산성수용매에서 이-μ-옥소비스-(아쿠아옥살라토옥소몰리브덴(V)) 산이온과 티오시안산이온의 반응

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Kinetic Studies on the Reaction of Thiocyanate with Di-μ-oxobis-(aquaoxalatooxomolybdate(V)) in Acid Media

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요 약. 산성용매에서 몰리브덴—옥살산 결합의 고리열림이 일어난 다음 티오시안산과 반응하는 속도를 460nm에서 분광학적으로 측정하였다. 산성용매에서 몰리브덴—옥살산의 해리와 이 해리된 착물과 티오시안산의 반응속도를 티오시안산 및 수소이온농도에 따라 연구하였다. 몰티브덴에 결합된 옥살산리간드에 양성자첨가가 되고 이 양성자 첨가된 착물은 티오시안산이온과 반응을 빠르게한다. 이들 결과에서부터 산성용매에서 옥살산리간드의 치환은 몰리브덴닐산소의 트란스에 결합된 산소의 결합이 끊어지는 과정과 관련되는 해리메카니즘에 의해서 설명할 수 있다.

ABSTRACT. Rate constants for complexing with thiocyanate after ring opening of molybdenum-oxalate in acid media were obtained spectrophotometrically at 460nm. The acid-assisted dissociation of molybdenum-oxalate and the reaction of thiocyanate with oxalatooxomolybdenum(V) complex in acid media were investigated with thiocyanate and hydrogen ion concentration. The kinetic data indicate that molybdenum-oxalate is protonated to a limited extent in acid media and the protonated complex is responsible for an increase in rate for the reaction of thiocyanate with oxalatooxomolybdenum(V) complex. Replacement of an oxalate ligand in acid media has been interpreted in terms of dissociative mechanism involving bond-breaking of the oxygen *trans* to the yl oxygen.

INTRODUCTION

The paramagnetic $MoO_{(aq)}^{3+}$ is the predominate species in high hydrochloric acid solution, but the diamagnetic $Mo_2O_{4(aq)}^{2+}$ is the predominate species in the lower hydrochloric acid solution (<4M) as shown by ^{18}O studies.[1] The reaction (1) of SCN^- with the molybdenum(V) aqua dimer, $Mo_2O_{4(aq)}^{2+}$ have been studied previously.[2]

$$Mo_2O_4(H_2O)_6{}^{2+}+SCN^- \longrightarrow$$

$$Mo_2O_4(H_2O)_5NCS^+ + H_2O \qquad (1)$$
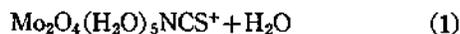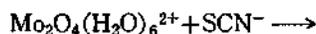
Molybdenum(V) complexes with oxalates were prepared by Bailhache[3] and characterized by Mitchell.[4] The structure(I) of $BaMo_2O_4(C_2O_4)_2$ $5H_2O$, which is a diamagnetic binuclear complex anion with a double oxygen bridge and two terminal oxygens, has been determined by X-ray crystallographic method.[5]

The rapid 1:1 equilibration(2) of thiocyanate
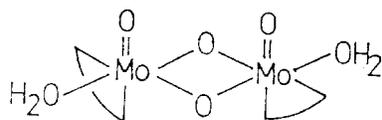
and pyridine with the di-μ-oxo-bis aqua-oxalatooxomolybdenum(V) complex in aqueous solution have already been studied by temperature-jump technique.[6]

$$Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}+SCN^- \longrightarrow$$
$$Mo_2O_4(C_2O_4)_2(H_2O)NCS^{3-}+H_2O \qquad (2)$$
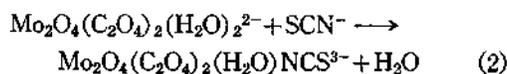
The kinetic results were interpreted in terms of the replacement of an H_2O ligand *cis* to a terminal oxo groups and a dissociative S_N1 nonlimiting mechanism for substitution.

