ESR Study of MoO_3 Obtained from Thermal Decomposition of Ammonium Molybdate

R. S. Mann and K. C. Khulbe
Department of Chemical Engineering, University of Ottawa, Ottawa, Canada

(Received August 7, 1974)

The thermal decomposition of ammonium molybdate, between 100—600°C was studied by ESR technique. At 250 °C all ammonium molybdate was decomposed into molybdenum trioxide. Samples taken at 250, 300, 350, 400 and 450 °C all gave ESR signals. Samples at other temperatures (higher and below of this temperature range) did not give any ESR signal. The ESR signals were due to the formation of Mo^{5+} and Mo^{3+} ions. The maximum ESR intensity was observed for the sample (MoO_3) at 300 °C. The different colouration of molybdenum trioxide formed at different temperature, was due to Mo^{5+} and Mo^{3+} ions.

Molybdenum trioxide catalyst is usually prepared in the laboratory by thermal decomposition of ammonium molybdate. Onchi and Ma[1] studied the gases evolved during thermal decomposition of ammonium molybdate by using the omegatron mass spectrometer at 395°C. No electron spin resonance (ESR) study has been reported during the formation of MoO_3 from thermal decomposition of ammonium molybdate. It is well known that pure MoO_3 does not give ESR spectra being a higher oxide[2]. In the present paper we report the formation of Mo^{5+} and Mo^{3+} during the MoO_3 formation from ammonium molybdate at different temperature.

Experimental

The MoO_3 was prepared by heating ammonium molybdate (B.D.H.A.R. Grade). Ammonium molybdate was dissolved in minimum quantity of warm water and the solution evaporated over a hot plate with a magnetic stirrer at low heat. The residue was dried for 12 hr at 60°C. The temperature was increased and maintained successively for 24 hr at 100, 150, 200, 250, 300, 350, 400, 450, 500, and 600°C. The samples were taken from the bulk before increasing the temperature. The ESR measurements were carried out by using Bruker 416 spectrometer in which the microwave frequency was in the X band. All measurements were made at room temperature. The Phillips difractometer was used for X-ray analysis of the samples. Measurements were carried out by Debye Sherrer method at room temperature using a cobalt target and an iron filter.

Results

a) X-Ray Analysis. The following table (Table 1) gives the results of X-ray analysis of the thermal decomposition of ammonium molybdate at different temperatures. At 250°C all ammonium molybdate was decomposed and pure MoO_3 formed. There were no other phases (other molybdenum oxides) present except molybdenum trioxide. The colour of the mass changed from white to bluish or gray and again to white as the temperature was raised. The colour of the molybdenum trioxide obtained at 300 °C was sharper than other samples of molybdenum trioxide obtained at other temperature.

Table 1. Results of the phase analysis

Sample at °C	Identified by	Colour
100	Molybdenum-Ammonia-Oxide-Hydrate (NH_3), $Mo_5O_{15}2H_2O$	White
150	$(NH_3)_4Mo_5O_{15}2H_2O$	White
200	$(NH_4)Mo_8O_{26}$[b]	Grayish white
250	Molybdite, (MoO_3)[c]	Grayish white
300	Molybdite	Gray or bluish
350	Molybdite	Gray or bluish
400	Molybdite	Grayish white
450	Molybdite	Grayish white
500	Molybdite	Grayish white
550	Molybdite	Yellowish white
600	Molybdite	White

a) ASTM-21-971. b) ASTM-18-117. c) ASTM-5-508.

Table 2. ESR Intensity with temperature

Sample at 0 °C	ESR signal intensity (main line) rel. units
100	0
150	0
200	4
250	11
300	54
350	13
400	6
450	2.5
500	2.0
550	~0
600	~0

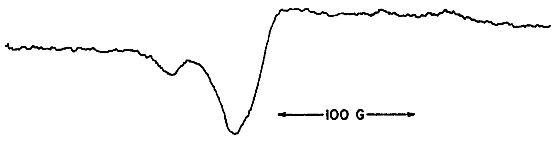

Fig. 1. ESR spectrum of MoO_3 formed at 300 °C.

