Bull. Inst. Chem. Res., Kyoto Univ., Vol. 55, No. 6, 1977

Kinetic Study of Salt Effect on Conversion Reaction of β to α-Dodecamolybdosilicate Complex

Taitiro FUJINAGA, Mutsuo, KOYAMA, and Toshitaka HORI*

Received October 22, 1977

In order to elucidate salt effects on conversion reaction of β to α-dodecamolybdosilicate complex, the conversion rate was measured kinetically in the presence of several kinds of neutral salts like as sodium chloride, sodium perchlorate, ammonium chloride, potassium chloride, and ammonium sulfate.

β-complex converts to α-complex by a first-order rate with respect to its concentration and the rate constant was evaluated as $k_{obs}=(2.13\pm0.03)\times10^{-3}\ min^{-1}$ in the absence of any salts except for an excess of sodium chloride introduced during the preparation of β-complex. The value of k_{obs} was a conditional constant and increased by the addition of the neutral salts in proportion to their concentration. The result can be formulated into a simple equation: $k_{obs}=k_{obs,extp}+b_s\cdot[C_s]$, where C_s: concentration of the added salt; b_s: a proportional constant which is specific to the salt: $k_{obs,extp}$: a conversion rate constant obtained by extrapolating k_{obs} toward $C_s=0$. On each salt, the magnitude of the salt effect was presented by the value of b_s and compared mutually, and it was concluded that the neutral salts, which have been considered to be inert, actually participate with the transition state of the conversion reaction.

INTRODUCTION

It is known that the rate of the conversion reaction of β to α-dodecamolybdosilicate complex (abbreviated as β-complex and α-complex hereafter, respectively) is affected by the presence of neutral salts in aqueous solutions. The effect was first pointed out by Strickland[1] with ammonium sulfate. The similar effects by the other neutral salts have been observed in the determinations of silicate ions based on the formation of β-complex,[2~5] and the effect has been called as salt effect or salt error. Recently, Fanning and Pilson investigated[6] the salt effect in seawater samples and correlated the effect to the salinity and hence to the ionic strengths of the media. However, the salt effect is not systematically investigated yet.

In the present paper, the authors determined the absorptivities of α and β-complex and established a spectrophotometric method for determining the concentration of each complex in their mixture. By the method, the decrease of β-complex due to the conversion can be monitored continuously and the conversion rate was determined kinetically. The kinetic analysis was carried out in the presence of neutral salts such as sodium chloride, sodium perchlorate, ammonium chloride, potassium chloride and ammonium sulfate, and the effects of the salts on the rate constants were systematically investigated. The participation of these salts with the conversion reaction is also discussed.

* 藤永太一郎, 小山睦夫, 堀 智孝: Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.

EXPERIMENTAL

Reagents. 0.01 M silicate standard solution containing sodium carbonate in a concentration of 0.1 M was prepared by fusing 0.3005 g of quartz wool with 5.3 g of Na_2CO_3, followed by diluting the resulted cake to 500 ml with water.

0.1 M molybdate solution was prepared by dissolving 24.195 g of $Na_2MoO_4 \cdot 2H_2O$ with water and diluting it to 1 liter.

1 M salt solutions of NaCl, $NaClO_4$ NH_4Cl, KCl, and $(NH_4)_2SO_4$ were prepared by dissolving the respective anhydrous salt with water.

Measurements. Measurements of absorbance and absorption spectra were carried out by using a UV-200 spectrophotometer (Shimadzu) at a constant temperature of $25 \pm 0.2°$. Quartz cells with path-lengths of 1, 0.2, and 0.1 cm were properly used according to the intensity of absorbance of sample solutions. The path-length of each cell was calibrated as 1×1.00, 0.2×1.02, and 0.1×1.02 cm, respectively.

RESULTS

1) Formation of α and β-complex and Their Absorptivity

It is known[1] that β-complex is formed predominantly in solutions acidified with more than two equivalents of H^+ per gram-atom of Mo, being accompanied by the spontaneous conversion to α-complex. Actually, in properly acidified solutions, the rate of formation of β-complex is quite larger than that of the conversion and, hence, the formation reaction can be easily distinguished from the conversion reaction. According to the following manner, the degree of the conversion occurred during the period of the complex formation (*ca.* 10 min) was corrected by a graphical extrapolation and the exact absorptivity of β-complex was determined.

