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Kinetic Studies of the Stripping of Bis(2,4-pentanedionato)beryllium in Various Liquid-Liquid Partition Systems

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The rate constant, k_{st}, for the stripping of bis(2,4-pentanedionato)beryllium from inert solvents into water or a mixed solvent of water with a miscible organic solvent, such as ethylene glycol, methanol, acetonitrile, and pimethyl sulfoxide, was determined and discussed in connection with the dissociation rate constant, k_d, of the chelate in the aqueous phase and the liquid-liquid partition coefficient, P, of the chelate. The $k_{st}=k_d/(1+P)$ relationship was found to hold true in all systems studied. The solvent effect of the aqueous mixed solvents on k_d was discussed in terms of the transfer activity coefficient.

The solvent extraction technique is widely employed in analytical chemistry to separate or concentrate a metal ion in an aqueous phase by removing it into an organic phase. Kinetic studies of a solvent-extraction mechanism of metal ions have been carried out by many workers. The rate-determining step of a chelate extraction has, in many cases, been reported to be a chelate-formation process in an aqueous phase.[1] The importance of an interfacial reaction for chelate formation has recently been pointed out for the extraction of calcium with bis(2-ethylhexyl)hydrogenphosphate[2] and copper with *o*-hydroxybenzaldehyde oximes.[3] On the other hand, the process of removing a metal compound from an organic phase into an aqueous phase, say stripping, is also important for an effective separation between metal ions.[4] However, on the stripping rate and the mechanism of the metal chelate there is no detailed information at present.

In this study, the rate and mechanism of the stripping reaction of the β-diketonato complex have been investigated utilizing bis(2,4-pentanedionato)beryllium as an example of the β-diketonates; it was chosen because of its moderate substitution lability and its simple dissociation behavior.[5] The stripping rate of the metal ion is expected to be influenced by the partition coefficient of the metal chelate and the dissociation behavior of the chelate in the aqueous phase. Therefore, the solvent effect of an aqueous phase is particularly interesting. In this study, various mixed solvents were used for the strip solution, *i.e.*, water–ethylene glycol, water–methanol, water–acetonitrile, and water–dimethyl sulfoxide. The stripping mechanism and solvent effect were studied from the measurements of the stripping rate constant, the hydrolysis rate constant in the aqueous phase, and the partition coefficient of the chelate. The partition coefficient is not only a measure of the extractability of a chelate from a nonpolar phase into a polar phase, but also a measure of the solution free-energy difference of the chelate in given solvents. With this in view, the kinetic solvent effect of the mixed solvent on the stripping rate will be discussed by correlating the rate constant with the partition coefficient.

Experimental

Chemicals. Bis(2,4-pentanedionato)beryllium(II) (Dotite, G. R.) was purified by vacuum sublimation at 80 °C. Organic solvents of dodecane, heptane, carbon tetrachloride, ethylene glycol, methanol, acetonitrile, and dimethyl sulfoxide were purified by ordinary methods.[6] Reagent-grade perchloric acid was used without further purification. Sodium perchlorate commercially purchased was purified by recrystallization. Redistilled water was used throughout. The stock solution of the acid was standardized by sodium carbonate titration. The mixed solvent of water and organic solvent was prepared by weight. The ionic strength in the aqueous phase used was adjusted to 0.1 M (1 M = 1 mol dm^{-3}) by the use of sodium perchlorate.

Kinetic Measurements. The stripping rates of beryllium were observed by means of an ordinary batch method, except for the experiment in the carbon tetrachloride/water system. An organic solution of Be(acac)$_2$ (10^{-4} M) was agitated with an aqueous phase. The shaking speed of the partition tube, which contained 5 ml for each phase, had to be as high as 430 tpm to establish a rapid mass transfer across the interface. Under these conditions, the observed stripping rate reflects purely the chemically rate-controlled process. In practice, a shaking rate of 460 tpm was adopted for all measurements. The stripping-rate constant was calculated from the absorbance decrease in the chelate in the organic phase. The absorbance change was observed intermittently at given shaking-time intervals. Although the absorption maximum of Be(acac)$_2$ in an inert solvent is at 293 nm, the absorbance change was observed at 310 nm to prevent any interference due to acetylacetone produced from the hydrolysis of the chelate. For the kinetic experiment in the carbon tetrachloride/water system, the continuous partition method, described previously in detail,[7] was applicable because of the large difference in the densities of the two phases. Fifty μl of 0.03 M Be(acac)$_2$ in carbon tetrachloride was spiked into the two-phase system which had been agitated in a continuous-partition vessel. The decrease in the absorbance of the complex in the organic phase, observed at 310 nm soon after the injection, was recorded as a function of the time. A first-order analysis of the results gave the stripping-rate constant. The sample preparation and the batch experiment were carried out in a thermostated room at 25 ± 1 °C.

