Copper(II) Catalyzed Oxidation of Molybdenum(V) in Aqueous Solutions[*1]

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Molybdenum(V) with the $4d^1$ electronic structure has been the subject of a number of recent studies from the viewpoints of magnetic susceptibility,1) ESR,2) electronic spectra3) and redox enzyme activity.4) In connection with these studies, it has been generally believed that molybdenum(V) in aqueous solutions is easily oxidized to molybdenum(VI) by atmospheric oxygen.5) During the course of investigating stabilization of molybdenum(V) by complex formation, we have found that the oxidation of molybdenum(V) is strongly catalyzed by the presence of metal cations, such as copper(II) and iron(III).

In order to clarify the nature of this reaction, kinetic measurements were carried out as follows. Standard molybdenum(V) solutions prepared by reduction of sodium molybdate(VI) solutions with mercury6) were used in the preliminary experiments. In the later runs, solid complex, $(NH_4)_2MoOCl_5$, prepared after Klason's method7) was conveniently employed. Copper(II) and iron(III) solutions were prepared from JIS[*2] special grade copper(II) sulfate pentahydrate and iron(III) alum, respectively. Other chemicals were all of JIS special grade and used after purifying by recrystallization or distillation. Thrice-distilled water was used for all experiments. Just before each run, a certain amount of $(NH_4)_2MoOCl_5$ was weighed out and dissolved in the acetate buffer solutions of appropriate pH and temperature. All experiments were conducted with dissolved molybdenum(V) concentration of about 2×10^{-4} M. The oxidation reaction was followed spectrophotometrically by measuring extinction at 320 mμ which is at the maximum of the absorption spectrum of molybdenum(V) species.

After a number of preliminary runs, it was found that, under the conditions given above, the rate of catalytic oxidation of molybdenum(V) was independent of the kind of standard molybdenum(V) species employed, and small amounts of anions, such as acetate, chloride, perchlorate, sulfate and nitrate, had no effect on the oxidation rate.

The results of systematic experiments showed that the rate of oxidation of molybdenum(V) was first order with respect to the concentration of molybdenum(V), when other conditions were kept the same. In the range of pH 2.4—5.2, the rate was inversely proportional to the square of hydrogen ion concentration.

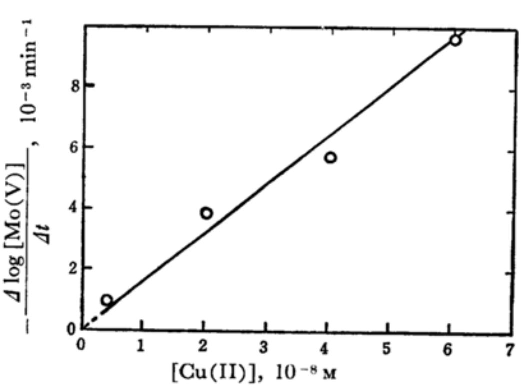

Fig. 1. A plot of the rate of oxidation of molybdenum(V) *vs.* concentration of copper(II).

0.01M acetate buffer, pH: 5.1, 25°C. Initial concentration of molybdenum(V): 2×10^{-4}M

As is seen from Fig. 1, it was also confirmed that under a definite condition the rate is proportional to the concentration of copper(II). In an extreme case where the concentration of copper(II) is less than 10^{-9} M, almost no oxidation of molybdenum(V) was seen to take place. It appeared that the rate is independent of the partial pressure of oxygen.

From the above-mentioned results, the experimental rate law may be expressed as follows:

$$-d[Mo(V)]/dt = k[Mo(V)][Cu(II)]/[H^+]^2.$$

The value of the apparent rate constant k was estimated as *ca.* 2×10^{-4} M min^{-1} at 25°C.

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[*2] Japanese Industrial Standards.