RATES OF REACTIONS IN Cu(II)–BENZOYLACETONE SYSTEM IN AQUEOUS PHASE

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The mechanism and rates of aqueous-phase reactions in cupric ion and benzoylacetone system were elucidated. The exchange reaction between enol and keto forms was expressed by

The rate constants for enol and keto forms were determined as $k_E = 81 \text{ s}^{-1}$ and $k_K = 0.018 \text{ s}^{-1}$, respectively. The reaction rate between enolate ion and cupric ion was well interpreted by Eigen's mechanism and the rate constant of second-order reaction was $k_{CB} = 1.1 \times 10^9 \text{ dm}^3/\text{mol} \cdot \text{s}$. Direct reactions between cupric ion and the enol and keto forms of benzoylacetone were observed. The rate constants for the enol and the keto forms were 2000 and $12 \text{ dm}^3/\text{mol} \cdot \text{s}$, respectively.

Introduction

Kinetics of metal extraction by chelating agents is important for solvent extraction and liquid membrane operations. Most workers have interpreted their data in terms of aqueous-phase reaction.^{15,17} For water-insoluble chelating agents, Flett *et al.*⁹ and Komazawa *et al.*¹⁶ asserted that the rate determining process would be interfacial in nature. A consistent explanation of the kinetics of metal extraction is lacking at present.

It would be difficult to elucidate the reaction locus of metal extraction based solely on information about the overall extraction rate. A more rational approach is first to determine the mechanism and the rate of metal chelate formation in the aqueous phase and then to study the extraction mechanism on the basis not only of the rate of metal extraction but also the information obtained from the reaction mechanism in the aqueous phase.

Several papers have reported the results of studies on the formation of 1:1 metal chelate complexes of various water-soluble β -diketones, e.g. acetylacetone (Acac) and thenoyltrifluoroacetone (TTA).^{2,4,13,14,20,21} β -diketone exists as enol and keto tautomers and the reaction routes to yield 1:1 complexes are very complicated.

The aim of the present work is the elucidation of the mechanism and the rate of 1:1 complex formation in the aqueous phase for less water-soluble benzoylacetone (BA) by measuring the chemical re-

action rate by use of the relaxation method.

1. Experimental

1.1 Procedures and reagents

BA aqueous solution and cupric perchlorate aqueous solution were mixed in a chamber using a four-jet mixer and the time course of light absorbance by the solution was measured by a rapid reaction analyzer of stopped-flow type (Union Giken Co. Ltd., PA-1100). The concentration of sodium perchlorate was adjusted to 0.1 mol/dm^3 after the aqueous solutions were mixed. The pH values of the aqueous solutions were adjusted to be in the range 2.5–4.5 using perchloric acid or sodium hydroxide. The reaction temperature was maintained at 25°C . All reagents used were the same as shown in the previous report.¹⁾

1.2 Experimental conditions

The equilibrium relationships of the reactions in the aqueous phase involving Cu(II) and BA have been determined by the authors.¹⁾

$$K_2 = [\text{H}][\text{B}]/[\text{HB}] = 1.6 \times 10^{-9} \text{ mol/dm}^3 \quad (1)$$

$$K_3 = [\text{CuB}]/[\text{Cu}][\text{B}] = 2.0 \times 10^8 \text{ dm}^3/\text{mol} \quad (2)$$

$$K_4 = [\text{CuB}_2]/[\text{B}][\text{CuB}] = 1.6 \times 10^8 \text{ dm}^3/\text{mol} \quad (3)$$

Here, HB and B represent neutral and dissociated benzoylacetone. The electrical valences of the ionic species are omitted hereafter for the sake of simplicity. The neutral form of BA consists of the

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Fig. 1. Experimental domains in this work. Domain I, CuB formation; Domain II, coexistence of CuB and HB; Domain III, CuB₂ is not neglected.

tautomers, enol and keto forms. The concentration of BA, [HB], is the sum of those of the two tautomers. The concentrations of the chemical species in the above equations are calculated from the equilibrium relation given in Eqs. (1)–(3). It is easily shown from Eq. (1) that [B] is negligibly small compared with [HB] when the pH is less than seven.

