MECHANISM OF CHARACTERISTIC DECOMPOSITION OF Cu(PCD)_2 EXTRACTED FROM HYDROCHLORIC ACID: CONTRIBUTION OF REACTION BETWEEN Cu(PCD)_2 AND CuClx^(2-x)

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Abstract

To study the decomposition mechanism of copper(II) pyrrolidinecarbodithioato chelate ($Cu(PCD)_2$) extracted into di-isobutylketone (DIBK) with 1-pyrrolidinecarbodithioate (APCD) from 0.01~8 M hydrochloric acid solution, the effect of the ligand concentration in organic phase on the decomposition of $Cu(PCD)_2$ has been studied. The concentration of the free ligand in the extract decreases with time; this decrease obeys good first-order kinetics, and depends on the acidity. On the other hand, the concentration of $Cu(PCD)_2$ is not seemingly altered as long as the free ligand is present in the extract; however, the copper chelate begins to react with hydrochloric acid as soon as the free reagent has run out due to its decomposition. Furthermore, the reaction of $Cu(PCD)_2$ with hydrochloric acid in IBMK solution has also been studied kinetically. To monitor the reaction, the molar absorption coefficients of some species [CuCl(PCD), $CuCl_2$, and $CuCl_3^-$], which are formed in the course of this reaction, at 350 - 500 nm are determined. It can be thought that the reaction consists of not only simple ligand substitution by Cl^- but also of the path which gives CuCl(PCD) by reaction between $Cu(PCD)_2$ and $CuCl_2$,, and the path can be regard as the practical motive force of the decomposition of $Cu(PCD)_2$ extracted from hydrochloric acid solution.

INTRODUCTION

Ammonium 1-pyrrolidinecarbodithioate (APCD) has been known as a chelating agent which has sufficient ability for formation of the chelate with some elements even in relatively low pH media (<1). We direct our attention to such characteristics of APCD, we have systematically studied the extraction of Cu(II) from highly acidic solution (0.01~8 M

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hydrochloric and nitric acid) into isobutyl methyl ketone (IBMK)[1,2] or di-isobutyl ketone (DIBK)[3,4] with APCD, and have applied APCD/DIBK system to direct extraction of copper and nickel from titanium metal samples which digested by concentrated hydrochloric acid[5].

Through the studies we found that taking due care on the concentration of the reagent was very important to stabilize the copper chelate and increase the upper limit of acidity for the extraction. In addition, the characteristic decomposition behaviour of the copper chelate in the extract was also noteworthy; it was observed that $Cu(PCD)_2$ extracted in the extract is stable for certain period of time, however, it suddenly begins to decompose. Such a period of time when the concentration of the chelate remains constant increases as the amount of the reagent is increased. In the preceding paper[6], we studied the decomposition mechanism of the copper chelate extracted into such solvents from hydrochloric acid solution. We specified the intermediate and the final product in the reaction by UV-visible and ESR spectrometry. In this system, CuCl(PCD) and $CuCl_x^{(2-x)}$ were observed as an intermediate and a final products; then, it was concluded that the decomposition reaction of $Cu(PCD)_2$ extracted from hydrochloric acid solution could be assumed as a ligand substitution with Cl^-. It is assumed that the "motive force" of such a ligand substitution is decomposition of the PCD^- ligand dissociated from $Cu(PCD)_2$, since the formation constant of series of copper(II) dithiocarbamato complexes are considerably larger than those of copper(II) chloro complexes; if the ligand is not decomposed immediately after its dissociation from the copper chelate, the ligand will be only slightly substituted with Cl^-.

However, the decomposition of copper chelate can not be explained only by this mechanism. If the decomposition of copper chelate depends on only the decomposition of the free ligand, the rate of copper chelate decomposition must be determined by that of the free ligand, since the rate of the ligand replacement is appreciably higher than that of the decomposition of the free ligand in the organic phase. However, it seems that the decomposition rate of $Cu(PCD)_2$ is considerably higher than that of the free ligand. Aspila and Chakrabarti[7] have reported that the half-lives of APCD become constant in strongly acidic solution (< pH 2), and it determined about 30 min. On the other hand, that of the copper chelate can be estimated about 1-2 min. at the most, when the chelate extract from 4M hydrochloric acid solution. Of course they does not compare straightly since they studied in different media each other, however, any studies on the decomposition of APCD in the extraction system has not been attempted; the systematic studies on the kinetic stability and decomposition mechanism of some dithiocarbamates were made by Aspila et. al.[8,9,10] but they studied only in aqueous and the methanol/water media.

Hence, in the present paper, the decomposition of free ligand and the copper chelate in the extract was studied kinetically. We have simultaneously determined the kinetic stability of the free ligand and the copper chelate in the extract, and the relation between the decomposition of the free ligand and that of the copper chelate have studied. Then,

the reaction of $Cu(PCD)_2$ with hydrochloric acid in IBMK solution was studied kinetically, and the scheme (and "true motiveforce") of this reaction are discussed.

EXPERIMENTAL

Reagents

All chemicals used were of reagents grade. Water was redistilled from an all-glass apparatus. The standard stock solution (1000-μg/ml) of copper was prepared from 99.99 % pure metal. All solvents were used without further purification.

Procedure

Extraction of $Cu(PCD)_2$. A 20 ml portion of hydrochloric acid of desired concentration, and 2.5 ml of 10-μg/ml) copper solution were transferred to a 100 ml separatory funnel, and 10 ml of DIBK and 2.5 ml of APCD solution were added. The mixture was mechanically shaken vigorously. Immediately after the aqueous phase had been withdrawn, the absorbance of the DIBK phase was measured at 433.5 nm in a 10-mm silica cell against DIBK as reference. For kinetic work, the sample was kept in the cell compartment of the spectrophotometer throughout the period, and the temperature was kept constant at 25 ℃. Timing was started when the reagent was added to the mixture.

