Thermochimica Acta, 124 (1988) 163–169
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

CHEMICAL REACTIONS BETWEEN MOLYBDENUM DISULFIDE AND SODIUM CHLORIDE IN A STREAM OF OXYGEN IN THE TEMPERATURE RANGE 470–900 K

S. RAJIĆ * and D. ZLATANOVIĆ

Department of Chemistry, Faculty of Science, University of Niš, Cirila i Metodija 2,
18000 Niš (Yugoslavia)

(Received 29 April 1987)

ABSTRACT

The system consisting of MoS_2 and NaCl was heated at 470–900 K in a flow of oxygen. Chemical reactions occurring in the investigated system were the subject of this study. Gaseous compounds containing chloride and/or chlorine begin to form at 470 K. Yields of those compounds rise at elevated temperatures. The solid sample remaining after heating was investigated by X-ray diffraction analysis. Some new phases were found, but chlorides and oxychlorides of molybdenum and sodium sulfate were not identified, in contrast to the literature data.

INTRODUCTION

The advantages of having a chlorination process in industrial manufacturing of many metals is widely known. There are several procedures of chlorination: by gaseous chlorine, by chlorine compounds including inorganic chloride salts, and finally chlorination in molten media [1,2].

Literature data concerning chlorine generation at elevated temperatures and the chemistry of reactions between chlorides of alkalis and alkaline earths with metal sulfides are scarce. Reactions between pyrites and sodium chloride at elevated temperatures were studied in the work by Rajić [3]: solid samples after heating and gaseous products of the mixture were investigated by X-ray diffraction. On heating MoO_3 and NaCl to 970 K Na-molybdates are formed, but after addition of pyrite Mo-chlorides are formed [4]. Methods of DTA and DTG corroborate three stages of chemical reactions; the energy of activation for each reaction is calculated by Kissinger's method [5].

The present paper further investigates chemical reactions in the mixture

---

* Present address: Metallurgical Department, Technical Faculty, Bor University of Beograd, 19210 Bor, Yugoslavia.

0040-6031/88/$03.50

of molybdenum disulfide and sodium chloride during heating in a stream of oxygen.

EXPERIMENTAL

Apparatus

The cylindrical, gradually heated furnace which was used for heating has been described earlier [3]. The mass of the sample was determined before and after heating. Gaseous chlorine-containing compounds were absorbed in distilled water contained in a washing bottle, and after heating was finished, the chlorine in the water was determined potentiometrically. A Philips X-ray diffractometer was used for identification of the products after sample heating.

Sample preparation

Molybdenum disulfide was mixed with sodium chloride in 2 : 1 and 1 : 1 ratios by weight. Molybdenum disulfide was synthetically prepared in the usual way. A sample of 1 g of the mixture was weighed in a quartz vessel, the vessel containing the sample was placed in the furnace and the flow of oxygen regulated. Each of the samples was heated to a selected temperature. Gaseous products were absorbed in distilled water by bubbling.

RESULTS AND DISCUSSION

Generation of gaseous compounds containing chlorine

During the heating of a mixture of molybdenum disulfide and sodium chloride in a stream of oxygen, gaseous compounds containing chlorine were

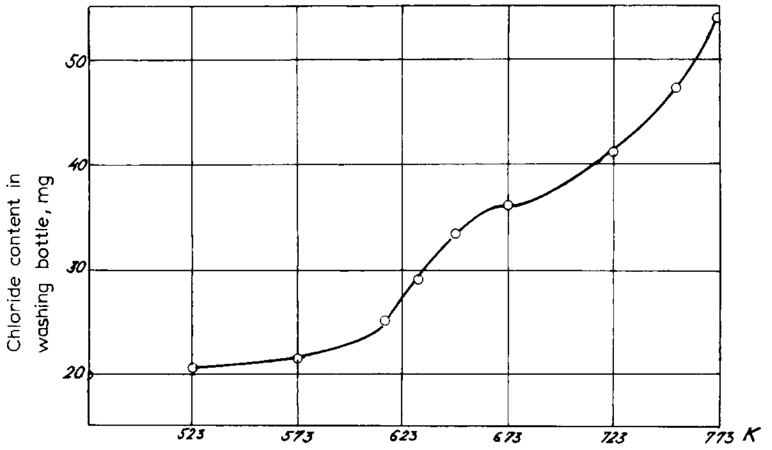

Fig. 1. Dependence of chlorine generation on heating temperatures.

