Thermochimica Acta, 58 (1982) 117–121
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

MASS SPECTRAL AND THERMOGRAVIMETRIC INVESTIGATIONS OF MOLYBDENUM OXINATES

M.R. UDUPA and K.S. NAGARAJA

Department of Chemistry, Indian Institute of Technology, Madras-600 036 (India)

(Received 23 March 1982)

The modes of ion dissociation in the mass spectra of metal complexes are largely dependent on the oxidation states usually preferred by the metal atom. This observation has been explained on the basis of the valence-change concept [1]. A ligand is capable of forming complexes with molybdenum in most of its oxidation states, 0–6. The complexes formed are mono-, bi- or polynuclear molybdenum units [2]. Molybdenum has seven naturally occurring isotopes with mass number ranging from 92 to 100 units. Thus, mononuclear molybdenum fragments consist of seven closely spaced peaks, whereas the dinuclear species exhibit 15 lines enveloping 17 mass number units. Recently Udupa and Nagaraja [3] have reported the mass spectral studies of molybdenum dithiocarbamates, and reported in this paper are the results of mass spectral and thermogravimetric investigations of molybdenum complexes of 8-hydroxyquinoline.

EXPERIMENTAL

The complexes—A, oxoisothiocyanatobis(oxinato)molybdenum(V) [MoO(NCS)(oxine)$_2$]; B, dioxobis(oxinato)molybdenum(VI) [MoO$_2$(oxine)$_2$]; and C, disulphidobis(oxinato)molybdenum(VI) [MoS$_2$(oxine)$_2$]—were prepared by the reported methods [4,5]. The mass spectra of the complexes were recorded on a VG micromass 70-70FF double focussing mass spectrometer with a VG 2235 data system. The thermogravimetric studies were carried out on a Stanton recording thermobalance in air at a linear heating rate of 6°C min^{-1}.

RESULTS AND DISCUSSION

The mass spectral data of compounds A, B and C are given in Table 1. The results suggest that the fragmentation of the oxoisothiocyanate com-

TABLE 1

Mass spectral data of molybdenum oxinates

m/e	m^+
A. $MoO(NCS)(C_9H_6ON)_2$	
412–420	$MoO_2(C_9H_6ON)_2$
396–404	$MoO(C_9H_6ON)_2$
380–388	$Mo(C_9H_6ON)_2$
268–276	$MoO_2(C_9H_6ON)$
252–260	$MoO(C_9H_6ON)$
209–217	$Mo(C_8H_7N)$
203–211	$MoO_2(C_5H_5N)$
198–206	$Mo(C_7H_6ON)$
185–193	$Mo(C_6H_5O)$
166–193	$Mo(C_6H_5O)$
166–174	$MoO(NCS)$
145	C_9H_7ON
144	C_9H_6ON
117	C_8H_7N
116	C_8H_6N
89	C_7H_5
63	C_5H_3
59	HNCS
58	NCS
32	S
28	CO
27	HCN
26	C_2H_2,CN
B. $MoO_2(C_9H_6ON)_2$	
412–420	$MoO_2(C_9H_6ON)_2$
396–404	$MoO(C_9H_6ON)_2$
380–388	$Mo(C_9H_6ON)_2$
268–276	$MoO_2(C_9H_6ON)$
209–217	$Mo(C_8H_7N)$
203–211	$MoO_2(C_5H_5N)$
198–206	$Mo(C_7H_6O)$
185–193	$Mo(C_6H_5O)$
124–132	MoO_2
145	C_9H_7ON
144	C_9H_6ON
117	C_8H_7N
116	C_8H_6N
89	C_7H_5
63	C_5H_3
28	CO
27	HCN
26	C_2H_2,CN

TABLE 1 (continued)

m/e	m^+
C. $MoS_2(C_9H_6ON)_2$	
256	S_8
192	S_6
160	S_5
145	C_9H_7ON
144	C_9H_6ON
128	S_4
117	C_8H_7N
116	C_8H_6N
96	S_3
89	C_8H_6N
64	S_2
63	C_7H_5
32	S
28	CO
27	HCN

pound does not give a parent molecular ion. The seven-line pattern fragmentation at *m/e* 396–404 is attributed to $MoO(C_9H_6ON)_2$, which results from the loss of the NCS group from the parent ion and loses oxygen to give $MO(C_9H_6ON)_2$. Mo(oxine)$_2$ dissociates an oxinate moiety followed by a molecule of CO to give $Mo(C_8H_6N)$. The spectral peaks at *m/e* 198–206 and 185–193 are assigned to $Mo(C_7H_6O)$ and $Mo(C_6H_5O)$, respectively, which probably result due to the cleavage of the N-containing ring of the oxinate group. The fragmentation of the oxinate anion is followed by the successive loss of CO, HCN and C_2H_2 finally to give C_5H_3, as observed in the mass spectrum of free oxine [6]. In the spectrum, peaks at *m/e* 412–420, 268–276 and 203–211 appear, which are assigned to $MoO_2(C_9H_6ON)_2$, $MoO_2(C_9H_6ON)$ and $MoO_2(C_5H_5N)$, respectively. The dioxomolybdenum fragments probably result from the inadequate evacuation of the system. This is also evident from the peak due to oxine at *m/e* 145, obtained by the protonation of the oxinate ion.