Determination of free ligand in extract. To determine the free ligand in the organic phase, copper(II) ion was made to react with the free ligand, and then the concentration of the free ligand was estimated from the concentration of copper chelate formed by this reaction. A 22.5 ml of hydrochloric acid of the desired concentration and 10 ml of DIBK was transferred to a 100 ml separatory funnel, 2.5 ml of APCD solution was added, and the mixture was mechanically shaken vigorously for 300 sec. It was allowed to stand until the layers separated clearly. After they had separated, 5ml of the upper phase and 10 ml of 0.01 M copper(II) solution, the pH of which had been adjusted to pH 2.0 with hydrochloric acid, were added to a 100 ml separatory funnel and the mixture was shaken vigorously for 300 sec. The upper phase was filtered through a phase separation filter paper, and the absorbance of the filtrate was measured at 433.5 nm.

Kinetic stability of free ligand in extract. A solution of 198 ml of the desired concentration of hydrochloric acid and 80 ml of DIBK were transferred to a 300 ml separatory funnel. To this was added 2 ml of 1.8×10^{-2} M APCD solution, and the mixture was mechanically shaken vigorously for 5 min. The timing was started when the reagent was added to the mixture. After the layers had separated, the upper phase was filtered through a phase separation filter paper, and the filtrate was transferred to a 100 ml conical flask and stored in a water bath thermostatted at 18.0 ℃. Portions (5 ml each) of this sample were

taken at appropriate time intervals, and the concentration of the free ligand was determined as described above.

Kinetic stability of free ligand and $Cu(PCD)_2$ in extract. A solution of 198 ml of 4 M hydrochloric acid solution containing 20 ml of 10-μg/ml) copper solution, and 80 ml of DIBK, were transferred to a 300 ml separatory funnel. To this was added 2 ml of 0.01 M APCD solution, and the mixture was then mechanically shaken vigorously for 5 min. The timing was started when the reagent was added to the mixture. After the layers had separated, the upper phase was filtered through a phase separation filter paper. A portion of the filtrate was transferred to a 10 mm silica cell, and kept in the cell compartment of a spectrophotometer throughout the measurement period at constant temperature (18.0 ℃). The remainder of the filtrate was transferred to a 100 ml conical flask and stored in a water bath thermostatted at 18.0 ℃. To measure the change in concentration of $Cu(PCD)_2$ in this sample, its absorbance during this kinetic run was monitored continuously at 433.5 nm, against DIBK as reference.

The change in concentration of free ligand was estimated by sampling 5 ml of this sample from the 100 ml in the conical flask at the appropriate time intervals. The free ligand reacted with copper(II) ion and the absorbance was measured as described above. In this case, the absorbance value obtained with this measurement gives the sum of the initial absorbance due to the copper chelate initially present in the sample, and the absorbance due to that formed from the free ligand. Thus the concentration of the free ligand could be estimated from the absorbance value given by subtracting the initial absorbance of the sample, which had been monitored at the sampling point, from this absorbance. All spectral measurements were made against DIBK as reference.

Formation of CuCl(PCD). The IBMK solution of mixture of $Cu(PCD)_2$ and CuCl(PCD) was prepared by the procedure as described in the previous paper[6].

Determination of total copper(II), $Cu(PCD)_2$, and CuCl(PCD). A 50 ml of the sample solution containing $Cu(PCD)_2$ and CuCl(PCD) was transferred to 1-mm i.d. quartz capillary cell, and ESR spectrum was measured at 3300 ± 500 G. In the present work, taking into account the sensitivity and the ease of integration, 20 G of the width of magnetic field modulation was used. The output signal of ESR spectrometer [see Fig. 3(1), given as first-order derivative form] integrated twice by using the handmade integrator[11]. To determine total copper(II) concentration, the integrated intensity [see Fig. 3(3)] was calibrated by using the working carve which was made from a know concentration of $Cu(PCD)_2$ in IBMK solutions as a spin standard. The concentration of each species in the mixture was made as following; the concentration of $Cu(PCD)_2$ was determined by measuring and calibrating of the peak-to-peak intensity of appropriate ESR spectra [see Fig. 3(1)], and then the

concentration of CuCl(PCD) was obtained by subtracting the concentration of $Cu(PCD)_2$ from that of the total copper(II).

Determination of ε of CuCl(PCD). The sample solution containing $Cu(PCD)_2$ and CuCl(PCD) was transferred to the 10-mm quartz cell, and the absorption spectrum was measured at 2.5-nm intervals, in the 350 to 500 nm wavelength region. The absorption spectrum of CuCl(PCD) alone was estimated by subtracting the spectral ingredient of $Cu(PCD)_2$ (it can be given from absorption spectrum of the standard sample and the concentration of $Cu(PCD)_2$ in the present sample determined as above) from the absorption spectrum. The molar absorption coefficient, ε, of CuCl(PCD) at any wavelength was calculated by dividing the absorbance of CuCl(PCD) alone by its concentration determined as mentioned above.

Kinetic works. A 2.0 ml of 1×10^{-4} M $Cu(PCD)_2$ IBMK solution and a teflon-coated micro stirrer bar were placed in a 10 mm quartz cell in the thermostated cell compartment of a spectrophotometer. The solution was stirred constantly throughout the reaction with a micro magnetic stirrer mounted under the cell holder and thermostated at 25 ± 0.1℃. The reaction was started by adding 2 ml of IBMK solution containing the desired concentration (1×10^{-4} -1×10^{-2} M) of hydrochloric acid, and 5 sec after that, the measurement was started.