The rate of the acid hydrolysis of Be(acac)$_2$ in the aqueous phase was observed photometrically. The absorbance change at 310 nm was observed as a function of the time after the injection of 15 μl of a 0.01 M dioxane solution of Be(acac)$_2$ into 3 ml of an aqueous solution contained in an optical cell thermostated at 25 ± 0.1 °C. The reproducibility of the rate constant thus determined is within $\pm5\%$.

Partition Experiment. The partition coefficient of Be(acac)$_2$ was determined by means of the kinetic method at 25 ± 1 °C. A 5-ml portion of an organic solution of the chelate was agitated with an equal volume of the aqueous phase for a given period, and then the absorbance of the organic phase was observed. From the absorbance change observed at four different periods at least, the absorbance at $t=0$ was estimated by extraporation and has then used to calculate the partition coefficient. All of the photometric measurements in this study was performed by means of a UVIDEC-2 or Hitachi 356 spectrophotometer.

Results

Stripping in Inert Solvent/Water Systems. Stripping-rate constant, k_{st}, in the carbon tetrachloride/water system is shown in Fig. 1 as a function of the hydrogen-ion concentration in the aqueous phase. The k_{st} is linearly proportional to $[H^+]$ in the concentration range from 0.001 M to 0.004 M. The observed rate constants for the acid hydrolysis of $Be(acac)_2$, shown in Fig. 2, are also linearly proportional to $[H^+]$ in the concentration range from 0.001 M to 0.012 M and coincide with those reported by Pearson and Moor.[5] The stripping data obtained in the three inert solvent/water systems are summarized in Table 1. The partition coefficients of $Be(acac)_2$ greatly depend on the solvents, and the stripping-rate constant appears to be proportional to the partition coefficient.

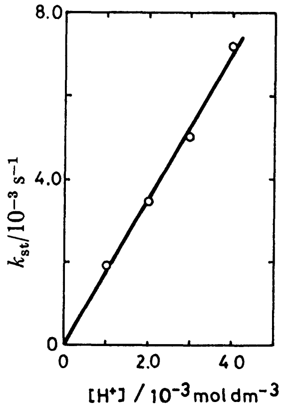

Fig. 1. Correlation between k_{st} and hydrogen ion concentration in aqueous phase. Organic phase: CCl_4.

Stripping in Dodecane/Water–Organic Solvent Mixture. The stripping-rate constants in the systems of dodecane/water–organic solvent mixtures at a constant hydrogen-ion concentration of 0.001 M are shown in Fig. 3.

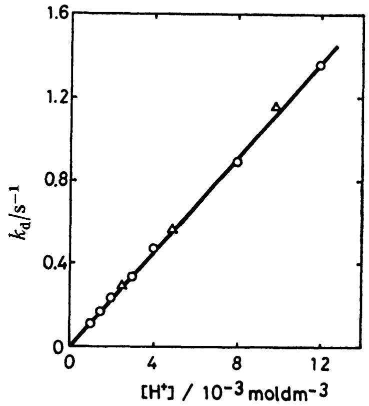

Fig. 2. Plot of k_d *vs.* hydrogen ion concentration for the acid hydrolysis of Be $(acac)_2$.
△: Pearson and Moore (1966), ○: this work.