We obtained the result that one coordinated water was substituted by thiocyanate and the other coordinated water was not displaced by SCN^-, but two thiocyanate are substituted in acid media. We now report here our results of studies on displacement of a site of an oxalate of Mo_2O_4 $(C_2O_4)_2(H_2O)_2{}^{2-}$ by SCN^- in acid media after dissociation of molybdenum-oxalate bond.

EXPERIMENTAL

Reagents. Distilled water was redistilled from alkaline permanganate solution. All chemicals were reagent grade. Analytical grade sodium molybdate was recrystallized from the distilled water and dried at 120 °C. Recrystallization of sodium thiocyanate was done in ethanol as described previously.[2] Sodium perchlorate was prepared from the solution of 60% perchloric acid and sodium hydroxide. Solution of sodium perchlorate was analyzed by acid titration after proton ion exchange replacements of sodium ion.

Stock Solution of $Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}$. The molybdenum(V) was obtained by reduction of sodium molybdate in 4M HCl with hydrazine

hydrochloride at 80 °C for about 2 hours.[1] Under these conditions the aquo dimer $Mo_2O_{4(aq)}^{2+}$ is formed. The $Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}$ was prepared by addition of oxalate to $Mo_2O_{4(aq)}^{2+}$ and adjusting $[H^+]$ to 0.1 M-1 M. The solution was vacuum-dried to yield brown crystals. Prolonged drying of these crystals *in vacuo* furnished a brown crystal. The aqueous solutions of the complex were made by dissolving freshly prepared crystals in water. The aqueous solutions when stored at 0 °C were stable for a few months. However, aqueous solutions were freshly prepared before use.

Kinetic Measurements. Perkin-Elmer Lambda 5 UV/VIS and Shimadzu UV 120-01 spectrophotometers were used to monitor the reaction of thiocyanate with $Mo_2O_4(C_2O_4)_2(H_2O)^{2-}$. Rates of anation were measured by adding $HClO_4$ of a given concentration with microburet to reaction cell after 1:1 equilibration of $Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}$ with SCN^- at constant temperature. All measurements were carrid out in a thermostatted quartz cell of 1cm path length. The temperature was controlled to within 0.1 °C by circulating water through cell compartment. Ionic strengths of all the measurements were adjusted with sodium perchlorate. The kinetics of the reactions were studied under pseudo-first order conditions at the desired temperatures. The rate constants were obtained by a linear least-squares analysis of the absorbance against time in accordance with the expression

$$-\ln(A_t-A_\infty)=k_{obsd}t-\ln(A_0-A_\infty) \qquad (3)$$

where A_t, A_0 and A_∞ represent the absorbance at time t, the initial absorbance and absorbance at effective infinite time, respectively. The relation between $\ln(A_t-A_\infty)$ versus t was straight line (correlation coefficient=0.999-0.995) for at least 3-4 half-lives. The wavelength was fixed at 460nm and the increase in optical density was monito-

red. A product of the 1:1 rapid equilibrium (2) before run has a negligible absorbance at 460 nm. Activation parameters were calculated from the equation (4)

$$k_{obsd} = \frac{kT}{h} e^{\Delta S^*/R_e - \Delta H^*/RT} \qquad (4)$$

where k_{obsd} is the observed first-order rate constant at Kelvin temperature T, k the Boltzmann constant, h the Planck constant, R the gas constant, ΔS^* the entropy of activation and ΔH^* the enthalpy of activation. A least-square analysis of $\ln(k_{obsd})$ vs. $1/T$ data was used over a temperature range of at least 20 °C.