The hydrochloric acid in IBMK solution was prepared as following. A 50-ml of IBMK and 0.5-ml of concentrated hydrochloric acid were transferred to 100 ml of separatory funnel, and were mechanically shaken vigorously. After the aqueous phase had been withdrawn the organic phase was filtered through a phase separation filterpaper (Whatman 1PS "phase separators"). The concentration of hydrochloric acid was made as mentioned in the preceding paper[6], and was adjusted to the desired concentration by dilution with pure IBMK.

A set of the measurement consist the absorbance measurement at 405 and 410 nm was taken automatically at intervals of 8.0 sec. The concentrations of $Cu(PCD)_2$ and CuCl(PCD) at each set were calculated with a correction in the time lag which needs to scan the spectrophotometer from 405 nm to 410 nm, and plotted as a function of time by a EPSON PC 286V micro computer.

RESULTS AND DISCUSSION

Kinetic stability of the free ligand

The change in the concentration of the free ligand with time was studied at various acidities. It was found that the concentration of the free ligand extracted into DIBK from such an acidic solution decreases exponentially with time; it obeyed good first-order

kinetics, and dependent on the acidity, as shown in Fig. 1. The half-life of the reagent extracted from 4, 6, and 8 M hydrochloric acid were listed in Table 1; in the case of 8 M acid, the decomposition was too fast to study with the present method and the half-life was roughly estimated about less than 2 min. These facts suggest that the free ligand which has been distributed to the organic phase reacts with the free hydrochloric acid contaminated into the organic phase and is decomposed.

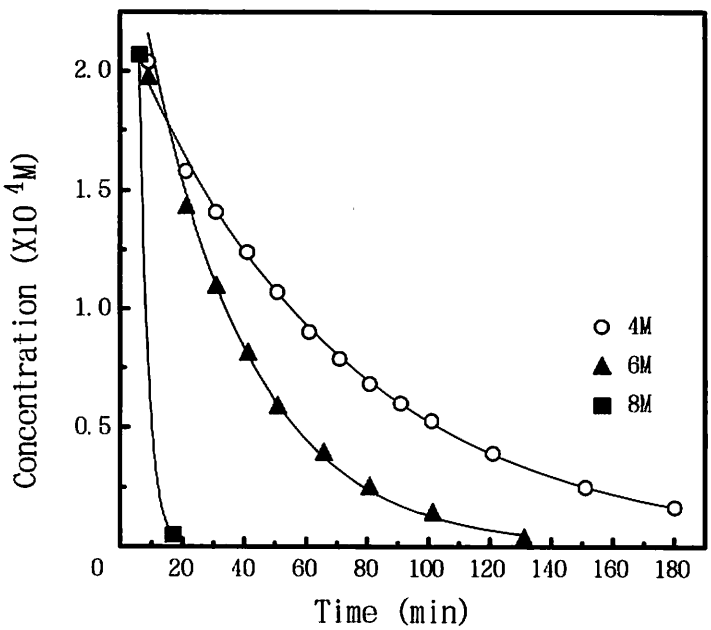


Figure 1. Kinetic stability of free PCD ligand extracted into DIBK from 4 M, 6 M and 8 M hydrochloric acid.

Table 1. Half-life (t1/2) for free PCD ligand extracted into DIBK.

Conc. of HCl (M)	t1/2 (min)
4	47.9
6	22.2
8	< 2

[APCD]: 2 $\times 10^{1}$ M; shaking time: 300 sec; temp: 18 ℃

The rate of decomposition of the free ligand in the organic phase is greater than that in aqueous solution at the same acidity. In our previous paper[6], the free acid concentrations in the DIBK phase at these acidities were estimated as follows: 2.9×10^{-4} M, 3.7×10^{-3} M, and 3.1×10^{-2} M, for 4, 6, and 8 M acid, respectively. The half-lives of the ligand in aqueous solution at about the same acidities as the above have been reported as follows: 91.76 min for pH 3.4 (3.98×10^{-4} M), 44.94 min for pH 2.6 (2.5×10^{-3} M), and 32.55 min for pH 1.4 (3.98×10^{-2} M)[7].

Such differences in the decomposition rate are attributable to the polarity of the solvent. Joris, Aspila and Chakrabarti[8] reported that the dielectric constant of the medium influences the decomposition rate of some dithiocarbamates (DTC), and indicated that in a water-methanol mixture the decomposition rate increases with decreasing dielectric constant of medium at higher fractions of methanol above 70 - 80 %. They concluded that this is due to the decrease in solvation of the DTC molecule; the solvation lowers the fractional charge in the molecule thereby stabilizing the DTC acid[9]. In IBMK or DIBK solution, an effective solvation as in aqueous medium can not be expected due to its considerably low dielectric constant and its bulkiness. Therefore, the decomposition rate of free PCD ligand in DIBK solution is higher than that in aqueous solution under the same conditions of hydrochloric acid concentration.

The present method to study the kinetic stability of free PCD ligand in the extract works effectively in the case of the ligand extracted from 4 - 8 M hydrochloric acid solution. However, it was observed that this method could not be applied to cases of acidity lower than 4 M. In these cases, an unexpected decrease in absorbance of the sample solution which had been shaken with copper(II) solution was observed in the course of the kinetic run. This was due to a change in the absorption spectrum, that is, a shift of the peak to a shorter wavelength and a decrease in absorbance. The fact indicates the composition of extracted copper chelate was changed; perhaps, it taken as the partial formation of the 1:1 complex of copper and PCD ligand. Because such a spectral change is similar to that observed when the 1:1 complex of copper and PCD ligand is formed in the decomposition of copper chelate extracted from hydrochloric acid media[6]. Such a spectral change in the measuring solution was not observed in the case above 4 M acid. Hence, the case to which the present method can be applied was estimated as above 4 M acid only.