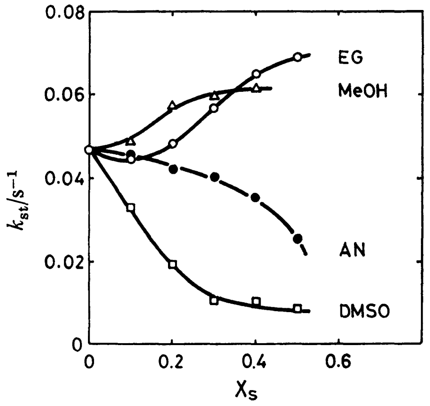

Fig. 3. Effect of aqueous mixed solvent on the stripping rate constant. $[H^+]=0.001$ M.

The stripping-rate constant is found to be greatly affected by the co-solvent. Remarkably, in system of the both H_2O-EG and H_2O-MeOH, the k_{st}'s increase with an increase in the mole fraction of the co-solvents. The rate constants for the solvolysis also greatly depend on the mixed solvent, as is shown in Fig. 4, where an increase of k_d in the H_2O–EG system is noticeable. In the mixed solvent systems also, the k_d raises with an increase in the hydrogen-ion concentration, as is shown in Fig. 5. The variation of the partition coefficient of $Be(acac)_2$ with the mole fraction of the co-solvent in

TABLE 1. THE PARTITION COEFFICIENTS, P, THE DISSOCIATION RATE CONSTANTS, k_d, AND THE STRIPPING RATE CONSTANTS, k_{st}, OF $Be(acac)_2$ AT 25 °C

Organic solvent	Acid concentration/M[a)]	P	k_d/s^{-1}	k_{st}/s^{-1}	$k_{st,calcd}/s^{-1}$[b)]
Dodecane	0.0010	1.61	0.115	0.0471	0.044
	0.0020		0.220	0.0876	0.084
Heptane	0.0005	3.15	0.060	0.0145	0.015
	0.0010		0.115	0.0258	0.028
	0.0020		0.220	0.0535	0.053
Carbon tetrachloride	0.0010	70.8	0.115	0.00192	0.0016
	0.0020		0.220	0.00347	0.0030
	0.0030		0.337	0.00501	0.0047
	0.0040		0.478	0.00722	0.0067

a) $I=0.1$ M by $NaClO_4$. b) $k_{st,calcd}=k_d/(1+P)$.

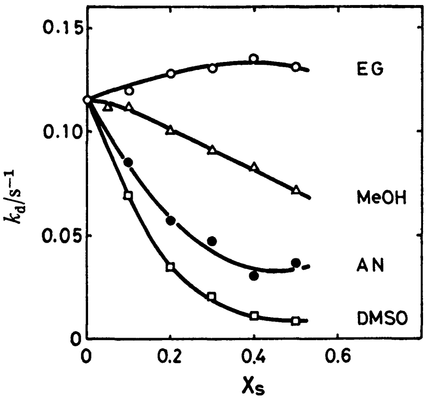

Fig. 4. Effect of aqueous mixed solvent on the rate constant of dissociation of Be $(acac)_2$. $[H^+]=0.001$ M. $I=0.1$ M by (H, Na) ClO_4.

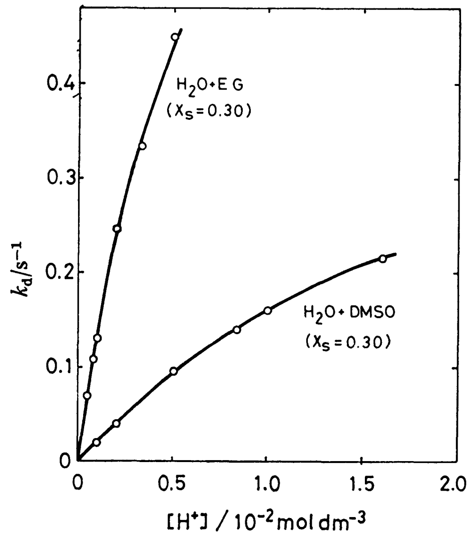

Fig. 5. Plot of k_d *vs.* hydrogen ion concentration.

