BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1435—1436 (1971)

The Thermochromism of Molybdenum(V) in Hydrochloric Acid Solutions

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(Received December 14, 1970)

During a systematic study of the autoxidation of molybdenum(V) in aqueous solutions,[1] it was found that the color of the hydrochloric acid solutions of molybdenum(V) changes remarkably with a rise in temperature. It was established that the change is prominent in the concentration range of 4—6 molar HCl, and is reversible between room temperature and 100°C. These observations have been explained on the basis of temperature dependence of the monomer-dimer equilibrium[2]

$$(MoOCl_4)_2O^{4-} + 2HCl \rightleftarrows 2MoOCl_5^{2-} + H_2O$$

Experimental

Molybdenum(V) solutions were prepared by dissolution of $(NH_4)_2MoOCl_5$[3] in an appropriate concentration of hydrochloric acid. Thrice distilled water was used throughout the experiment. The absorbance measurements were carried out by an Ito model QU-3 spectrophotometer using 1-cm stoppered quartz cells. The temperatures were controlled by circulating ethylene glycol from a Haake thermostat.

Results and Discussion

Figure 1 shows the effect of temperature on the visible spectra at 5 molar HCl. The molybdenum(V) solution has two absorption maxima at 450 mμ (I) and at 720 mμ (II), both of which are assigned to *d–d* transition in $4d^1$ electronic configuration.[4] It will be seen that the absorbance at 450 mμ decreases strikingly with a rise in temperature, while at 720 mμ absorbance remains almost unchanged. The net result is that the solution is yellow at room temperature but turns to light green at higher temperatures.

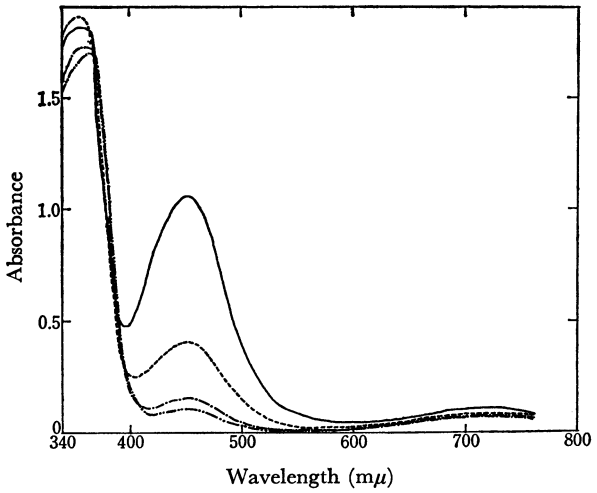

Fig. 1. The spectrum of 5×10^{-3} M $(NH_4)_2MoOCl_5$ in 5M HCl at various temperatures.
a) —— 33.5°C, b) ---- 57.5°C, c) ····· 78.6°C, d) -·-·-· 94.0°C

It was established that, when the hot solution is allowed to cool to room temperature, the original pattern of spectra is recovered with slight decrease of absorbance. It was noted that the patterns of spectra at lower and higher temperatures are quite similar to those observed at lower and higher concentration ranges of hydrochloric acid.[2]

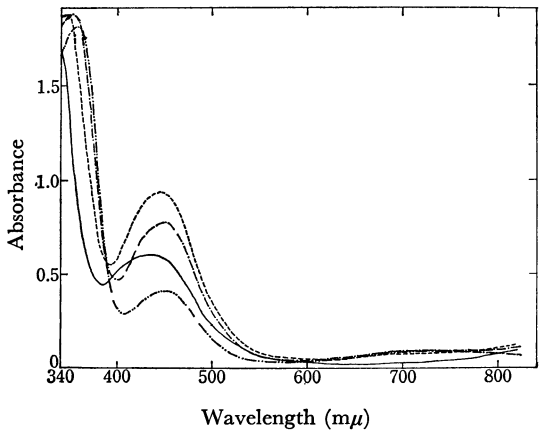

Fig. 2. The spectrum of 5×10^{-3} M $(NH_4)_2MoOCl_5$ in 4 M HCl at various temperatures.
a) —— 25.7°C, b) ---- 58.6°C, c) ····· 78.2°C, d) -·-·-· 93.2°C

In a 6 molar HCl solution, the color of the solution is light green at room temperature, but with a temperature rise a slight decrease in absorbance is still observable at 450 mμ.