The condition that 95% of BA in the aqueous phase is converted to CuB complex can be determined from Eqs. (2)–(3) and is shown in Fig. 1 as the solid line where the total concentration of BA, C_B , is fixed at 4.8×10^{-5} mol/dm³. The broken curve is the condition that 5% of BA remains in the form HB in the aqueous phase and the dotted curve represents the condition that 5% of BA exists in the form CuB₂. In domain I in Fig. 1, the reaction to form CuB is considered to all intents and purposes to be an irreversible reaction. In domain II, the reaction to form CuB is considered as a reversible reaction, where HB is not completely converted to CuB. In domain III, the formation of CuB₂ is not negligible. In this experiment, the reaction to form CuB was carried out in domains I and II.

As shown in the previous report,¹⁾ the molar extinction coefficient of CuB is about 100 times greater than that of HB at a wavelength of 360 nm, and is about the same value as that for CuB₂. When the experiments are performed at the conditions in domains I and II, the absorbance of the solution at 360 nm is almost completely due to the formation of CuB except for the early period of the reaction. The absorbance due to Cu ion is also negligibly small at 360 nm. Therefore, the process to form CuB can be measured directly.

2. Results and Discussion

2.1 Reaction path

The tautomerization rate of enol–keto forms of

Fig. 2. Postulated reaction paths to yield CuB.

Fig. 3. Typical example of time course of absorbance at initial pH: 3.5.

acetylacetone is expressed in acidic aqueous solution^{6,12)} by

Here, the rate constants are

$$k_K = 2.1 \times 10^{-2} \text{ s}^{-1}, \quad k_K' = 6 \times 10^6 \text{ dm}^3/\text{mol} \cdot \text{s}$$

$$k_E = 1.4 \times 10^2 \text{ s}^{-1}, \quad k_E' = 3 \times 10^{10} \text{ dm}^3/\text{mol} \cdot \text{s}$$

HK and HE represent keto and enol form, respectively. Taking this into account, we can postulate the paths of the reaction to form CuB as shown in Fig. 2.

The chemical reaction to form CuB via path I would be very rapid compared with the reactions via paths II and III, because the water coordinated to Cu ion is easily detached from Cu. Taking into account that the dissociation of β -diketone in enol form is much faster than for the keto form, the BA in enol form first reacts with Cu rapidly and approaches quasi-equilibrium. Thereafter, the BA in keto form reacts with Cu slowly and approaches thermodynamic equilibrium.

To ensure the presence of the above two steps, the reactions to form CuB were performed at such conditions that the final state of the reactions were in domains I or II in Fig. 1. A typical example of the change of absorbance is shown in Fig. 3 together with the experimental conditions. The ordinate E is the absorbance of the reaction mixture at 360 nm and the abscissa is reaction time t . For a short time span, the

Fig. 4. Enol-keto tautomerization equilibrium.

absorbance rapidly increased with time and attained quasi-equilibrium (curve a). For a large time span, the absorbance initially agreed with the value in the above quasi-equilibrium state (curve b). This experimental result ensures the presence of the two steps in the aqueous-phase reaction. It also ensures that the rate process by intramolecular tautomerization is much slower than the rate processes of Eq. (4).