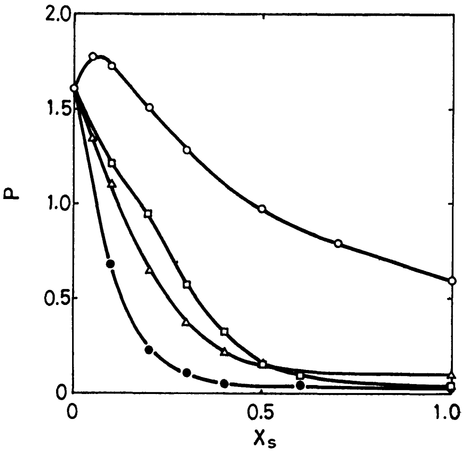

Fig. 6. Variation of partition coefficient of Be $(acac)_2$ with solvent composition.
Organic phase: dodecane. Aqueous phase: ○; H_2O–EG, □; H_2O–DMSO, △: H_2O–MeOH, ●; H_2O–AN.

the mixed-solvent phase is shown in Fig. 6. A maximum in the partition coefficient was observed in the dodecane/H_2O–EG system.

Discussion

Mechanism of the Stripping Reaction. As is shown in Figs. 1 and 2, both k_{st} and k_d depend on the hydrogen-ion concentration. The plot of k_{st} against k_d showed a simple linear relationship, $k_{st}=C\ k_d$, where C is a proportional constant. Therefore, we assumed the following scheme for the stripping reaction:

$$Be(acac)_{2,org} \rightleftharpoons Be(acac)_{2,aq} \qquad (1)$$

$$Be(acac)_2 + H^+ \longrightarrow Be(acac)^+ + Hacac. \qquad (2)$$

Processes 1 and 2 are represented by the partition coefficient, $P=[Be(acac)_2]_{org}/[Be(acac)_2]_{aq}$, and the dissociation rate constant, k_d, respectively. The rate equation for the stripping reaction:

$$-d[Be(acac)_2]_{org}/dt = k_{st}[Be(acac)_2]_{org} \qquad (3)$$

gives the relation among k_{st}, k_d, and P:

$$k_{st} = k_d/(1+P). \qquad (4)$$

Equation 4 strongly supports the proportionality between k_{st} and k_d observed experimentally. According to this equation, k_{st} was calculated and compared with the observed one. The results for the three solvent systems are listed in the last column of Table 1. The agreement between $k_{st,calcd}$ and k_{st} is satisfactory; this confirms the proposed scheme of Eqs. 1 and 2. For the mixed solvent systems also, the linear relationship between k_{st} and $k_d/(1+P)$ was confirmed, as is shown in Fig. 7, and the proposed mechanism was supported.

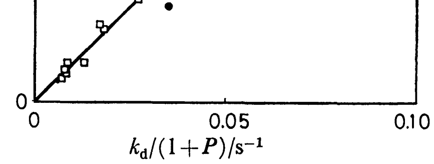

Fig. 7. Correlation between k_{st} and $k_d/(1+P)$.
Solid line represent an expected relation with unit slope. Organic phase: dodecane. Aqueous phase: ○; H_2O–EG, □; H_2O–DMSO, △; H_2O–MeOH, ●: H_2O–AN.

Solvent Effect on the Acid Solvolysis. Equation 4 indicates that the solvent effect on the stripping rate is due to the effects on the dissociation rate and the partition equilibrium. The partition coefficient of $Be(acac)_2$ in the dodecane/aqueous mixed solvent system is related to the transfer-activity coefficient, y_s, of $Be(acac)_2$ from water to a mixed solvent by means of Equation 5:[8]

$$y_s = P/P_o, \qquad (5)$$

where the subscript o denotes the reference value observed in a pure-water system. On the other hand, the rate equation for the acid hydrolysis can be represented by the following equation under the conditions of a dilute acid concentration:

$$-\mathrm{d}[\mathrm{Be(acac)_2}]/\mathrm{d}t = k[\mathrm{H^+}][\mathrm{Be(acac)_2}], \qquad (6)$$

where k is a constant in the equation of $k_d=k[\mathrm{H^+}]$. In terms of the transfer-activity coefficient, the solvent effect on the dissociation rate can be represented by the next equation:[9]

$$k_d/k_{d,o} = y_s y_{\mathrm{H^+}}/y_{\ddagger}, \qquad (7)$$

where $y_{\mathrm{H^+}}$ and $y_{\ddagger}$ are the transfer-activity coefficients from water to a mixed solvent of proton and the transition state. Equation 7 shows that the solvent effect of the mixed solvent on k_d can be represented by the three transfer-activity coefficients of y_s, $y_{\mathrm{H^+}}$, and $y_{\ddagger}$. The substitution of Eq. 5 for y_s in Eq. 7 gives the next equation:

$$\log(y_{\ddagger}/y_{\mathrm{H^+}}) = \log(P/P_o) - \log(k_d/k_{d,o}). \qquad (8)$$