RESULTS AND DISCUSSION

The equilibrium constant for the reaction (5) will be

$$K = \frac{[Complex(product)]}{[Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}]^m [SCN^-]^n}$$

$$mMo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-} + nSCN^- \xrightleftharpoons{K}$$

$$Complex(product) \qquad (5)$$
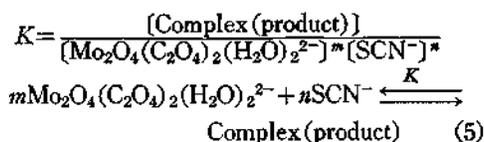
Is we take the logarithms of left and right sides of this equation we may write

log [complex] = log$K$ + $m$log [Mo$_2$O$_4$ (C$_2$O$_4$)$_2$ (H$_2$O)$_2{}^{2-}$] + $n$log [SCN$^-$] The slope of plot of the logarithms of the absorbance of the complex and the concentration of the SCN$^-$ ion gives the value of $n=2$ (*Fig.* 1). In nonacidic media one water ligand of Mo$_2$O$_4$(C$_2$O$_4$)$_2$(H$_2$O)$_2{}^{2-}$ is displaced by a thiocyanate ion, but in acidic media ([H$^+$] = 0.3−0.85) one water molecule and a coordinated site of molybdenum−oxalate bond are substituted with two thiocyanate ions.

Rate constants for complexing with thiocyanate after ring opening of molybdenum-oxalate in acid media were obtained spectrophotometrically at 460nm. *Table* 1 summarizes all of the rate runs obtained with the various conditions. The acid−assisted dissociation of Mo$_2$O$_4$—C$_2$O$_4$ and the reaction of SCN$^-$ with Mo$_2$O$_4$(C$_2$O$_4$)(HC$_2$O$_4$)
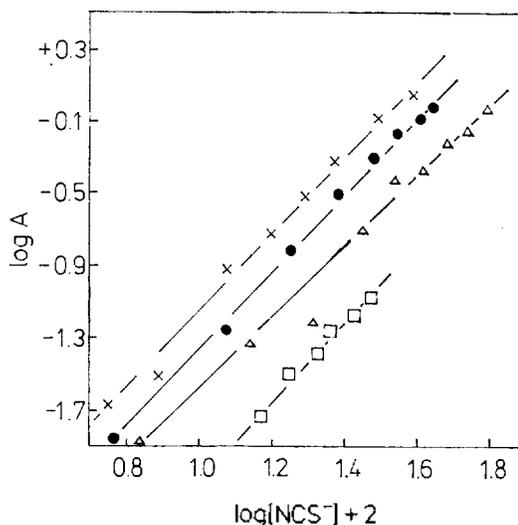
Fig. 1. Plots of logarithms of absorbances against logarithms of concentration of thiocyanate for the reaction (5) at 25°C. (H$^+$): 0.85, (×); 0.61, (●); 0.48, (△); 2.14, (□).
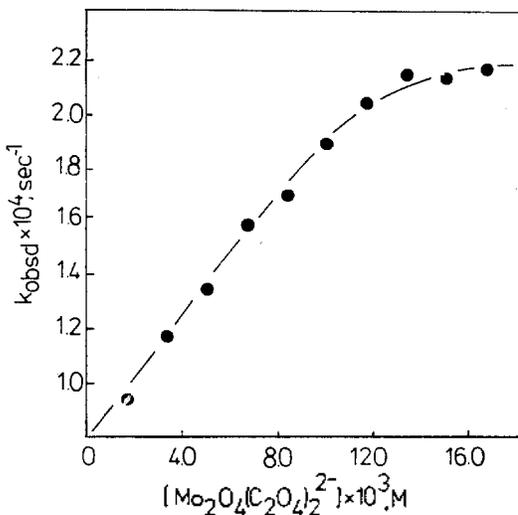
Fig. 2. Plot of first-order rate constants against concentration of Mo$_2$O$_4$ (C$_2$O$_4$)$_2$ (H$_2$O)$_2{}^{2-}$ for the reaction(5) at 25 °C. [SCN$^-$]=0.62 M. [HClO$_4$] = 0.26 M.