20 ml of 0.1 M sodium molybdate solution and 10 ml of 1 M hydrochloric acid solution were taken into a 50 ml of volumetric flask. A calculated amount (0.2–

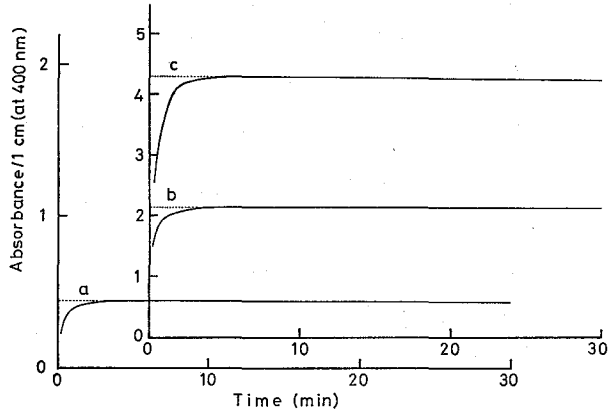

Fig. 1. Formation of β-complex
[molybdate]$=4.0 \times 10^{-2}$ M (constant); [HCl]$=0.2$ N; 25°
(a) [silictac]$=2.0 \times 10^{-4}$ M, light path-length$=1.00$ cm
(b) [silicate]$=1.0 \times 10^{-3}$ M, light path-length$=0.204$ cm
(c) [silicate]$=2.0 \times 10^{-3}$ M, light path-length$=0.204$ cm

17.5 ml) of the silicate standard solution was added to the flask and the solution was diluted quickly to the mark with water. Then, the time was set to zero and the absorbance change at 400 nm of the solution was recorded. At the preparation of the sample solutions, the amount of the acid added was devised to be sufficient enough to keep the ratios of $[H^+]/[MoO_4^{2-}]$ more than two in all of the solutions and, in consequence, the formation of β-complex was favorable in every solution. The absorbance changes observed at silicate concentrations of 2×10^{-4}, 1×10^{-3} and 2×10^{-3} are represented in Fig. 1, where the absorbances are normalized with respect to the path-length of the cell used. It can be seen in the Figure that each absorbance increases rapidly corresponding to the formation of β-complex and becomes maximal between t=9 and 10 min, and then decreases quite slowly due to the conversion to α-complex. The absorbance of each solution at t=0, which absorbance corresponds to the initial concentration of β-complex, can be determined by a linear extrapolation of the respective absorbance curve toward t=0 as shown by a broken line in Fig. 1. These measurements were performed at various silicate concentrations between 4×10^{-5} and 3.5×10^{-3} M and the initial absorbance thus read out from each intercept is plotted against the silicate concentration in Fig. 2. The plot gives a straight line in a range of the silicate concentration from 2×10^{-4} to 2.5×10^{-3} M, since β-complex is formed quantitatively in proportion to the total amount of silicate ions present. By the least square method, the absorptivity of the complex at 400 nm was determined as $\varepsilon_{\beta,400}=(2.18\pm0.04)\times10^3\ l\cdot mole^{-1}\cdot cm^{-1}$ from the slope of the fitted line. Precision given above is the confidence limit of the regression coefficient at the 95% confidence level. The straight line obtained here passes through the origin of Fig. 2, but some deviations from the line appear in lower silicate concentration than 2×10^{-4} M because of the absorbance of uncomplexed molybdate ions present in excess. As the silicate concentration is increased, the excess of molybdate ions are consumed for the complex formation and the absorbance of the molybdate ions is diminished to a negligible extent. In higher silicate concentration than 3.3×10^{-3} M, in turn, the total amount of molybdate ions, which is kept constant at 2×10^{-2} M in the solutions, limits the formation