The quasi- and pure thermodynamic states provide information for the reaction from enol to keto exchange. We can postulate the chemical reactions:

The following relationship exists for the equilibrium constants, K_{2e} , K_{2k} and K_2 :

$$1/K_2 = 1/K_{2e} + 1/K_{2k} \quad (7)$$

We define the tautomerization equilibrium constant K_T as

$$\text{HK} \rightleftharpoons \text{HE}; \quad K_T = K_{2k}/K_{2e} = [\text{HE}]/[\text{HK}] \quad (8)$$

In thermodynamic equilibrium, the following equation is satisfied because $[\text{CuB}_2]$ is negligibly small in this experiment.

$$(1/[\text{CuB}]) = (1/[\text{CuB}]_{r^* \rightarrow 0})(1 + r^*/K_2K_3) \quad (9)$$

Here, $r = [\text{H}]/[\text{Cu}]$ and the asterisk represents the value at thermodynamic equilibrium. The above equation is rewritten with use of the absorbances as

$$\frac{1}{E^*} = \left(\frac{1}{E^*} \right)_{r^* \rightarrow 0} \left(1 + \frac{r^*}{K_2K_3} \right) \quad (10)$$

At quasi-equilibrium Eqs. (5) and (2) hold and these give

$$\frac{1}{E^\circ} = \left(\frac{1}{E^\circ} \right)_{r^\circ \rightarrow 0} \left(1 + \frac{r^\circ}{K_{2e}K_3} \right) \quad (11)$$

Fig. 5. Observed overall reaction rate coefficients for first step.

where the superscript of open circle represents quasi-equilibrium. The absorbances E^* and E° observed are plotted according to Eqs. (10) and (11) in Fig. 4. The tautomerization equilibrium constant K_T can be determined from the intercepts $(1/E^\circ)_{r^\circ \rightarrow 0}$ and $(1/E^*)_{r^* \rightarrow 0}$ and also from the products of the slope of the straight lines, S , by $E_{r \rightarrow 0}$:

$$K_T = [E^\circ/(E^* - E^\circ)]_{r^*, r^\circ \rightarrow 0} = 1/[S^*E_{r^* \rightarrow 0}/S^\circ E_{r^\circ \rightarrow 0} - 1] \quad (12)$$

The K_T value is obtained so that the values evaluated from Eq. (12) agree with each other. The resultant value is given as

$$K_T = 0.43 \quad (13)$$

This value compares well with the values 0.52 in water⁵⁾ and 0.41 in 1 mol/dm³-NaClO₄ aqueous solution,²³⁾ which were determined from static equilibrium experiments. The agreement of these results of two different techniques ensures that the reaction between Cu ion and the enol form is much faster than that for the keto form.

2.2 Reaction mechanism and rates

Consider first the rate of the reaction to form CuB from BA in enol form. The measured course of this reaction is given by curve a in Fig. 3. This time course was for a linear process and $\ln[(E^\circ - E)/E^\circ]$ changed linearly with reaction time t . In these experiments, the total concentrations of copper C_c were much greater than C_B and $[\text{Cu}]$'s were kept nearly constant during the course of the reactions. The $[\text{H}]$ values were also kept nearly constant except for the experiment at pH = 4.5, where $[\text{H}]$ increased by 30% compared with their initial values. The sole factor changing with time was $[\text{HE}]$ as an approximation. The overall reaction rate coefficient k_e which is evaluated from the gradient of the straight line of $\ln[(E^\circ - E)/E^\circ]$ against t is shown in Fig. 5.

As mentioned previously, the major path to form CuB from HE would be path I in Fig. 2. Since $[\text{B}]$ is much less than $[\text{HE}]$, a stationary-state method with respect to B would be usable. In this case, the rate of formation of CuB is described as

$$\begin{aligned}
d[\text{CuB}]/dt &= k_{CB}[B][\text{Cu}] - k'_{CB}[\text{CuB}] \\
&\quad + k_{CE}[\text{HE}][\text{Cu}] - k'_{CE}[\text{CuB}][\text{H}] \\
d[B]/dt &= k_E[\text{HE}] - k'_E[\text{H}][B] \\
&\quad + k'_{CB}[\text{CuB}] - k_{CB}[B][\text{Cu}] = 0 \quad (14)
\end{aligned}$$