(H$_2$O) (NCS)$^{2-}$ in acid media was investigated by varying [H$^+$] from 0.1 to 0.8M. The nonlinear dependence of k_{obsd} on Mo$_2$O$_4$ (C$_2$O$_4$)$_2$ (H$_2$O)$_2{}^{2-}$ ion concentration is illustrated in *Fig.* 2. The reaction, as well as all studied in this

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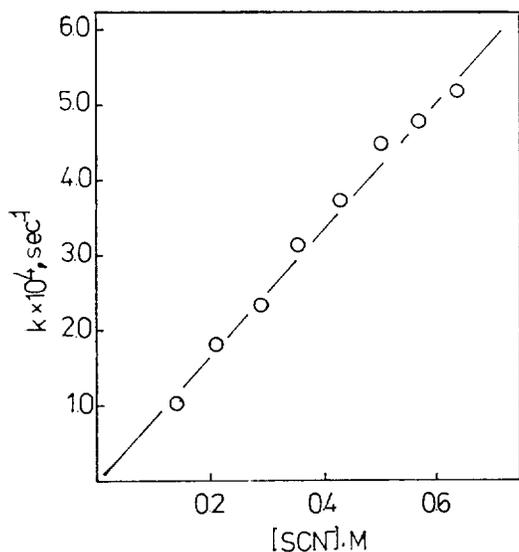
Fig. 3. Dependence of rate constants on thiocyanate ion concentration for the reaction(5). $[Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}] = 2.03 \times 10^{-3}M$, $[HClO_4] = 0.61\ M$.
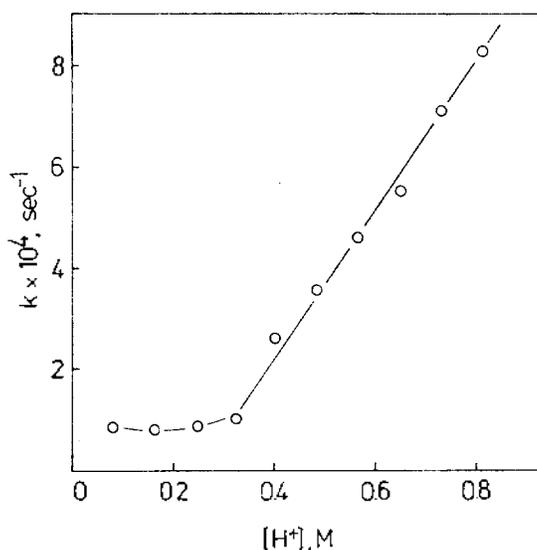
Fig. 4. Dependence of rate constants on hydrogen ion concentration for the reaction (5) at 25°C. $[Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}] = 2.61 \times 10^{-3}M$, $[SCN^-] = 0.47M$, $\mu = 0.8$.

investigation, followed pseudo-first order kinetics with SCN^-

$$k_{obsd} = k_{-1} + k_1[SCN^-] \tag{6}$$

Table 1. Rate constants of the reaction of $Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}$ with thiocyanate at 25 °C

| no.	$[Mo_2O_4(C_2O_4)_2(H_2O)_2{}^{2-}]_{added} \times 10^3,\ M$	$[SCN^-]_{added},\ M$	$[HClO_4]_{added},\ M$	$[NaClO_4]_{added},\ M$	$k_{obsd} \times 10^4,\ sec^{-1}$
1	1.37	0.62	0.26		0.93
2	2.73	0.62	0.26		1.17
3	4.11	0.62	0.26		1.34
4	5.48	0.62	0.26		1.58
5	6.84	0.62	0.26		1.70
6	8.21	0.62	0.26		1.90
7	9.58	0.62	0.26		2.05
8	10.95	0.62	0.26		2.15
9	12.32	0.62	0.26		2.13
10	13.68	0.62	0.26		2.17
11	2.61	0.47	0.81		8.47
12	2.61	0.47	0.73	0.08	7.13
13	2.61	0.47	0.65	0.16	5.68
14	2.61	0.47	0.56	0.24	4.61
15	2.61	0.47	0.48	0.32	3.54
16	2.61	0.47	0.40	0.40	2.59
17	2.61	0.47	0.32	0.48	1.04
18	2.61	0.47	0.24	0.56	0.89
19	2.61	0.47	0.16	0.65	0.81
20	2.61	0.47	0.08	0.73	0.84
21	2.03	0.64	0.61		5.35
22	2.03	0.57	0.61		4.72
23	2.03	0.50	0.61		4.43
24	2.03	0.43	0.61		3.70
25	2.03	0.36	0.61		3.10
26	2.03	0.29	0.61		2.44
27	2.03	0.21	0.61		1.68
28	2.03	0.14	0.61		0.96
29	7.60	0.68	0.47		0.25[a]
30	7.60	0.68	0.47		0.55[b]
31	7.60	0.68	0.47		1.05[c]
32	7.60	0.68	0.47		2.95[d]
33	7.60	0.68	0.47		3.79[e]

