Vacuum Sublimation Behavior of Molybdenum(VI) and Tungsten(VI) Chelates with 8-Quinolinol

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Synopsis. A vacuum sublimation apparatus with a continuous-temperature gradient (30—280 °C) along the glass tube (60—0 cm) at 10^{-2} and 10^{-1} Torr (1 Torr=133.322 Pa) was used. 8-Quinolinol (Oxine, ox) and its Mo^{6+} and W^{6+} chelates ($MoO_2(ox)_2$ and $WO_2(ox)_2$) in milligram amounts were sublimed without any thermal decomposition. The Mo^{6+} chelate (orange yellow) forms large, rectangular crystals in the crossed state, while the W^{6+} chelate (pale yellow) forms small, rectangular crystals in the scattered states after vacuum sublimation.

8-Quinolinol (Oxine, ox) forms extractable chelates with at least 50 metals.[1-3] Of these chelates, Al^{3+}, Fe^{3+}, $Co^{2+,3+}$, Ni^{2+}, Cu^{2+}, Zn^{2+}, and In^{3+} oxinates have been found to be useful for the purification and separation of metals by means of the vacuum sublimation method.[4] Now, the present authors have found that the Mo^{6+} and W^{6+} oxinates ($MoO_2(ox)_2$ and $WO_2(ox)_2$) in milligram amounts sublime without any thermal decomposition; their vacuum-sublimation behavior has been studied in detail with a continuous-temperature gradient under low pressure.

Experimental

Apparatus. A model PD-51 Yamato Vacuum Pump; a model PM-12 Shimadzu Pirani Gauge; a model CL Yamato Denki Mantle Heater; a model 105-A Tokyo Shibaura Electric Voltage Stabilizer; a model FPW-4 Hitachi Voltage Stabilizer; a model MP-S2 Yanagimoto Melting Point Measuring Apparatus; a model M-7_{II} Hitachi-Horiba pH meter, and a model BH Olympus System Microscope were used.

Materials. The 8-quinolinol (Oxine, ox), purchased from the Wako Junyaku Kogyo Co., was a guaranteed-grade material. The metal oxinates were generally prepared by the addition of an acetic-acid solution of oxine to an aqueous solution of an excess of both metal salts, $Na_2MoO_4 \cdot 2H_2O$ and $Na_2WO_4 \cdot 2H_2O$, adjusted to pH 3—5 by adding 6M (1M=1 mol dm^{-3}) hydrochloric acid or 6M ammonia. After aging overnight on a water bath, the products were filtered off with a glass filter (1G4), washed with hot distilled water, and finally dried in a desiccator under low pressure or on heating at 100—120 °C.[2] The Mo^{6+} and W^{6+} oxinates ($MoO_2(ox)_2$ and $WO_2(ox)_2$) were decomposed at 291—295 °C and about

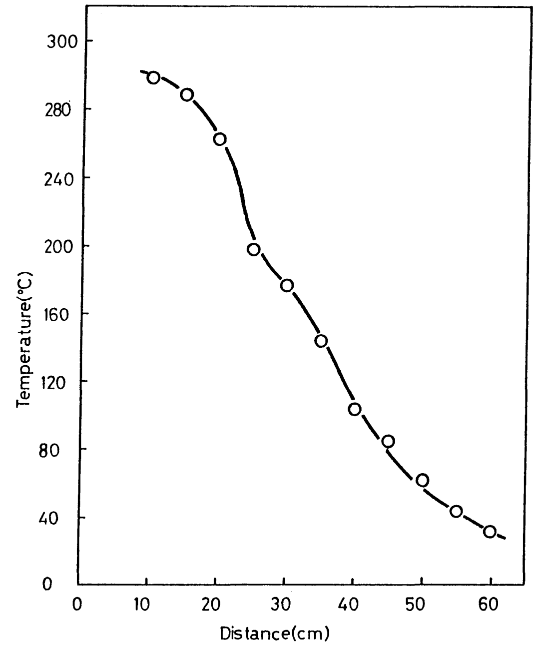


Fig. 1. Continuous temperature gradient along vacuum sublimator.