b) ESR Measurements. Samples taken at 250, 300, 350, 400, and 450 °C all gave ESR signals. Samples at other temperatures (higher and below this range) did not give any ESR signals. Well resolved hyperfine structure was obtained for molybdenum trioxide at 300 °C obtained from the thermal decomposition of ammonium molybdate (Fig. 1), after which the individual hyperfine line broadened out

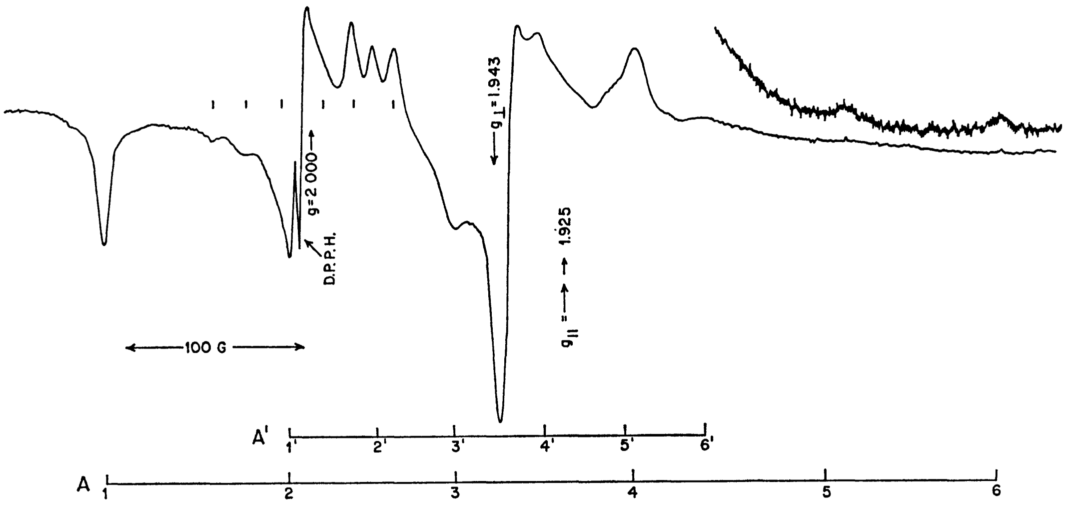

Fig. 2. ESR spectrum of MoO_3 formed at 450 °C.

to form a single broad line near the centre of the spectral pattern (Fig. 2). On the spectrum of the even numbered isotopes there is superimposed hyperfine structure from the uneven numbered isotopes ^{95}Mo and ^{97}Mo (Fig. 1). The quantum number which describe the spectrum are $S=1/2$ and $I=5/2$, and the appropriate axial spin Hamiltonian is:

$$H = \beta[g_{\parallel}H_zS_z + g_{\perp}(H_xS_x+H_yS_y)] + AI_zS_z + B(I_xS_x+I_yS_y)$$

where the terms have their usual meaning. The spin Hamilton parameters were calculated as shown in Table 3.

Table 3. A comparison of results obtained

Ref.	$g_{\perp}$	$g_{\parallel}$	A	B
Maksimovskya *et al.*[5]	1.932	1.88	98±3	52±3
Sultanov *et al.*[6]	1.93	1.88		
Present case	1.943	1.925	100±6	49±2

The effect of the temperature on the ESR signal was investigated. It is apparent from Table 1 and Table II that the maximum signal intensity is observed for a sample at 300 °C when the colour of the molybdenum trioxide was sharper (bluish) than others.

Discussion

Natural molybdenum is a mixture of isotopes, 25% of which consists of two isotopes (^{95}Mo—15.7 and ^{97}Mo—9.4) with nuclear spin of 5/2. The interaction of an unpaired electron with the nuclear magnetic moments of these two isotopes should lead to hyperfine splitting of the spectrum into six components. The remaining isotopes do not have nuclear spins, and should give a spectrum consisting of one line only. Accordingly, the ESR spectrum of the Mo ion should consist of seven lines, the central line being about 25 times as intense as others.