From the above relationships, the rate of CuB formation is easily expressed when $[\text{CuB}]$, $[\text{HB}] \gg [\text{CuB}_2]$, $[B]$:

$$d[\text{CuB}]/dt = p - k_e[\text{CuB}] \quad (15a)$$

$$p = \{k_E/(1 + k'_E r/k_{CB}) + k_{CE}[\text{Cu}]\} K_T C_B / (1 + K_T) \quad (15b)$$

$$k_e = (1 + r/K_{2e}K_3) \{k_E/(1 + k'_E r/k_{CB}) + k_{CE}[\text{Cu}]\} \quad (15c)$$

Equation (15) can easily be solved if r is constant:

$$\begin{aligned}
\{[\text{CuB}]^\circ - [\text{CuB}]\} / [\text{CuB}]^\circ &= (E^\circ - E) / E^\circ \\
&= \exp(-k_e t) \quad (16)
\end{aligned}$$

The measured k_e values are replotted according to Eq. (15c) in Fig. 6, where the k'_E/k_{CB} value was determined to be 13.5 so that the plotted points change linearly, satisfying Eq. (15c). k_E and k_{CE} can also be determined from this figure. The other rate constants are obtained with the help of equilibrium constants K_{2e} and K_3 . The resultant rate constants are

$$\begin{aligned}
k_E &= 81 \text{ s}^{-1}, \quad k'_E = 1.5 \times 10^{10} \text{ dm}^3/\text{mol} \cdot \text{s}, \\
k_{CB} &= 1.1 \times 10^9 \text{ dm}^3/\text{mol} \cdot \text{s} \\
k'_{CB} &= 5.7 \text{ s}^{-1}, \quad k_{CE} = 2 \times 10^3 \text{ dm}^3/\text{mol} \cdot \text{s}, \\
k'_{CE} &= 2 \times 10^3 \text{ dm}^3/\text{mol} \cdot \text{s} \quad (17)
\end{aligned}$$

Next, we consider the second step of CuB formation from HK. As mentioned previously, the first step of CuB formation approached quasi-equilibrium and thereafter the second step of CuB formation occurred slowly. Thus, quasi-equilibria between B, CuB and HE would be attained during whole course of the second step.

$$[B] = [\text{CuB}]/K_3[\text{Cu}] = K_{2e}[\text{HE}]/[\text{H}] \quad (18)$$

The change of the sum of $[B]$, $[\text{CuB}]$ and $[\text{HE}]$ can be described as follows because the formation of CuB_2 is negligible in this experiment.

$$\begin{aligned}
\frac{d}{dt}([B] + [\text{HE}] + [\text{CuB}]) &= k_K[\text{HK}] - k'_K[\text{H}][B] \\
&\quad + k_{CK}[\text{HK}][\text{Cu}] - k'_{CK}[\text{CuB}][\text{H}] \quad (19)
\end{aligned}$$

The terms $d[B]/dt$ and $d[\text{HE}]/dt$ are related to $d[\text{CuB}]/dt$ by differentiating Eq. (18) with respect to time and the introduction of these relations into Eq. (19) yields

$$\begin{aligned}
(1 + r/K_3K_{2e} + 1/K_3[\text{Cu}])d[\text{CuB}]/dt &= (k_{CK}[\text{Cu}] + k_K) \\
&\quad \times [\text{HK}] - (k'_{CK} + k'_K/K_3[\text{Cu}])[\text{H}][\text{CuB}] \quad (20)
\end{aligned}$$

Fig. 6. Validity of Eq. (15c). Symbols are same as in Fig. 5. Cross symbol represents data by Pearson²¹⁾ at 25°C and ionic strength 0.1 mol/dm³.