Decomposition of the free ligand and $Cu(PCD)_2$

To elucidate the relationship of the free ligand concentration in the extract on the decomposition of $Cu(PCD)_2$, the changes in the absorbance of $Cu(PCD)_2$ and the concentration of the free ligand with time were simultaneously measured. Figure 2 shows that the absorbance of $Cu(PCD)_2$ (△) is not altered as long as the free ligand is present; however, the concentration of the free ligand (○) in the extract is exponentially

decreasing with time (the half-life is 48.8 min), and the absorbance of copper chelate begins to decrease as soon as the free ligand has run out.

From these results, it was concluded that the absorbance of copper chelate is maintained by the existence of a surplus of the free ligand. This can be explained as follows: $Cu(PCD)_2$ undergoes a very rapid ligand replacement reaction in the organic phase; the copper chelate begins to reacts with Cl^- remaining in the organic phase provided that the PCD^- ligand molecule, which dissociates in the replacement process, is decomposed and that another molecule of the ligand is not supplied. Such an above ligand replacement reaction of the copper(II)-dtc chelate was reported by Khodzhaeva and Kissin[12].

In the preceding paper6, we found that PCD^- ligand in $Cu(PCD)_2$ chelate was substituted with Cl^- step by step, and CuCl(PCD) and Cu(II)-chloride complex ($CuCl_2$ or $CuCl_3^-$) were formed. However, it seems that the decomposition behavior of copper chelate after the free ligand has run out can not be explained only by this mechanism. If the decomposition of copper chelate depends on only the decomposition of the free ligand, the rate of copper chelate decomposition must be determined by that of the free ligand, since the rate of the ligand replacement is appreciably higher than that of the decomposition of the free ligand in the organic phase. However, in practice, the decomposition rate of $Cu(PCD)_2$ is considerably higher than that of the free ligand, as shown in Fig. 2. This considerable difference between the decomposition rate of the free ligand and that of copper chelate indicates that another reaction is present in this decomposition reaction.

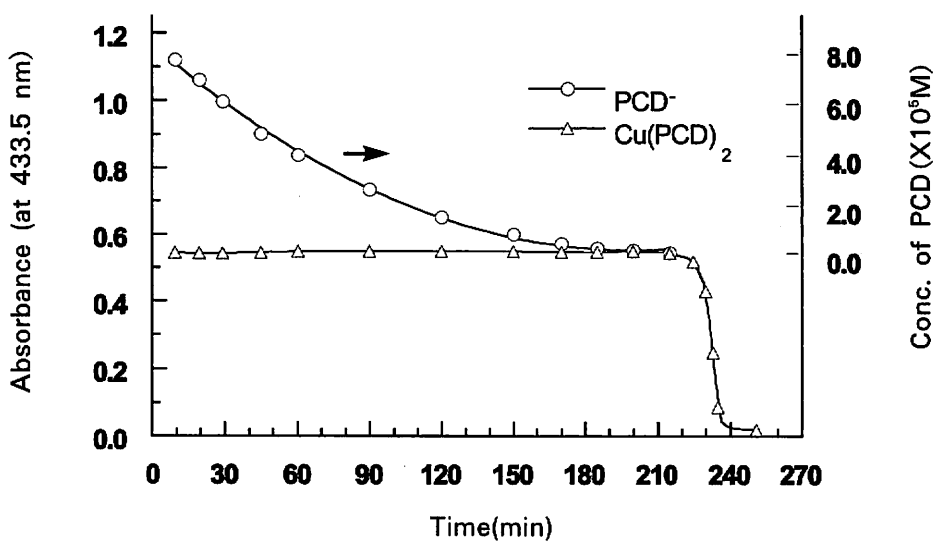


Figure 2. Relationship between time stability of Cu(PCD)2 chelate and decomposition of free PCD ligand in organic phase.

Thus, the reaction of $Cu(PCD)_2$ with hydrochloric acid in IBMK solution has kinetically been studied and then the possible mechanism of the reaction has also been discussed.

Kinetic study on the reaction between $Cu(PCD)_2$ and hydrochloric acid. Determination of ε of CuCl(PCD). In this reaction process, several kinds of copper species were observed, namely, $Cu(PCD)_2$ as a starting material, CuCl(PCD) as an intermediate product, and $CuCl_2$ or $CuCl_3$ as a final product. In order to follow this reaction, $Cu(PCD)_2$ and CuCl(PCD) must be simultaneously determined as a function of time. However, for the determination of CuCl(PCD), one of the major problems was the lack of its concentration standard; although CuCl(PCD) can be easily produced in non-aqueous solution, it has not yet been isolated since it is too unstable to isolate. Hence, we have developed the method that allows the estimate of the concentration of CuCl(PCD) without its standard by using ESR spectrometry, and we also determined the molar absorptivity of CuCl(PCD) in order to allow spectrophotometrical monitoring of the reaction.