Table 1. Sublimation-Recrystallization-Zone Temperatures, Amounts Remaining, and Colors of Mo^{6+} and W^{6+} Oxinates after Sublimation at 10^{-2} and 10^{-1} Torr

Metal chelate	Sublimation pressure/Torr	Recrystallization-zone temperature /°C	Color	Chelate taken /mg	Metal compound remained[a]
Oxine(ox)	10^{-1}	<31	White	9.60	—
	10^{-2}	<31	White	9.60	—
$MoO_2(ox)_2$	10^{-1}	222—185	Orange yellow	6.18	A little
	10^{-2}	221—136	Orange yellow	6.30	A little
$WO_2(ox)_2$	10^{-1}	232—204	Pale yellow	3.43	Much
	10^{-2}	224—187	Pale yellow	3.85	Much

a) A little, 10—30%; much, <30%.

All the chelates taken were sublimed a few times without thermal decomposition. The examination of the metal compounds remaining in the sample tubes after every sublimation gave different values, depending on the state of their packing in the sample glass tube.

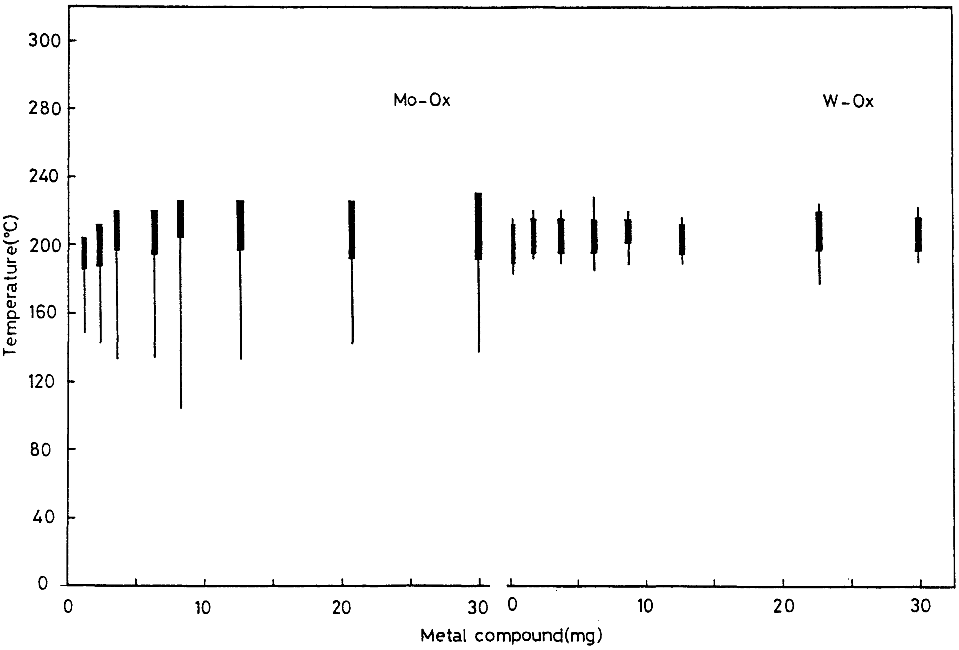
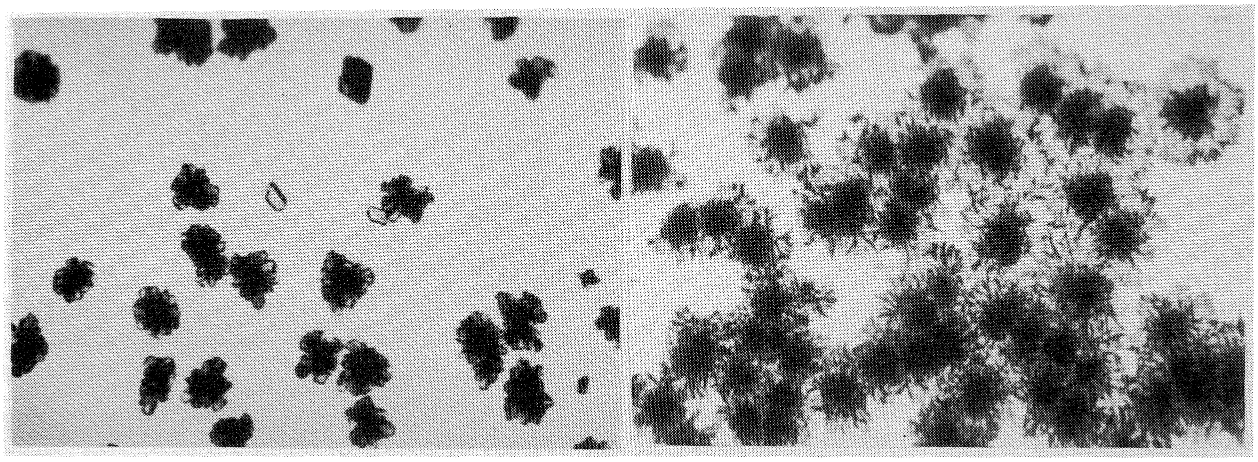


Fig. 2. Sublimation-recrystallization zone of Mo^{6+} and W^{6+} oxinates in various quantities.