In the above derivation, we assumed that the values $[\text{H}]$ and $[\text{Cu}]$ are constant in the course of the second-step reaction. Employing Eq. (7) and the relationships

$$k_K/k'_K = K_{2k}, \quad k_{CK}/k'_{CK} = K_3K_{2k} \quad (21)$$

the rate of CuB formation is given from Eq. (20):

$$\begin{aligned}
d[\text{CuB}]/dt &= p' - k_k[\text{CuB}] \quad (22) \\
p' &= (k_{CK}[\text{Cu}] + k_K)C_B / (1 + 1/K_3[\text{Cu}] + r/K_3K_{2e}) \\
k_k &= \frac{(k_{CK}[\text{Cu}] + k_K)(1 + 1/K_3[\text{Cu}] + r/K_3K_{2e})}{1 + 1/K_3[\text{Cu}] + r/K_3K_{2e}} \quad (23)
\end{aligned}$$

Here, we assumed

$$C_B = [\text{CuB}] + [\text{HE}] + [\text{HK}] + [B]$$

Integration of Eq. (23) on the postulation that $[\text{Cu}]$ and $[\text{H}]$ are independent of time gives

$$(E^* - E)/(E^* - E^\circ) = \exp(-k_k t) \quad (24)$$

The experimental values of $\ln(E^* - E)/(E^* - E^\circ)$ were linear with respect to time and the reaction to form CuB in the second step is of first order with respect to BA. The values of overall reaction rate coefficient, k_k , obtained are shown in Fig. 7 where the r value was approximated as r^* . The result shown in Fig. 7 satisfies the relationship of Eq. (23). From this result the reaction rate constants are determined with help of Eq. (21):

$$\begin{aligned}
k_{CK} &= 11.6 \text{ dm}^3/\text{mol} \cdot \text{s}, \quad k'_{CK} = 25.3 \text{ dm}^3/\text{mol} \cdot \text{s} \\
k_K &= 0.018 \text{ s}^{-1}, \quad k'_K = 7.86 \times 10^6 \text{ dm}^3/\text{mol} \cdot \text{s} \quad (25)
\end{aligned}$$

Watarai *et al.*²²⁾ determined the rate constant of the tautomerization from enol to keto forms by mixing BA in dioxane solution with water. The k_K value evaluated from their result with use of K_T in Eq. (13) is

Fig. 7. Overall reaction rate coefficients for second step. Cross symbol represents data by Pearson²¹⁾ at 25°C and ionic strength 0.1 mol/dm³.

$$k_K = 0.025 \text{ s}^{-1} \quad (26)$$

This value is a little greater than that obtained in this work.

We compare the results of the present work with those of Acac. Pearson *et al.*²¹⁾ reported data for the reaction of cupric ion with Acac. They analyzed these data on the assumption that reaction path I in Fig. 2 was neglected. This assumption is not rigorous and we re-analyzed their data according to Eqs. (15c) and (23). The results are shown in Figs. 6 and 7. From these figures, the rate constants can be obtained. The resultant values are shown in Table 1 together with the results of Eigen⁶⁾ and Munakata *et al.*¹⁸⁾

The k_{CB} values for these two systems agree with each other and this rate process would proceed according to Eigen's mechanism,⁷⁾ which involves the loss of water molecule from the metal ion as the rate-determining step. The reaction rate constant is given in this case by

$$k_{CB} = K_{OS} k_{H_2O} \quad (27)$$

K_{OS} is the formation constant of the outer sphere complex and is given by Fuoss¹⁰⁾ as

$$K_{OS} = (4\pi N a^3 / 3000) \exp(-U/kT), \quad (28)$$

$$U = -2e^2(1 + \kappa a) / Da$$

N is the Avogadro number and the a -value is minimum separation distance between ions. The e -value represents the elementary electric charge. U represents the electrostatic effect. D and $1/\kappa$ are the dielectric constant and Debye's screening length, respectively. k_{H_2O} is the rate constant of dehydration and is given for cupric ion¹¹⁾ as

$$k_{H_2O} = 3 \times 10^8 \text{ s}^{-1} \quad (29)$$

The k_{CB} value calculated from Eq. (27) with use of Eqs. (28) and (29) is given by