Compound B gives a peak at *m/e* 412–420 due to the parent molecular ion, $MoO_2(C_9H_6ON)_2$. The fragmentation products suggest that successive loss of oxygen occurs to give Mo(oxine)$_2$. The *m/e* value at 124–132 is attributed to MoO_2 obtained by the loss of oxinate groups. The other fragments are similar to those of compound A.

Compound C does not give fragmentation of mass number higher than 256, for which the parent molecular ion would cover the mass number

444–452, probably due to the non-volatility of the compound as observed [7] in Mo_2O_3 $(Et_2NCS_2)_2$. The peaks at 256, 192, 160, 128, 96, 64 and 32 originate from sulphur due to polymerization. The fragments of Mo are too weak and are not located. The peaks of oxinate anion are similar to those of other oxinate compounds.

The TG plots of the three compounds are given in Fig. 1. $MoO(NCS)(oxine)_2$ apparently decomposes in three stages and $MoO_2(oxine)_2$ and $MoS_2(oxine)_2$ in two stages. Compound A registers a loss of 13% weight in the temperature range 300–360°C which agrees with the dissociation of the NCS group as the calculated weight loss is found to be 12.6%. $MoO(oxine)_2$ thus formed loses 3% of the initial weight in the temperature 360–400°C which agrees with the overall calculated weight loss of 16.1% for the formation of $Mo(oxine)_2$. In the final stage of decomposition, between 420 and 600°C, the oxinate moiety is oxidized to give MoO_3 as the final residue. The observed total loss of 69% is in good agreement with the calculated value of 68.6%.

Compound B loses 8% weight between 300 and 400°C to give $Mo(oxine)_2$, as the calculated weight loss for the dissociation of the two oxo groups is 77%. $Mo(oxine)_2$ decomposes to MoO_3 between 420 and 600°C.

The disulphido compound loses 14% weight between 280 and 400°C which corresponds to the value of 14.3% for the removal of two sulphido groups. $Mo(oxine)_2$ is oxidized to MoO_3 as observed in the other two cases between 420–600°C. It is interesting to note that S-containing Mo com-

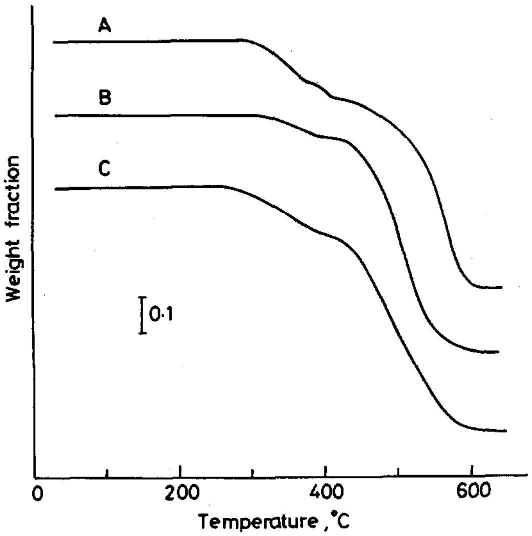

Fig. 1. TG plots of A, $MoO(NCS)(oxine)_2$; B, $MoO_2(oxine)_2$; and C, $MoS_2(oxine)_2$.

pounds generally decompose in air to give MoO_3 through the intermediate molybdenum sulphides. However, in the present case the expulsion of sulphur takes place, probably due to the higher thermal stability of the Mo-oxinate chelate. Further, the dissociation temperatures of the dioxo and the disulphido compounds suggest that $MoO_2(\text{oxine})_2$ is more stable than $MoS_2(\text{oxine})_2$.

ACKNOWLEDGEMENT

The authors wish to thank Dr. M.A. Hitchman, Australia, for providing mass spectra of the compounds.

REFERENCES

1 I.S. Shannon and J.M. Swan, Chem. Commun., (1965) 33.
2 E.I. Stiefel, Prog. Inorg. Chem., 22 (1971) 1.
3 M.R. Udupa and K.S. Nagaraja, Thermochim. Acta, 56 (1982) 241.
4 F.M. Moore and R.E. Rice, Inorg. Chem., 7 (1968) 2511.
5 K.S. Nagaraja, Ph.D. Thesis, Indian Institute of Technology, Madras, India, 1982.
6 D.M. Clugston and D.B. Maclean, Can. J. Chem., 44 (1966) 781.
7 A.T. Casey, D.J. Mackey, R.L. Martin and A.H. White, Aust. J. Chem., 25 (1972) 477.