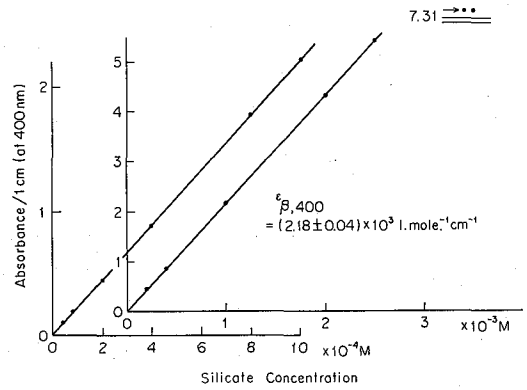

Fig. 2. Determination of absorptivity of β-complex at 400 nm
[molybdate]$=4.0\times10^{-2}$ M (constant); [HCl]=0.2 N; 25°

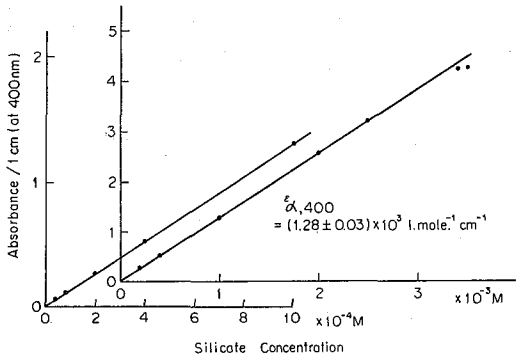

Fig. 3. Determination of absorptivity of α-complex at 400 nm
[molybdate] $=4.0\times10^{-2}$ M (constant); [HCl] $=0.2$ N; 25°

of the molybdosilicate complex and deviated plots from the extrapolated line appear as shown at the top right of Fig. 2.

By standing the same solutions as those prepared for β-complex for more than 40 hours at room temperature, α-complex is entirely formed in every solution through the conversion of β-complex. The absorbances of the resulted solutions were measured at 400 nm and plotted similarly against the silicate concentration. As shown in Fig. 3, the plot gives a straight line according to the adherence to the Beer-Lambert law with respect to α-complex. From the slope of the line, the absorptivity of the complex was determined as $\varepsilon_{\alpha,400}=(1.28\pm0.03)\times10^3\ l\cdot\text{mole}^{-1}\cdot\text{cm}^{-1}$. The precision has the same significance as described for β-complex.

The absorptivities thus determined can be successfully applied for determining each concentration of α or β-complex in their mixtures. In solutions including the both complexes, the following equations are conformed:

$$A_{400}=\varepsilon_{\alpha,400}\cdot C_\alpha+\varepsilon_{\beta,400}\cdot C_\beta \quad (1)$$

$$C=C_\alpha+C_\beta \quad (2)$$

here, A_{400}: the absorbance at 400 nm of a mixture of α and β-complex; C_α and C_β: the respective concentration of α and β-complex in the mixture; C: total concentration. These equations are solved with respect to C_α and C_β and resulted into

$$C_\alpha=(\varepsilon_{\beta,400}\cdot C-A_{400})/(\varepsilon_{\beta,400}-\varepsilon_{\alpha,400}) \quad (3)$$

$$C_\beta=(A_{400}-\varepsilon_{\alpha,400}\cdot C)/(\varepsilon_{\beta,400}-\varepsilon_{\alpha,400}) \quad (4)$$

When absorbance of a mixture of α and β-complex is measured at 400 nm and the total concentration of the complexes is known, the concentration of each complex can be calculated according to Eqs. 3 and 4. The total concentration in above equations can be easily known either from the amount of silicate ions initially added or from the actual analysis of the complexes by a solvent extraction method with methyl isobutyl ketone, which method will be reported elsewhere.