[a,b,c,d] and [e] are 25.0, 30.0, 35.0, 40.0 and 45.0°C, respectively.

It is clear that the reaction is first order in $[SCN^-]$ as shown in Fig. 3. Also the intercept obtained from Fig. 3. implies a reverse reaction.

The values of k_1 evaluated from a linear least squares fit of the k_{obsd} against $[SCN^-]$ are constant within the experimental errors. k_1 and
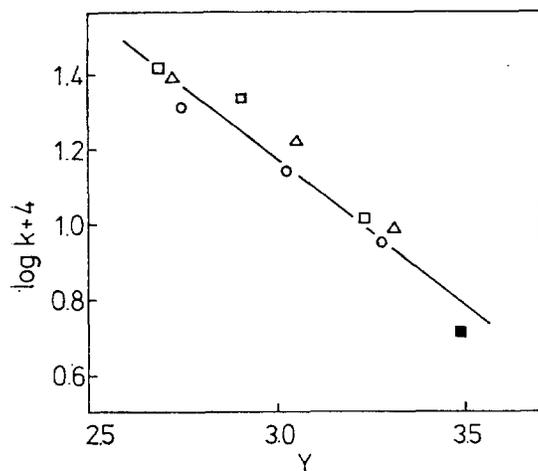
Fig. 5. Grunwald-Winstein plot for the reaction(5) at 25°C. Cosolvent: methanol, (○); ethanol, (△); acetone, (□); water, (■).

Table 2. First-order rate constants for the reaction of SCN⁻ with $Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$ at 25°C. [SCN⁻] $=0.50M$, [HClO₄] $=0.83 M$, [$Mo_2O_4(C_2O_4)_2^{2-}$] $=5.23 \times 10^{-3}M$

Organic component	V/V, %	Y	$k_{obsd} \times 10^3$, sec⁻¹
Menthanol	0	3.49	0.51
	10	3.28	0.88
	20	3.03	1.39
	30	2.75	2.04
Ethanol	10	3.31	0.95
	20	3.05	1.62
	30	2.72	2.47
Acetone	10	3.23	1.24
	20	2.91	2.14
	30	2.69	2.61
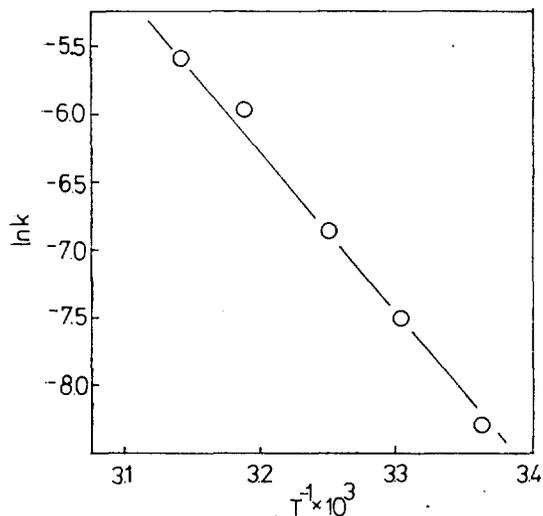
Fig. 6. Temperature dependence of first-order rate constants for the reaction(5). [$Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$] $=7.66 \times 10^{-3}M$, [SCN⁻] $=0.68M$, [HClO]₄ $=0.47M$.