First, an IBMK solution of mixture of $Cu(PCD)_2$ and CuCl(PCD) was prepared, and a total copper(II) concentration in the mixture was determined from the integral intensity of the whole ESR spectrum of the mixture [Fig. 3(3)]. The integral intensity of an ESR

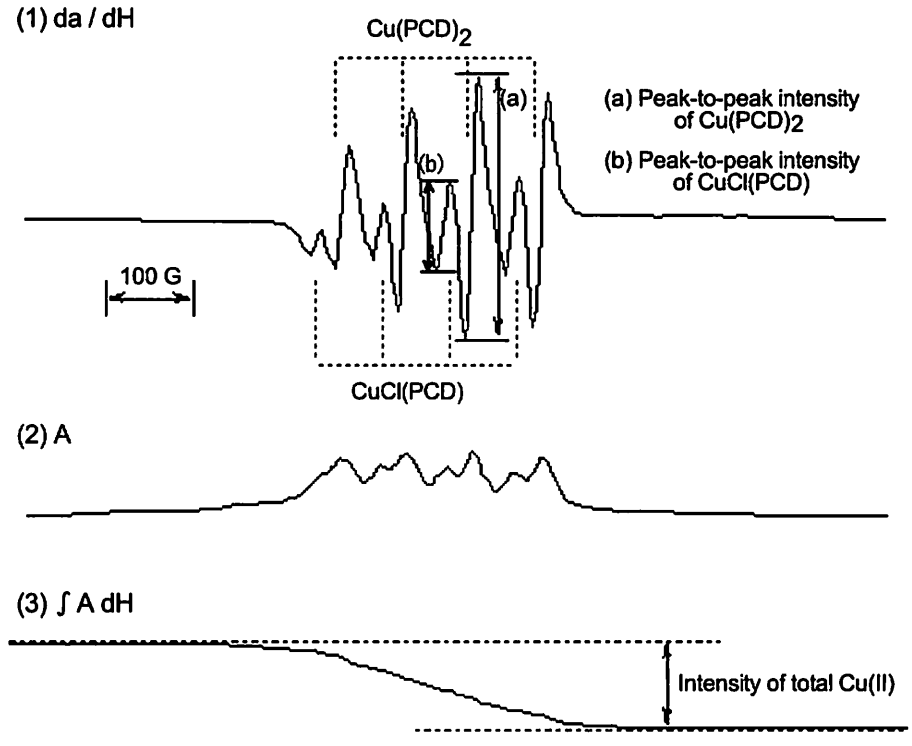


Figure 3. Determination of total Cu(II) and CuCl(PCD).

spectrum is proportional to only the concentration of unpaired electrons, viz., the spin concentration. Therefore, it can be determined by using an appropriate standard material containing a known amount of spin; It should be noted that it is unnecessary to use a same species as the analyzed one, as the standard. Thus, in this case, the total concentration of copper(II) can be determined by using an IBMK solution which contain known concentration of $Cu(PCD)_2$ as the spin standard, without the concentration standard of CuCl(PCD). Next, we determined the $Cu(PCD)_2$ alone from its peak intensity of ESR spectra of the mixture [Fig. 3(1)], and finally we could estimate the concentration of CuCl(PCD) by subtracting the concentration of $Cu(PCD)_2$ alone from that of the total copper(II). The molar absorption coefficient, ε, of CuCl(PCD) was determined at various wavelengths, by measuring the absorbance of the mixture of both species and determining the concentrations of each species in this mixture as mentioned above.

Figure 4 (O) shows the absorption spectrum of CuCl(PCD) in IBMK solution. The absorption maximum appeared at 407.5 nm, and its molar absorption coefficient was determined to be 8100 ± 70 $M^{-1}\cdot cm^{-1}$, the mean of seven replications. The wavelength at which the molar absorption coefficient of CuCl(PCD) was equal to that of $Cu(PCD)_2$ was about 408 nm, and it agrees closely with that of the isosbestic point, which was observed in the early stages of the decomposition of $Cu(PCD)_2$[6]. This fact suggests that the value of ε of CuCl(PCD) obtained by this method are reasonable.

By using the molar absorption coefficients of CuCl(PCD) and $Cu(PCD)_2$, both species

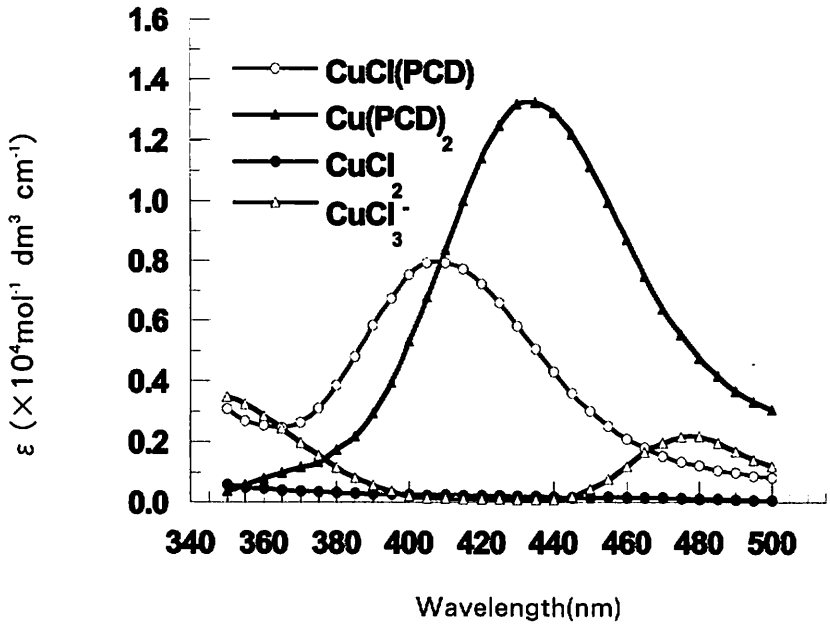


Figure 4. Absorption spectrum of CuCl(PCD), $Cu(PCD)_2$, $CuCl_2$ and $CuCl_3^-$.

can be simultaneously determined with spectrophotometric measurement at two wavelengths, since the final product of $CuCl_2$ or $CuCl_3$ only slightly absorbed light in the region from 350 to 500 nm. The value of their molar absorption coefficients were much smaller than that of CuCl(PCD) and $Cu(PCD)_2$, as shown in Fig. 4. Hence, 405 and 410 nm were selected as the wavelengths for measuring the absorbance.