2) Evaluation of Conversion Rate Constant

By the same manner as described in the preceding paragraph, a 50 ml solution of β-complex with the concentration of 2×10^{-3} M was prepared by adding 10 ml of the 10^{-2} M silicate standard solution to a mixture of 20 ml of 0.1 M sodium molyb-

date and 10 ml of 1 M hydrochloric acid solution. Only when the conversion rate in sodium perchlorate medium is examined, 1 M perchloric acid was used in place of hydrochloric acid. After standing the solution for 9 min at 25°, which solution thus prepared will be called as "β-original solution" hereafter, a 5 ml aliquot of the solution was transferred into a 50 ml of volumetric flask and diluted quickly to the mark with water; This solution ought to contain dodecamolybdosilicate complex in a concentration of 2×10^{-4} M as a whole. Then, the time when the final dilution was performed was set to zero and the measurement of the absorbance at 400 nm was started by using the 1 cm-cell. The absorbance changes were automatically recorded for 150 minutes. By reading out the absorbance value of A_{400} from the recorder chart at appropriate intervals, the concentration of β-complex at each time, $[C_\beta]_t$, was calculated from Eq. 4. As suggested by Strickland,[1] β-complex decreased by a first-order with respect to its concentration and a plot of $\ln[C_\beta]_t$ against time gives a straight line according to the equation of

$$\ln [C_\beta]_t = -k_{obs}\cdot t + \ln [C_\beta]_0 \qquad (5)$$

where k_{obs} and $[C_\beta]_0$ denote the first-order rate constant and the initial concentration of β-complex, respectively. In practice, sixteen different points of data at 10 minute intervals were treated by the least square method, and the values of k_{obs} and $[C_\beta]_0$ were determined as $(2.13\pm0.03)\times10^{-3}$ min^{-1} and $(2.03\pm0.03)\times10^{-4}$ M, respectively. The result is listed in the first row of Table I together with the other kinetic data. The plot and the fitted line are demonstrated in Fig. 4.

The initial concentration of β-complex determined by such kinetic analysis was in good agreement with the total concentration of dodecamolybdosilicate complex (2×10^{-4} M) in the sample solution. This fact means that the absorptivity of β-complex had been determined truely based on the assumption that all of the dodecamolybdosilicate complex existed in a form of β-complex at the initial stage of the conversion.

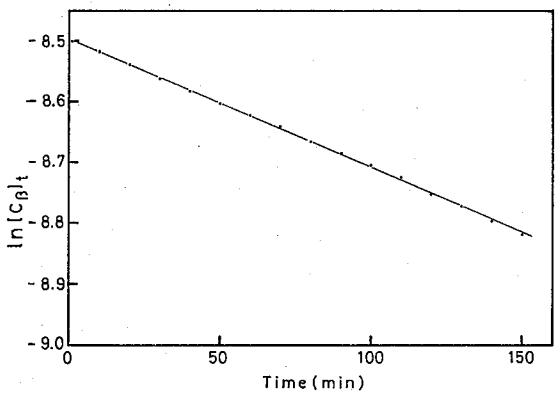

Fig. 4. Evaluation of the first-order rate constant of conversion of β-complex [β-complex]$=2\times10^{-4}$ M (at initial stage); pH=2.06; [uncomplexed free molybdate]$=1.6\times10^{-3}$ M; [Na^+]$=1.0\times10^{-2}$ g-ion$\cdot l^{-1}$; 25°.

3) Effect of Neutral Salts on the Conversion Rate

The rate constant evaluated above is a conditional constant which is observed

under solution conditions such as pH=2.06, concentration of excess molybdate (uncomplexed free molybdate)$=1.6\times10^{-3}$ M, concentration of sodium chloride (an excess sodium chloride introduced during the preparation of β-complex)$=1.0\times10^{-2}$ M, and at 25°. Although the rate constant changed actually depending on these solution conditions, the dependence on the neutral salts was specifically investigated by keeping the other conditions unchanged.

A 5 ml aliquot of freshly prepared "β-original solution" was transferred into a 50 ml volumetric flask, in which a calculated amount of solutions of neutral salts had been taken and diluted up to approximately 40 ml with water. Then, the solution was quickly made up to 50 ml with water and the absorbance change at 400 nm was recorded by the same manner as described before. As for the neutral salts, NaCl, $NaClO_4$, NH_4Cl, KCl, and $(NH_4)_2SO_4$ were employed, and the rate constant was observed at the concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 M of each salt; only for $(NH_4)_2SO_4$, the concentration was changed from 0.05 to 0.25 M. The kinetic data thus obtained are summarized in Table I together with pH values which were usually measured after the kinetic measurements. The values of k_{obs} are plotted against the salt concentration in Fig. 5. In the Figure, it can be seen that a linear relation between k_{obs} and C_s is conformed on every salt except for

Table I. Dependence of k_{obs} on Salt Concentration ([uncomplexed molybdate]$=1.6\times10^{-3}$ M, [dodecamolybdosilicate complex]$=2.0\times10^{-4}$ M, 25°).