The values of $\log(y_{\ddagger}/y_{\mathrm{H^+}})$ calculated from the above equation are plotted in Fig. 8 for the four mixed-solvent systems. This figure shows that $\log(y_{\ddagger}/y_{\mathrm{H^+}})$ decreases in the order of H_2O–DMSO>H_2O–EG> H_2O–MeOH>H_2O–AN in every solvent composition studied and that the value of the ratio of $y_{\ddagger}/y_{\mathrm{H^+}}$ is larger than unity for H_2O–DMSO and smaller than unity for the other systems. The large value of $y_{\ddagger}/y_{\mathrm{H^+}}$ observed in H_2O–DMSO system can be explained by the small value of $y_{\mathrm{H^+}}$ in the mixed solvent.[10] However, for the H_2O–EG and H_2O–MeOH systems, the reported order of $y_{\mathrm{H^+}}$, *i.e.*, H_2O–EG>H_2O–MeOH,[11,12] is in disagreement with the order of $-\log(y_{\ddagger}/y_{\mathrm{H^+}})$ in the two systems. This suggests that the solvent effect on $y_{\mathrm{H^+}}$ is not the only factor governing the solvent effect on the solvolysis of Be(acac)$_2$, the variation in $y_{\ddagger}$ with the solvent composition being also an important factor. At the present stage, the evaluation of $y_{\ddagger}$ is difficult because of the lack of reliable data for $y_{\mathrm{H^+}}$. However, a test of the correlation between $\log(y_{\ddagger}/y_{\mathrm{H^+}})$ and $\log y_s$ will be worthwhile in order to get a clue as to the solvent effect on the transition state. Figure 9 shows the linear proportionality of $\log(y_{\ddagger}/y_{\mathrm{H^+}})$ to $\log y_s$ in the three systems except H_2O–DMSO, which shows a curved line with a maximum and a great difference from the others. Because the transition state in the acid hydrolysis can be expected to be a positively charged species, $\log y_{\ddagger}$ can be expected to include the two contributions to solute-solvent interaction, *i.e.*, ionic and nonionic interaction. The linear relationship, shown in Fig. 9, suggests that the ionic contributions to $\log y_{\ddagger}$ and $\log y_{\mathrm{H^+}}$ may be compensated for each other and/or be proportionate to $\log y_s$ which is a measure of the nonionic interaction between Be(acac)$_2$ and a polar solvent. The great discrepancy in the plot in H_2O–DMSO suggests a strong proton affinity of the mixed solvent.[10]

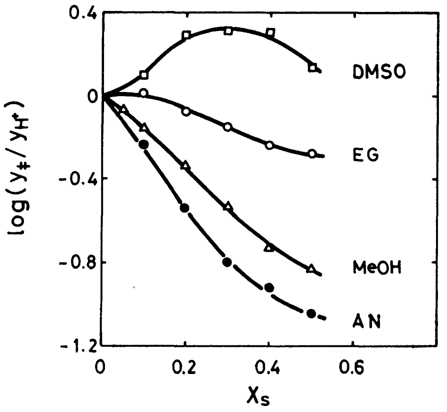

Fig. 8. Variation of log $(y_{\ddagger}/y_{\mathrm{H^+}})$ with solvent composition.