Rate profiles of $Cu(PCD)_2$ and CuCl(PCD)

Figures 5~9 show the change in concentration of both species with time at various initial concentrations of hydrochloric acid. Characteristic profiles were observed in the change in the concentration of $Cu(PCD)_2$ with time over the entire range of hydrochloric acid concentration. The rate of $Cu(PCD)_2$ disappearance increased with time until it reached a maximum; this was observed at the point of time when the concentration of $Cu(PCD)_2$ decreased to about half its initial value. Figure 10 shows the effect of the initial hydrochloric acid concentration on the rate of $Cu(PCD)_2$ disappearance at the point of time when $Cu(PCD)_2$ had decreased to half its initial concentration. The rate was reached a maximum at higher acid concentration (> about 6 fold ratio to copper), although the rate almost linearly increased as increasing the acid concentration up to 2-fold ratio to copper.

The change in the concentration of CuCl(PCD) was also characteristic. The concentration of CuCl(PCD) reached a maximum at the time when $Cu(PCD)_2$ had almost

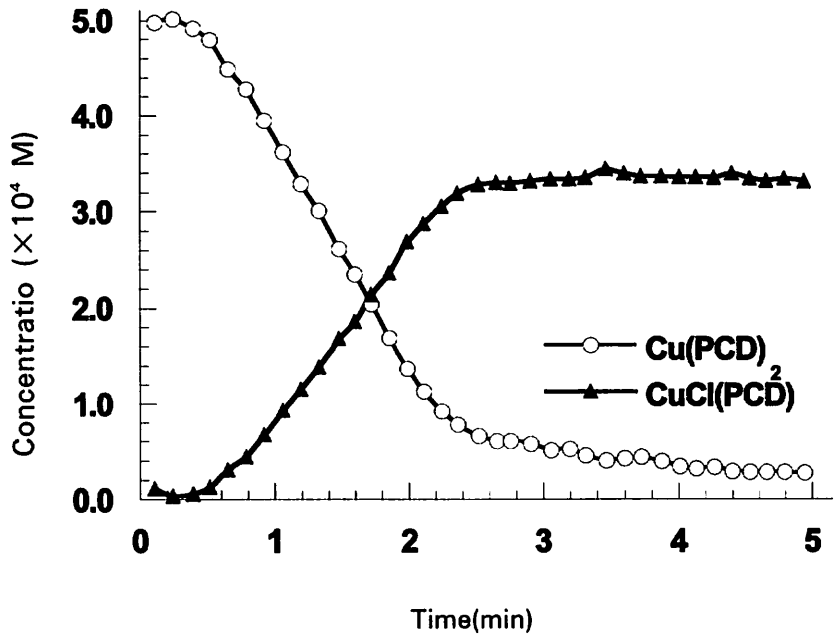


Figure 5. Concentration - time profiles of $Cu(PCD)_2$ and CuCl(PCD) during reaction of $Cu(PCD)_2$ with HCl (7.83×10^{-5} M, 1.55-fold ratio to Cu(II)) in MIBK, at 25.0 ℃.

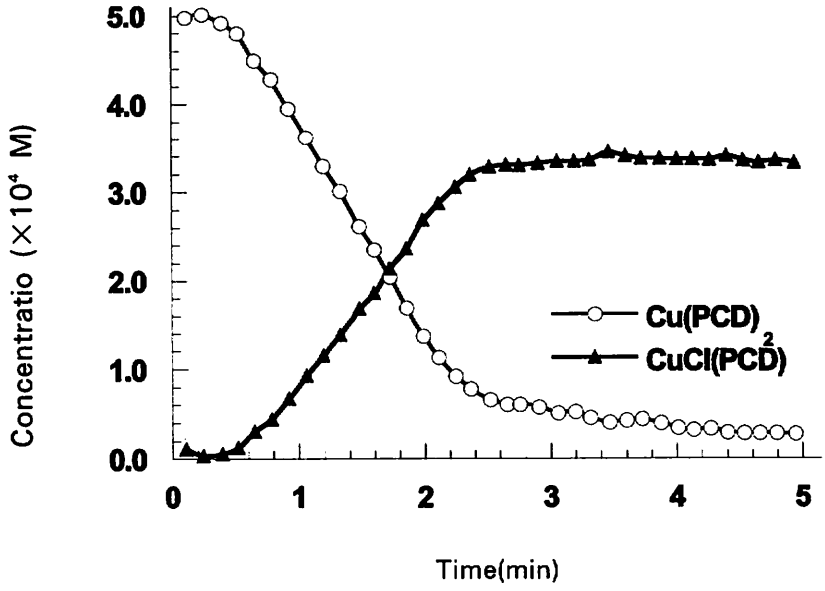


Figure 6. Concentration - time profiles of $Cu(PCD)_2$ and CuCl(PCD) during reaction of $Cu(PCD)_2$ with HCl (1.91×10^{-4} M, 3.67-fold ratio to Cu(II)) in MIBK, at 25.0 ℃.