Run #	Concentration of additional salt	pH	k_{obs} ($\times10^{-3}$ min^{-1})	b_s ($\times10^{-2}$ $l\cdot$mole$^{-1}\cdot$min^{-1})	k_{obs} ($\times10^{-3}$ min^{-1})
1	no additional salt	2.06	2.13±0.03		
2	0.1 M NaCl	2.08	3.32±0.07		
3	0.2 M 〃	2.08	4.64±0.08		
4	0.3 M 〃	2.03	5.82±0.09	1.21±0.05	2.13±0.02
5	0.4 M 〃	2.03	6.70±0.11		
6	0.5 M 〃	2.00	8.32±0.13		
7	0.1 M $NaClO_4$	2.06	3.47±0.05		
8	0.2 M 〃	2.05	4.77±0.08		
9	0.3 M 〃	1.95	5.90±0.10	1.12±0.09	2.44±0.03
10	0.4 M 〃	1.80	6.90±0.12		
11	0.5 M 〃	1.70	8.02±0.13		
12	0.1 M NH_4Cl	2.10	5.19±0.08		
13	0.2 M 〃	2.18	8.70±0.09		
14	0.3 M 〃	2.19	12.5 ±0.2	3.64±0.02	1.53±0.57
15	0.4 M 〃	2.19	16.3 ±0.2		
16	0.5 M 〃	2.20	19.6 ±0.6		
17	0.1 M KCl	2.15	5.62±0.07		
18	0.2 M 〃	2.10	11.2 ±0.2		
19	0.3 M 〃	2.21	15.0 ±0.3	4.47±0.47	1.7 ±1.5
20	0.4 M 〃	2.20	19.5 ±0.5		
21	0.5 M 〃	2.18	23.8 ±0.7		
22	0.05 M $(NH_4)_2SO_4$	2.51	12.5 ±0.02		
23	0.1 M 〃	2.51	20.3 ±0.02		

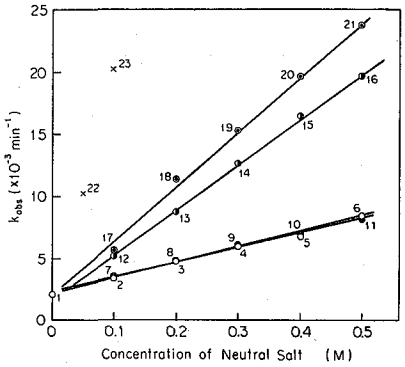

Fig. 5. Dependence of k_{obs} on the concentration of neutral salts at 25°
(○) NaCl; (●) $NaClO_4$; (◑) NH_4Cl; (◉) KCl; (×) $(NH_4)_2SO_4$
The run numbers in Table I are demonstrated in this Figure.

ammonium sulfate. In summary, the salt effect was formulated into a simple equation as

$$k_{obs}=k_{obs,extp}+b_s\cdot[C_s] \tag{6}$$

here, $k_{obs,extp}$: an intercept of the straight line; C_s: concentration of the salt; b_s: a slope of the line. The values of b_s and $k_{obs,extp}$ on each salt were evaluated by least square method and listed in the fifth and sixth column of Table I, respectively. As shown in the third column of Table I, on each series of experiments the pH was slightly changed by increasing the salt concentration and the pH changes may affect the emperical constant of b_s through the variation of rate constant. At present, however, no corrections for the pH changes were performed on b_s and, therefore, it partly includes such pH effect.

