this summary.