k_{-1} are $8.75 \times 10^{-4}M^{-1}sec^{-1}$ and $k_{-1} = -1.41 \times 10^{-5}sec^{-1}$, respectively. Although k_{-1} is significant the slightly negative value is obtained with various errors including inaccurate SCN⁻ in equilibration of SCN⁻ with $Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$. Value of k_1 is real but k_{-1} is not large enough to detect.

Fig. 4. summarizes the variance of k_{obsd} with [H⁺] at a constant concentration of $Mo_2O_4(C_2$

$O_4)_2(H_2O)_2^{2-}$ and SCN⁻. It is obtained that the anation of SCN⁻ ligand at the low acidic region [H⁺] $<0.25 M$ is independent on [H⁺] but at the higher acidic region [H⁺] $>0.25M$ the rate is dependent on [H⁺]. Hydrogen ion dependence was highly reproducible and definitive.

$$k_1 = k_2 + k_3[H^+] \tag{7}$$

A straight line of *Fig.* 4 was obtained with $k_2 = 8.45 \times 10^{-5}sec^{-1}$ from intercept and $k_3 = 1.11 \times 10^{-2}M^{-1}sec^{-1}$ from slope, showing k_{obsd} to be first order function of [H⁺]. This was confirmed by kinetic study at the various [H⁺].

Rate constants in aqueous organic solvents are given in *Table* 2 and correlation of the logarithms of the rate constants for anation with the solvent ionizing power, Y was shown in *Fig.* 5 The slope of the straight line for the reaction of SCN⁻ with $Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$ was found to be $m = -0.4$. The negative m values are associated with reactions in which one of the separating moieties is a charged species containing the hydrophilic groups[8]. The agreement in the m values for dissociatin of Mo–C_2O_4 and the anation of SCN⁻ with magnitude reported for the other complexes as shown in *Table* 3

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Table 3. m values of thereaction of the complexes with water or anions

Reactant	m	ref.
$Fe(CN)_5(3,5-Me_2py)^{3-}$, CN^-	-0.10	8
$Co(NH_3)_5Cl^{2+}$, H_2O, $Hg(II)$	-0.35	11
$Rh(NH_3)_5Cl^{2+}$, H_2O, $Hg(II)$	-0.25	11
$ReCl_6^{2-}$, H_2O, $Hg(II)$	-1.70	9
$ReBr_6^{2-}$, H_2O	-0.55	9
$Mo_2O_4(C_2O_4)_2(H_2O)_2^{2-}$, SCN^-, H^+	-0.41	This work

indicates that the degree of dissociation in the activated state is similar for aquation of all systems[9]. This is consistent with an essentially dissociative mechanism.

The activation enthalpy, $\Delta H^* = 105.11 kJmol^{-1}$ was obtained from the slope of *Fig.* 6. The corresponding entropies of activation at 30 °C were calculated by using the equation (4) to be $\Delta S^* = 38.85 J/mol K$. The positive entropy of activation is expected a dissociative process for this reaction as have previously been suggested[10].

A mechanism consistent with the kinetic data can be suggested that the anation consists of paths (a) and (b). It is reasonable to suggest that protonation of an oxygen of the $C_2O_4^{2-}$ helps to accelerate dissociation of $C_2O_4^{2-}$ and to be displaced a coordinated site of oxalate ligand by thiocyanate ion. At high acidity ($>0.4M$) where the k_3 term predominates, we suggest that the protonation of the oxygen of $Mo-OC_2O_3$ precedes substitution through a site of protonated oxalate ligand