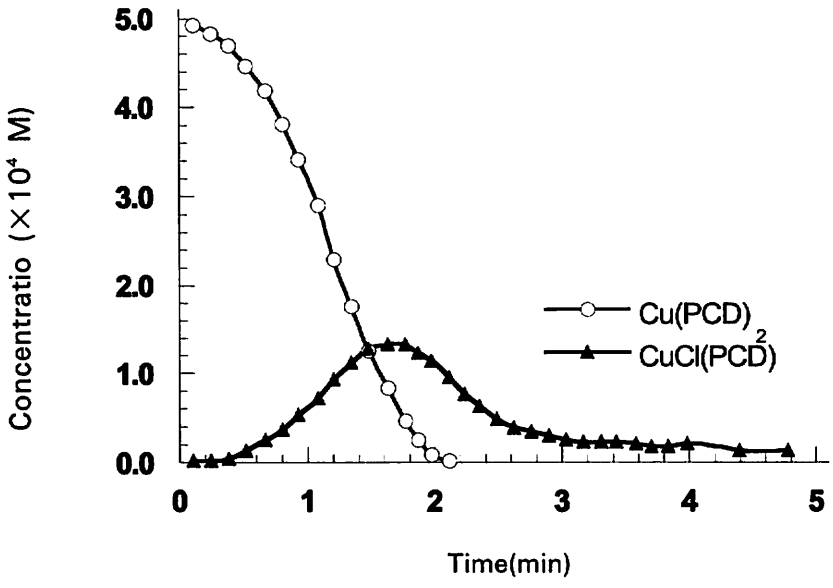


Figure 7. Concentration - time profiles of $Cu(PCD)_2$ and CuCl(PCD) during reaction of $Cu(PCD)_2$ with HCl (5.36×10^{-4} M, 10.7-fold ratio to Cu(II)) in MIBK, at 25.0℃.

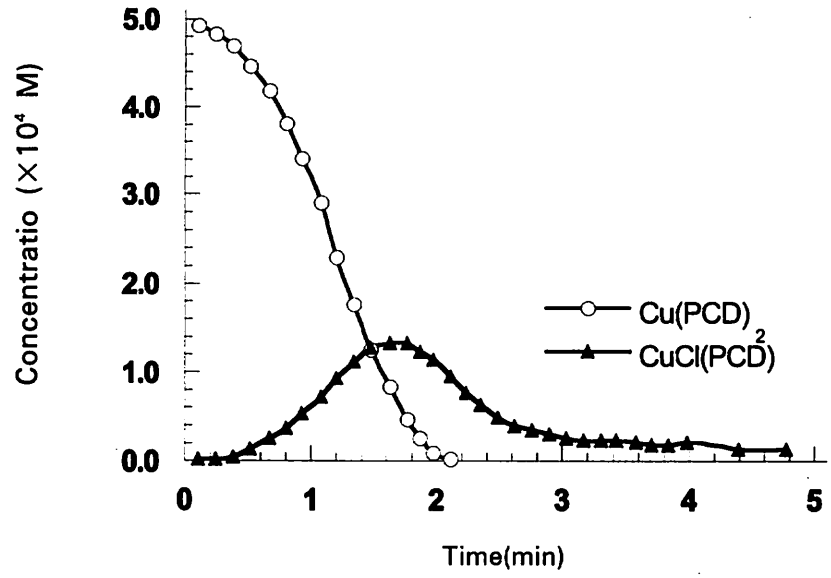


Figure 8. Concentration - time profiles of $Cu(PCD)_2$ and CuCl(PCD) during reaction of $Cu(PCD)_2$ with HCl (1.98×10^{-3} M, 36.0-fold ratio to Cu(II)) in MIBK, at 25.0℃.

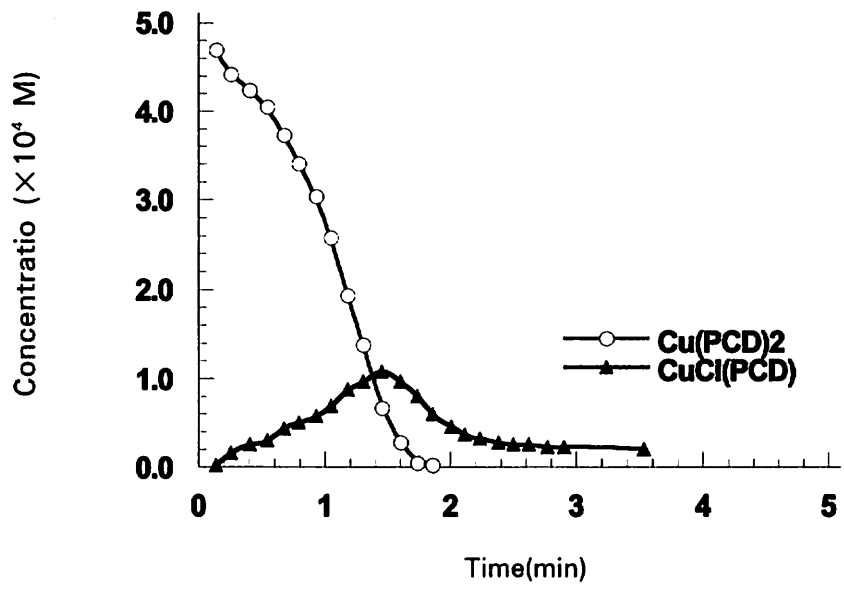


Figure 9. Concentration - time profiles of $Cu(PCD)_2$ and CuCl(PCD) during reaction of $Cu(PCD)_2$ with HCl (4.65×10^{-3} M, 93.0-fold ratio to Cu(II)) in MIBK, at 25.0℃.