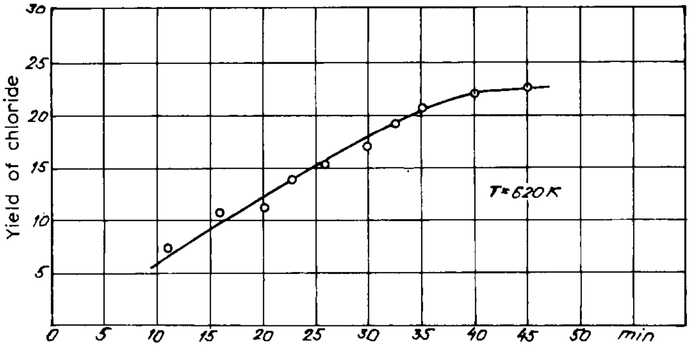

Fig. 2. Kinetic curve: yield of chloride vs. time.

formed, and those compounds can be absorbed in distilled water. From the chloride content of the water, data can be obtained about chlorine generation in those chemical reactions. It was found that with increasing temperature of the mixture, the amount of chloride absorbed in the water increased rapidly (Fig 1). The term chloride in this case is used because of the form of chlorine determination. The experimental results show that chlorine or gaseous compounds containing chlorine start to form at about 470 K, and from about 670 K the yield of chlorine rapidly increases. The kinetic curve showing the yield of chloride vs. time of heating is presented in Fig. 2. According to the kinetic results obtained, it is found that the optimum time of heating is 60 min. Molybdenum and chlorine evaporation contribute to a decrease in the total mass. The extent of molybdenum evaporation is presented as total evaporation and can be seen in Fig. 3. Molybdenum was not found in the water contained in the washing bottle, and molybdenum

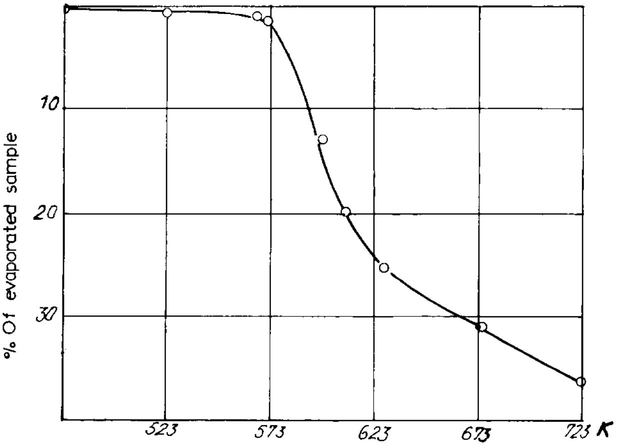

Fig. 3. Mass change of mixture of molybdenite and sodium chloride during heating. ($MoS_2 : NaCl = 2:1$).

compounds condensed only on the cold parts of the tube or remained partly in the vessel depending on the temperature of heating.

X-ray diffraction analysis

Solid samples from the vessel or samples from the cold parts of the tube after heating were analyzed by X-ray diffraction. The X-ray results obtained are listed in Table 1. In addition to sodium chloride, there are many new phases which are formed during the heating. The new phases are not the same in samples which were heated at different temperatures. The first new phase appears at about 470 K. All phases were very well crystallized having sharp reflections. Molybdenum chlorides or oxychlorides were not found by X-ray detection. From the X-ray diffraction analysis we note that sodium sulfate was not identified in any sample, in contradiction to literature data. A system consisting of molybdenum disulfide and sodium chloride was heated under the same experimental conditions as a system consisting of pyrites and sodium chloride. At 470 K samples undergo crystallochemical transformations as is shown by the disappearance of the X-ray reflections of both compounds contained in the mixture. At higher temperatures reflections of newly formed phases and sodium chloride start to increase. The newly formed phase remains stable up to 660 K. At higher temperatures the

TABLE 1

X-ray diffraction analysis of solid samples after heating at different temperatures. Oxygen flow, 12–16 cm^3 min^{-1}

Mixture	Temperature (K)	Reflections at θ	Remarks
MoS_2 + NaCl	470	$\theta_1 = 31.75$ weak $\theta_2 = 45.40$ weak $\theta_3 = 56.30$ weak	Decreasing of NaCl reflection intensities. Reactions begin
MoS_2 + NaCl	570	$\theta_1 = 27.10$ strong $\theta_2 = 23.25$ medium $\theta_3 = 25.60$ medium $\theta_4 = 12.75$ medium $\theta_5 = 33.65$ weak	Intensities of NaCl are stronger. New phase appears
MoS_2 + NaCl	640	The same reflections as in the previous sample.	
MoS_2 + NaCl	660	Reflections as in previous sample, but reflections of NaCl are stronger.	Reflections of following compounds are not found: Na_2SO_4, $Na_2S_2O_3$, $MoOCl_2$, $MoCl_3$, $MoCl_4$, etc.