$$Mo_2O_4(C_2O_4)(H_2O)(NCS)^{3-} + H^+ \xrightarrow{K_H}$$
$$Mo_2O_4(C_2O_4)(HC_2O_4)(H_2O)(NCS)^{2-}$$
$$\text{(I)}$$
$$\text{I} + SCN^- \xrightarrow{k} Mo_2O_4(C_2O_4)(HC_2O_4)(H_2O) \quad \text{(a)}$$
$$(NCS)_2^{3-}$$
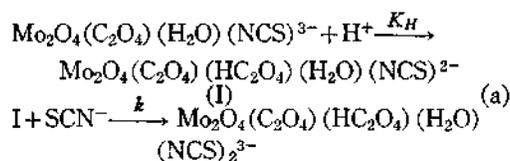
From the above reactions
$$R = k[\text{I}][SCN^-] = K_H k[Mo_2O_4(C_2O_4)_2(H_2O)$$
$$(NCS)^{3-}][H^+][SCN^-] \text{ and } K_H k = k_3.$$

In the less acidic region the anation is gover-

ned by the rate law
$$Rate = k_2[Mo_2O_4(C_2O_4)_2(H_2O)(NCS)^{3-}][SCN^-]$$
This rate comes about through the hydrolysis product:

$$Mo_2O_4(C_2O_4)_2(H_2O)(NCS)^{3-} + H_2O \xrightarrow{K_0}$$
$$Mo_2O_4(C_2O_4)(OC_2O_3)(H_2O)(NCS)^{3-}$$
$$\text{(II)}$$
$$\text{II} + SCN^- \xrightarrow{k} Mo_2O_4(C_2O_4)(OC_2O_3)(H_2O) \quad \text{(b)}$$
$$(NCS)_2^{4-}$$
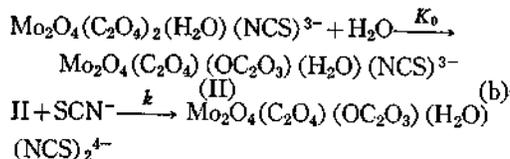
Thus, $R = k[\text{II}][SCN^-] = K_0 k[Mo_2O_4(C_2O_4)_2(H_2O)(NCS)^{3-}][SCN^-]$ and $K_0 k = k_2$

In summary, the kinetic data in this paper indicate that oxalate ligand is protonated to a limited extent in acid media and this form is responsible for an increase in dissociation at transition state. Replacement of an oxalate ligand in acid media by SCN^- has been interpreted in terms of dissociative mechanism involving bond breaking of the oxygen *trans* to the yl oxygen.

REFERENCES

1. (a) C. S. Kim and R. K. Murmann, *Inorg. Chem.*, **23**, 263(1984); (b) C. S. Kim, R. K. Murmann and E. O. Schlemper, *Transition Met. Chem.*, **9**, 260(1984).
2. Y. Sasaki, R. S. Taylor and A. G. Sykes, *J. Chem. Soc. Dalton Trans.*, 396(1975).
3. M. G. Bailhache, *Bull. Soc. Chim. France*, **68**, 161(1903).
4. P. C. H. Mitchell, *J. Chem. Soc.* (A), 146(1969).
5. F. A. Cotton, *Inorg. Chem.*, **4**, 1377(1965).
6. G. R. Cayley and A. G. Sykes, *Inorg. Chem.*, **15**, 2882(1976).
7. A. Bino, F. A. Cotton and Z. Dori, *J. Amer. Chem. Soc.*, **100**, 5252(1978).
8. M. J. Blandamer, J. Burgess and R. I. Haines, *J. Chem. Soc. Dalton Trans.*, 1293(1976).
9. J. Burgess, R. D. Peacok and A. M. Petric, *J. Chem. Soc. Dalton Trans.*, 902(1973).
10. J. Ojo, Y. Sasaki, R. S. Taylor and A. G. Sykes, *Inorg. Chem.*, **15**, 1006(1976).
11. J. Burgess and M. G. Price, *J. Chem. Soc.* (A), 3108(1971).