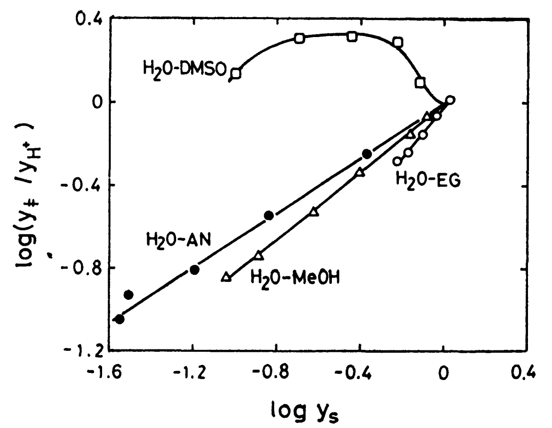

Fig. 9. Correlation between log $(y_{\ddagger}/y_{\mathrm{H^+}})$ and $\log y_s$.

The hydrogen-ion-concentration dependence of k_d in the H_2O–EG (X_s=0.30) and H_2O–DMSO (X_s=0.30) mixed solvents was discussed according to the general scheme proposed for the acid hydrolysis of acetylacetonates in an aqueous solution:[5]

$$\mathrm{Be(acac)_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Be(acac)(acac')} \qquad (9)$$

$$\mathrm{Be(acac)(acac')} + \mathrm{H^+} \overset{K_1}{\rightleftharpoons} \mathrm{Be(acac)(Hacac)^+} \qquad (10)$$

$$\mathrm{Be(acac)(Hacac)^+} \xrightarrow{k_2} \mathrm{Be(acac)^+} + \mathrm{Hacac}, \qquad (11)$$

where (acac′) denotes a half-bonded acetylacetone. This mechanism is represented by the next equation:

$$\frac{1}{k_d} = \frac{k_{-1}}{k_1 k_2 K_1}\frac{1}{[\mathrm{H^+}]} + \frac{1}{k_1}. \qquad (12)$$

Following Eq. 12, the dissociation-rate constants in H_2O–EG and H_2O–DMSO systems, shown in Fig. 5, were analyzed. An intercept of the linear plot between k_d^{-1} and $[\mathrm{H^+}]^{-1}$ gave the values of k_1; 0.75 s^{-1} for H_2O–DMSO (X_s=0.30) and 1.10 s^{-1} for H_2O–EG (X_s= 0.30). Both of these values are smaller than the reported value in an aqueous solution, 6.5 s^{-1}.[5] The decreasing order of k_1 values: H_2O (P=1.61)>H_2O–EG (X_s= 0.30) (P=1.28)>H_2O–DMSO (X_s=0.30) (P=0.58) corresponds to that in the partition coefficient. This indicates that the larger the solvation free energy of Be(acac)$_2$ in the mixed solvent, the slower the rate of the Be–O bond rupture.

In this study, the kinetic mechanism of the stripping of Be(acac)$_2$ was elucidated. For the purpose of practical separation using the stripping method, a solvent system with a smaller P value and a larger k_d value is promised from the present results. A further investigation of the other metal chelates will provide insight into the solvent's role in the solvolysis of metal chelate and into the separation mechanism of metal ions in extraction chromatography.

References

1) T. Sekine and Y. Hasegawa, "Solvent Extraction Chemistry: Fundamentals and Applications," Mercel Dekker, New York, N. Y. (1977).

2) G. F. Vandegrift and E. P. Horwitz, *J. Inorg. Nucl. Chem.*, **39**, 1425 (1977).

3) J. S. Preston and Z. B. Luklineka, *J. Inorg. Nucl. Chem.*, **42**, 431 (1980).

4) D. S. Flett, *Chem. Ind, (London)*, **3**, 706 (1977).

5) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **5**, 1528 (1966).

6) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Technique of Organic Chemistry," Interscience, New York (1955), Vol. 7.

7) H. Watarai and N. Suzuki, *J. Inorg. Nucl. Chem.*, **43**, 761 (1981).

8) H. Watarai and N. Suzuki, *J. Inorg. Nucl. Chem.*, **38**, 1683 (1976).

9) B. G. Cox and P. T. McTigue, *Aust. J. Chem.*, **20**, 1815 (1967).

10) Von D. Geheb, N. F. Kasanskaja, and I. W. Beresin, *Chem., Ber.*, **76**, 160 (1972).

11) C. Kalidas, P. Sivaprasad, and U. V. Venkatram, *Z. Naturforsch., Teil A*, **32**, 791 (1977).

12) V. S. Rao and C. Kalidas, *Ind. J. Chem.*, **13**, 1303 (1975).