TABLE 2

Part of diffractogram of the blue–green condensate from the cold part of a tube

θ	Relative intensities	Reticular distance d ($\text{nm} \times 10^{-1}$)
5.95	2	8.9
6.40	5 d [a]	6.87
11.77	6 d	3.78
13.02	11	3.42
13.85	10	3.22

[a] d, Diffuse.

newly formed phase evaporates from the mixture and condenses on cold parts of the tube. The condensate was also analyzed. It may have different colours, ranging from blue to blue–green to yellow–green. X-ray analysis shows that different compounds are present in the condensate, depending on experimental conditions during heating. Part of a diffractogram of a green condensate is given in Table 2. A diffractogram of the heated mixture is presented in Fig. 4. This sample was then treated with water in order to dissolve sodium chloride. Undissolved compounds were analyzed by X-ray. The diffractogram is presented in Fig. 5. No sulfate or other sulfur-containing sodium compounds were found in any of the samples investigated, so that the chemistry is not as described in Babenko and Smirnov's paper [8].

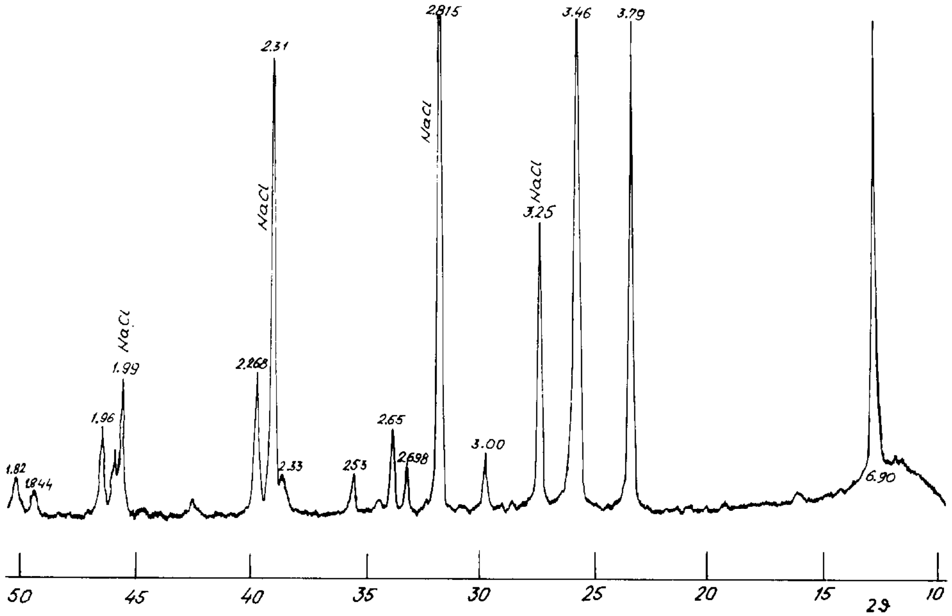

Fig. 4. Diffractogram of mixture of MoS_2 and NaCl after heating.