$MoO_2(ox)_2$ $WO_2(ox)_2$

Fig. 3. Microphotographs of metal chelates. Hox: Oxine, Magnification: X32.

300 °C respectively under normal pressure; the materials were purified by vacuum sublimation before use, and were identified by means of spectrophotometry (λ_{max}=373 nm for $MoO_2(ox)_2$ and 367.5 nm for $WO_2(ox)_2$ in chloroform[2]).

Sublimation Procedure. A vacuum-sublimation apparatus which provided a continuous-temperature gradient (30—280 °C) along the tube (70—0 cm) at 10^{-2} and 10^{-1} Torr (1 Torr=133.322 Pa) was used, as has previously been described.[4-7] The temperature gradient along the sublimator, which consists of a Pyrex glass tube (3 cm in outer diameter; 100 cm in length) covered with a heating mantle, is shown in Fig. 1; it was obtained after the thermal equilibrium had been kept for 4 h. These patterns were obtained by supplying the following electric power through the heating mantle; 20, 10, and 4 V at 1.30 A. A small glass sample tube (0.6 cm in inner diameter; 5 cm in length) containing an individual chelate (0.5—30 mg) and an attached long glass tube (0.5 cm in outer diameter; 55 cm in length), wrapped tightly with Teflon tape, were inserted into the higher-temperature end of the sublimator. Metal chelates were placed inside of the apparatus for 5 h after the thermal equilibrium had been established. The sublimate zone along the sublimation tube was decided from the color of the chelate and its position. The thermal conditions of the sublimator were always checked from the sublimation zone of a definite amount of copper(II) acetylacetonate after sublimating it by the use of another sublimation tube with the metal chelates to be investigated, as has previously been described.[7] The sublimation-recrystallization-zone temperatures of copper(II) acetylacetonate (in 12 mg amounts) were about 89—60 °C at 10^{-2} Torr and 120—66 °C at 10^{-1} Torr (bluish rectangular crystal).

Results and Discussion

The temperature range of the deposited zones, the recovery, and the colors of the Mo^{6+} and W^{6+} oxinates

($MoO_2(ox)_2$ and $WO_2(ox)_2$) after sublimation at 10^{-2} and 10^{-1} Torr are summarized in Table 1. The Mo^{6+} chelate was almost sublimed without any thermal decomposition, while the W^{6+} chelate was thermally stable, but did not sublime completely. The sublimation-recrystallization temperatures of these chelates gave lower values under low pressures. This may have been caused by the rate of the sublimation of the chelate compounds, which depends upon the temperature established at the high-temperature end of the sublimator.[3-7] The sublimation-recrystallization zones for Mo^{6+} and W^{6+} oxinates in varying quantities (0.5—30 mg) at 10^{-2} Torr are graphically presented in Fig. 2. In general, the sublimation-recrystallization temperature of the Mo^{6+} chelate (0.5—6 mg) and the W^{6+} chelate (0.5—2 mg) gave higher values with an increase in the quantity of the chelates, while that of the Mo^{6+} chelate (6—30 mg) and the W^{6+} chelate (2—30 mg) gave almost invariable values. In cases where the recrystallization-zone pattern was not uniform, the deposition zones (where more than 90% of the chelates were found) are indicated by thicker lines.

Representative photomicrographs of metal oxinates deposited on the glass wall inside the sublimation tube are given in Fig. 3. The Mo^{6+} chelate forms large rectangular crystals in the crossed states, while the W^{6+} chelate forms small, rectangular crystals in the scattered states. Both of the metal chelates generally form large crystals under higher pressures. Therefore, it is evident that sublimation is useful for the purification of milligram amounts of both the Mo^{6+} and W^{6+} oxinates because of the sublimation of only mg amounts of metal compounds. The oxinates can be obtained as uniform and beautiful crystals by the use of the present experimental apparatus.

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