Molybdenum can exist in any of four valency, 6+, 5+, 4+ and 3+ corresponding to d^0, d^1, d^2 and d^3 configuration. Hexavalent molybdenum if diamagnetic and, therefore gives no ESR signal. The tetravalent molybdenum, even if it were paramagnetic would not be observed except at very low temperatures. Also it would be expected that any observed resonance due to d^2, would have a large zero field splitting and therefore would give a very broad signal. Hence the observed signals must be due to Mo(V) and Mo(III).

The patterns of line shown in Fig. 1 are characteristic of Mo^{5+} ion and Mo^{3+}. Landry[3] studied Mo(III) in Al-Zn-phosphate-glass and reported a very broad spectrum at g_{eff} of 4.19. Griffiths, Owen and Ward[4] studied hydrated and unhydrated chloro and fluro complexes of Mo(III) and have reported isotropic g value around 1.96. In the present spectra there are six hyperfines including the main signal at around $g=2.000$. Further the hyperfine lines are approximately at equal spacing *i.e.* around 20±.5 G. Thus it is confirmed that this line *i.e.* at around $g=2.000$ with 6 hyperfine lines is due to Mo^{3+} ion and is not from a free electron.[5] The rest of the spectra is due to Mo^{5+} ion. The g value and other parameters are calculated and are given in Table 3. These are approximately the same as observed by others.[6,7] Thus it is confirmed that the Mo^{5+} and Mo^{3+} are formed during the thermal decomposition of ammonium molybdate.

It is well known that molybdenum trioxide (MoO_3) forms a number of nonstoichiometric oxides on heat treatment in vacuum or in a reducing atmosphere. The departure from stoicheometry is generally associated with the formation of colour centre or can acquire a blue colouration, the so called "Molybdenum blue". The general interpretation had been that the colouration is due to crystal field spectra of electrons in the Mo^{5+} state. The mechanism of the colouration process is not well understood. Deb and Chopoorian[5] suggested that the colour centres in MoO_3 are formed as a result of the free electrons being trapped in oxygen ion vaccancies. An attempt to detect the presence of a one electron centre by the ESR studies on UV irradiated thin film of MoO_3 had failed. In the repeated experiment[8] a new weak ESR absorption at $g = 2.000 \pm 0.005$ was observed which is close to the free electron value. In the present study the absorption at $g = 2.00$ has six hyperfine lines (Fig. 1) which are due to Mo,$^{3+}$ not a free electron. The maximum ESR intensity was observed for the sample MoO_3 at 300 °C (Table 2) and also the colour of the sample was sharper than others (Table 1). The intensity of the ESR signals and the colour decreased with the increase of temperature. It may be possible that the colouration is due to Mo^{5+} and Mo^{3+} (may be Mo^{4+} ion too) ions, and not due to the trapped electrons at anion vaccancies as suggested by Deb and Chopoorian.[5]

We are greatly indebted to Dr. A. Manoogian (Physics Department, University of Ottawa, Ottawa) for discussion and encouragement. The authors are also grateful to National Research Council for financial assistance for the project.

References

1) M. Onchi, and E. Ma, *J. Phys. Chem.*, **67**, 2240 (1963).

2) Y. I. Petcherskaya, V. B. Kazansky, and V. V. Veovodsky, Proc. 2nd Inter. Cong. Cat. Paris, 2nd Edition, Technip 1961, 2121—2134.

3) R. J. Landry, *J. Chem. Phys.*, **48**, 1422 (1968).

4) J. H. E. Griffiths, J. Owen, and I. M. Ward., *Proc. Roy. Soc. Ser. A*, **219**, 526 (1953).

5) S. K. Deb, and J. A. Chopoorian, *J. Appl. Phys.*, **37**, 4817 (1966).

6) R. I. Maksimovskaya, V. F. Anufrienko, and G. D. Kolovertnov, *Kinet. Katal.*, **9**, 1186 (1968).

7) A. S. Sultanov, G. Talipore, M. Inoyatore, V. P. Tatarskii, and K. A. Samigov, *ibid.*, **12**, 1259 (1971).

8) S. K. Deb, *Proc. Roy. Soc., Ser. A*, **304**, 211 (1968).