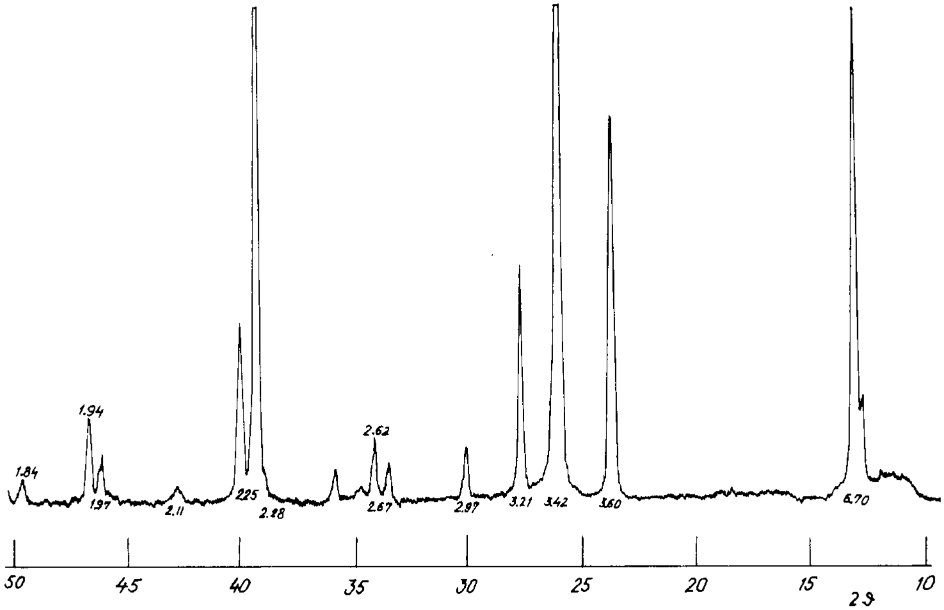

Fig. 5. Diffractogram of the sample presented in Fig. 4 after treatment with water.

In order to understand chemical processes which take place in the mixture of sodium chloride and molybdenum disulfide during heating, different samples were heated: (a) a mixture of MoO_3 and NaCl, (b) MoO_3 and NaCl with the addition of carbon powder, (c) MoO_3 and NaCl with the addition of sulfur powder, and (d) MoS_2 and NaCl. The amount of chlorides formed after heating of the samples is given in Table 3.

The results obtained show that only in the presence of sulfur or sulfides in a mixture with sodium chloride were chlorine-containing compounds formed. But, if compounds were separately heated in two vessels, chlorine-containing compounds were not formed in the case when oxygen passed first over sodium chloride and after that over sulfides or sulfur. However, if oxygen passes first over sulfides or sulfur, chlorine-containing compounds were formed just as in a mixture of sulfide and sodium chloride. This indicates a

TABLE 3

Chloride content in the washing bottle from mixture of molybdenum compounds and sodium chloride

Mixture	Cl^- content (mg)
$MoO_3 + NaCl$	0.2
$MoO_3 + NaCl + C + O_2$	0.3
$MoO_3 + NaCl + S + O_2$	6.5
$MoS_2 + NaCl + O_2$	11.6

role of SO_2 and SO_3 gases in a chemisorption process. The role of sulfur is not explained although it is similar to the role of carbon in chlorination, when using a chloride [9].

Figures 4 and 5 are diffractograms of a mixture after heating. It is seen that reflections of chlorides and oxychlorides or molybdenum do not appear; sodium sulfate also is not formed. Our model of the chemistry of chloride formation on the basis of our results is rather different from those based on results described in the literature [8]. The investigated system is similar to processes in a system consisting of pyrites and sodium chloride [3].

REFERENCES

1 V.P. Ozechov, T.M. Shverchov, K.V. Petrova and E.Ya. Shvelev, Tr. Nauchno Issled. Proektn. Inst. Redkomet. Prom., 44 (1972) 95.
2 A.N.N. Zelikman, S.L. Stefanyuk and I.K. Mataros, Nauchn. Tr. Mosk. Inst. Stali i Splav., 75 (1972) 71.
3 S. Rajić, Zb. Rad. Tehn. Fak. Bor, 19 (1983) 91.
4 A.S. Sinakecich and M.N. Zeryanov, Sb. Nauchn. Tr. Irkutsk. Gos. Nauchno Issled. Inst. Redk. Met., 7 (1958) 181.
5 D. Zlatanović, S. Rajić and Ž. Živković, to be published in Tehnika.
6 S.H. Pivneva, V.V. Gavrilov and A.M. Gurevich, Neorg. Mater., 13 (1970) 233.
7 A.N. Zelikman, O.E. Krein and G.V. Samsonov, Metallurgia Redkih Metall., Ed. Metallurgia, Moscow, 1978.
8 A.P. Babenko and V.I. Smirnov, Izv. Vyssh. Uchebn. Zaved. Tsvetn. Metall., 3 (1970) 34.
9 E. Barchese, Metal. ABM, 31 (1975) 219; Chem. Abstr., 85 (1976) 97262.