As shown in Fig. 2, when the concentraton of HCl is kept at 4 molar, the absorption maximum (I) decreases and shifts to shorter wave length at room temperature. When the temperature is raised, the absorption maximum (I) at first shifts to 450 mμ and increases in intensity, and then begins to decrease. By comparing such a change to that in a 5 molar HCl solution, it is suggested that another form of polymeric species (D_2) exists in the 4 molar HCl solution at room temperature, and that with a rise in temperature this species at first changes into yellow dimer (D_1), and then to green species (M). Moreover, it was confirmed that the spectral change is reversible with respect

1) Y. Yoshino, T. Takeuchi, H. Kinoshita, and S. Uchida, This Bulletin, **41**, 765 (1968); *Sci. Pap. Coll. Gen. Educ. Univ. Tokyo*, **19**, 71 (1969).
2) J. P. Haight, Jr., *J. Inorg. Nucl. Chem.*, **24**, 663 (1962).
3) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge, England (1954), p. 408.
4) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962).

to temperature.

To summarize the above observations, it may be concluded that the thermochromism of molybdenum(V) in approximately 5 molar HCl solution is due to the shift of equilibria between monomeric and dimeric species of molybdenum(V), and is the same sort of change observed in varying concentrations of hydrochloric acid. On this basis, the apparent equilibrium constants, K of the monomer (M)-dimer (D_1) equilibria,

$$D_1 \rightleftarrows 2M$$

were calculated according to Haight's approach.[2] The results are summarized in Table 1.

Table 1. Apparent equilibrium constants for dimer-monomer equilibria at various temperatures

6M HCl		5M HCl		4M HCl	
t°C	$K\times10^3$, M	t°C	$K\times10^3$, M	t°C	$K\times10^3$, M
23.8	3.18	33.5	0.368	25.7	(0.853)
56.3	14.9	57.5	1.37	58.6	(0.442)
75.5	30.0	78.6	5.78	78.2	5.79
92.5	54.2	94.0	12.1	93.2	1.37

Total concentration of molybdenum(V): 5×10^{-3}M.

Using these values, $-\log K$ was plotted against the reciprocal absolute temperature; the plots are shown in Fig. 3.

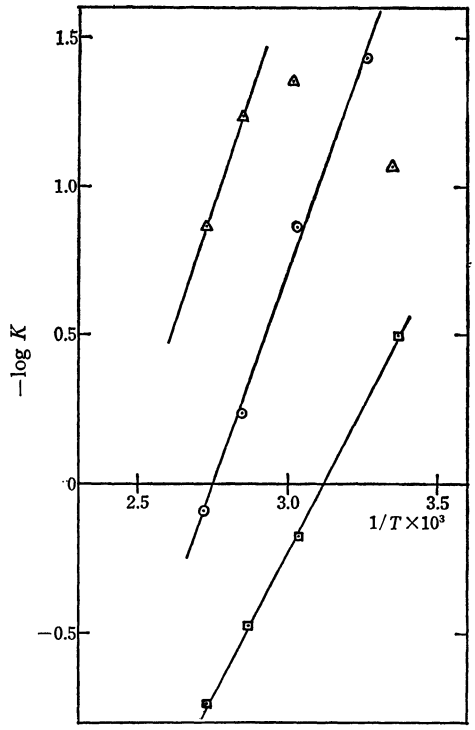

Fig. 3. The plots of $-\log K$ against $1/T$.
5×10^{-3} M Mo(V) in 4 M (△), 5 M (⊙), 6 M HCl (⊡)

Linear relations were found to hold in the cases of 6 and 5 molar HCl solutions over the temperature range studied, and this confirms the existence of monomer-dimer equilibria in these solutions. In the case of 4 molar HCl solution, however, the linear relation no longer holds in the lower temperature range as would be expected from the above-mentioned experiments.

From the slopes of the straight lines, the values of enthalpy change, ΔH, were evaluated as 8.9, 13.3, and 14.3 kcal/mol for 6, 5 and 4 molar HCl solutions respectively. These values are somewhate larger than Haight's, $\Delta H=6.0\pm0.2$ kcal/mol in 5 molar HCl solutions. The variation of the enthalpy values seems understandable in light of the possible overlapping of further hydrolytic equilibria in a relatively low concentration range of acid such as 4 to 6 molar HCl.