$$k_{CB} = 1.4 \times 10^9 \text{ dm}^3/\text{mol} \cdot \text{s}$$

Table 1. Comparison of reaction rate constants for Acac with BA at 25°C

Reactions	Acac	Ref.	BA	Ref.
$H^+ + B^- \rightarrow HE, k_E'$	3×10^{10}	a	1.5×10^{10}	d
$H^+ + B^- \rightarrow HK, k_K'$	6×10^6	a	7.9×10^6	d
$Cu^{++} + B^- \rightarrow CuB^+, k_{CB}$	9×10^8	b	1.1×10^9	d
$Cu^{++} + HE \rightarrow CuB^+, k_{CE}$	1.5×10^4	c	2×10^3	d
$Cu^{++} + HK \rightarrow CuB^+, k_{CK}$	11	c	12	d

a, Eigen *et al.* (1963); b, Munakata *et al.* (1978); c, Pearson *et al.* (1970); d, this work.

where we assumed that the a -value was $4.8 \times 10^{-10} \text{ m}$ and the ionic strength was 0.1 mol/dm³. This calculated value agrees well with the experimental result.

The reaction of cupric ion with enol form of BA is considered to be abnormally slow and this has been interpreted in terms of three factors²¹⁾: a) relatively strong intramolecular hydrogen bonds which may convert the protonated ligand into a poor entering group³⁾; b) sterically controlled six-membered chelate ring closure; and c) the energetics of the proton release from half-bonded intermediate which slows down the rate of ring closure.

A pure sterically controlled mechanism predicts that the enolate ion should also react at an abnormally slow rate, and mechanism b) seems to be unreasonable.¹³⁾ The present result shows that the effect of the substitution from methyl- to phenyl-group on the k_{CE} value would be large. Systematic study of this substitution effect would give information as to the cause of the slow rate, but a detailed discussion is left to future work.

The reaction rate constant k_{CK} is much smaller than k_{CE} . The k_{CK} for BA differs little from that for Acac. This reaction with keto form proceeds through an intermediate in which the metal ion is bonded to keto groups. This would be controlled by the slow metal-catalyzed proton release.²¹⁾

The reaction important for the extraction of metals would be the reaction of metal ions with enol or enolate ionic forms of β -diketone from the viewpoint of the extraction kinetics of metals. At relatively high pH, the reaction of metal ions with enolate ion would be important. At lower pH and relatively large concentration of metal ions, the direct reaction of metal ion with the enol form would be of primary concern in the kinetics of metal extraction.

Conclusion

The reaction mechanism of the reactions concerned with cupric ion and benzoylacetone was elucidated and the reaction rates in the aqueous phase were determined. The reaction of cupric ion with enolate ion proceeded according to Eigen's mechanism and

the reaction rate constant is very large. Direct reactions of cupric ion with molecular enol and keto forms were observed. These rate constants are abnormally small compared with that of the reaction with enolate ion.

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Nomenclature

a	= minimum separation distance between ions	[m]
C_B	= total concentration of benzoylacetone	[mol/dm ³]
C_C	= total concentration of copper	[mol/dm ³]
D	= dielectric constant	[—]
E	= absorbance	[—]
e	= elementary electric charge	
K_i	= equilibrium constants for reaction of Eqs. (1)–(3), (5), (6), (8)	[in mol and dm ³ units]
k_i	= reaction rate constants defined in Fig. 2 or in Eq. (29)	[in mol, dm ³ and S units]
k_e	= reaction rate coefficient for first step of reaction to form CuB	[s ^{−1}]
k_k	= reaction rate coefficient for second step of reaction to form CuB	[s ^{−1}]
N	= Avogadro number	[mol ^{−1}]
r	= $[H]/[Cu]$	[—]
t	= time	[s]
U	= electrostatic effect of outer sphere coordination of ligand with metal ion	[J/mol]
[]	= molar concentration	[mol/dm ³]
κ	= inverse of Debye's screening length	[m]
<Superscripts>		
*	= value at thermodynamic equilibrium state	
°	= values at quasi-equilibrium state	
<Subscript>		
0	= initial value	

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