DISCUSSION

Generally, effects of inert salts on a reaction rate are explained in terms of the change of activity coefficient of the reactants. Since the activity coefficient is related to ionic strength of the medium according to the Debye-Hückel theory, logarithm of the observed rate constant appears to depend linearly on the ionic strength by the term of its square root in relatively dilute ionic media. In the relatively high ionic media, it is known that logarithm of the rate constant is proportional to the ionic strength. On the other hand, in the case that ion-pair formation between the intermediate species in the transition state and the ions dissociated from the salts is extensive, it is known[7] that the rate constant is proportional to the salt concentrations and the following equation conforms:

$$k_{obs}=k_0+b\cdot[\text{salt}] \tag{7}$$

where k_0 is the rate constant in the absence of salt and b is an emperical constant specific to the salt present in the solution.

In the conversion reaction examined here, the rate constant itself depends on the concentrations of the salt, showing the definite linear relation represented by Eq. 6, and the relation is quite identical with Eq. 7. Moreover, the magnitude of the dependence, *i.e.*, value of b_s, is characteristic to the employed salt. By using

b_s value as a measure for the salt effect, the magnitude of the effect can be ordered as $KCl > NH_4Cl > NaCl = NaClO_4$. Among these chloride salts, the salt effect is the largest in the presence of potassium ion, and it becomes small in ammonium and further small in sodium ion. And also, the salt effects observed in both sodium chloride and sodium perchlorate are almost identical, the anions being different. This fact seems to suggest that the cations in the salts have more intensive effect on the conversion reaction rather than the counter anions. Although Fanning *et al.* reported[6] that salt effect depends only on the ionic strengths but not on the nature of the component salts of the solution, the present kinetic study shows evidently that the salt effect depends on the kind of the salt in the medium. In the conversion reaction of β-complex, there may appear several types of polymolybdosilicate intermediates with high ionic charges and each of them probably forms ion-pair with dissociated cations from the neutral salt. Therefore, the conversion process is so complicated that the detailed mechanism is not elucidated yet, but at least it can be said that these neutral salts do not only function to change the activity coefficient of the reactant species, but also participate with the transition state of the conversion reaction through the formation of ion-pairs with the intermediates.

Besides these results, a decomposition reaction of β-complex can be pointed out in the sulfate medium with a higher concentration than 0.1 M. The absorbance changes in ammonium sulfate medium are quite similar to those in the other media, but at the equilibriated state of the reaction the final absorbance at 400 nm reaches far lower than 0.256, which absorbance ought to be given by the entire α-complex with a concentration of 2×10^{-4} M. That is, β-complex in the medium does not completely convert to α-complex, but partly decomposes to silicate and molybdate ions. The partial decomposition caused by ammonium sulfate, probably caused by sulfate ion, gives a different type of salt effect to silicate analysis using the formation of molybdosilicate complex, and the decomposition reaction should always be considered in highly concentrated sulfate medium in addition to the ordinary salt effect. In a lower concentration of ammonium sulfate than 0.1M, however, the conversion reaction proceeds predominantly over the decomposition, and the rate constants are obtainable. The kinetic data at both 0.05 and 0.1 M of ammonium sulfate are listed in Table I for the comparison with those of ammonium chloride. As the result, it was found that the first-order rate constant in ammonium sulfate is approximately twice as large as that in ammonium chloride even at the same concentration of ammonium ion. This fact implies that sulfate ion also participates with the conversion reaction and acceralates the reaction still further.

Thus, the salt effect can be systematically investigated by such a spectrophotometric kinetic method and the result was formulated into an equation of 6 by introducing a term of b_s, the meaning of b_s being not thoroughly understood.

REFERENCES

(1) J. D. H. Strickland, *J. Amer. Chem. Soc.*, **74**, 868 (1952).
(2) I. Iwasaki and T. Tarutani, *Bull. Chem. Soc. Japan*, **32**, 32 (1959).
(3) K. Kato and Y. Kitano, *J. Earth Sci., Nagoya Univ.*, **14**, 151 (1966).
(4) D. T. W. Chow and R. J. Robinson, *Anal. Chem.*, **25**, 646 (1953).

(5) J. R. Morrison and A. L. Wilson, *Analyst,* **88,** 88 (1963).
(6) K. A. Fanning and M. E. Q. Pilson, *Anal. Chem.,* **45,** 136 (1973).
(7) A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.,* **78,** 2763 (1956).