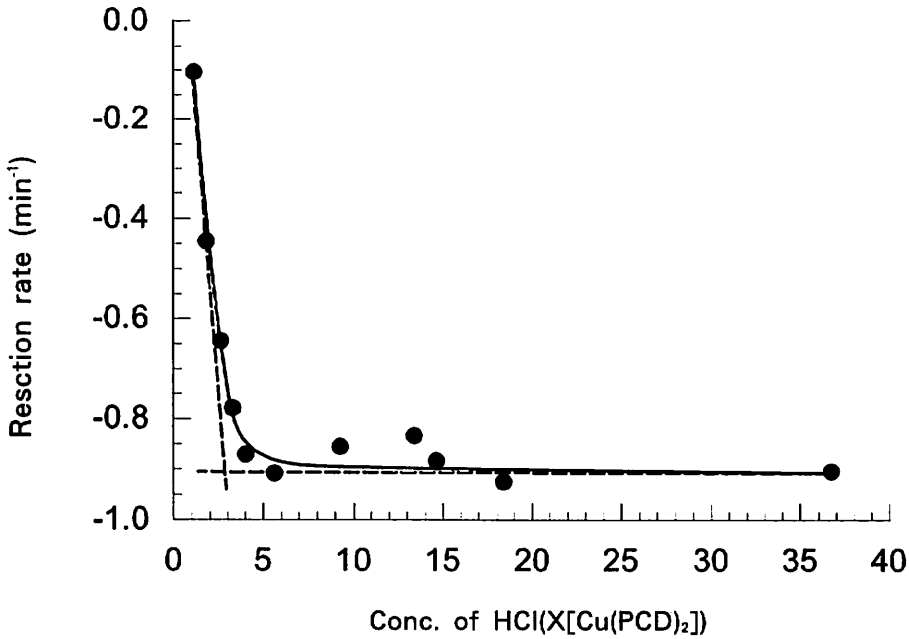


Figure 10. Relationship between the reaction rate of $Cu(PCD)_2$ at the point which is half of its initial concentration and initial concentration of HCl.

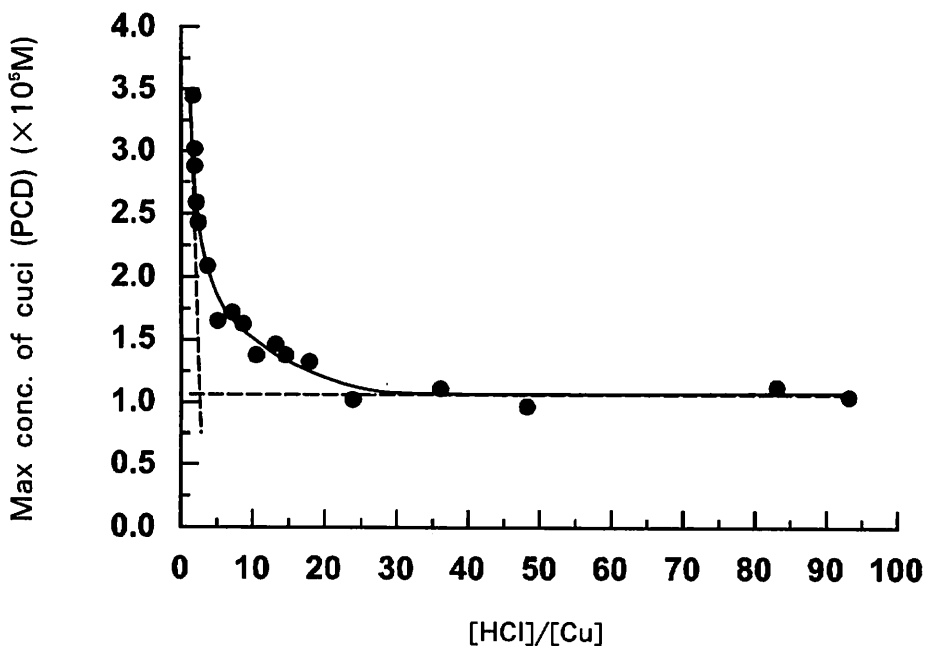


Figure 11. Relationship between the maximum concentration of CuCl(PCD) and the molar ratio of initial concentration of HCl to that of Cu

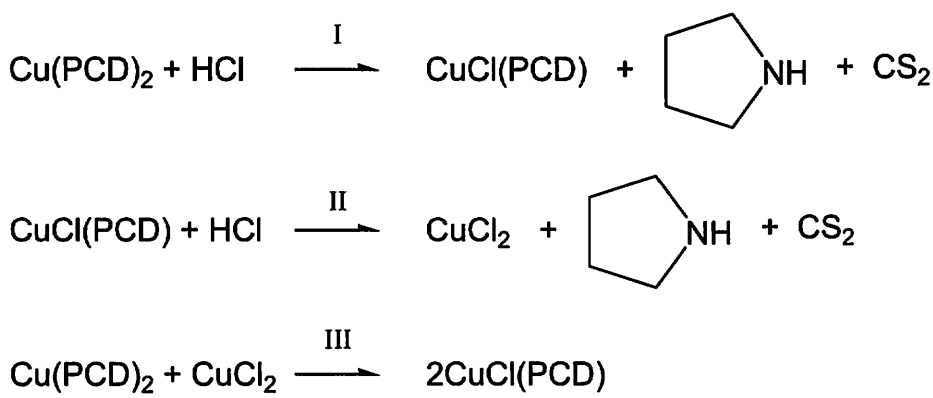
disappeared, and then it decreased with time, provided that the initial hydrochloric acid concentration was sufficiently high (Fig. 6 - 9). On the other hand, when the hydrochloric acid concentration decreased to less than about 2 fold ratio to copper, attaining of equilibrium of the concentration changes of both species was observed (Fig. 5). This agrees with the stoichiometric amount of hydrochloric acid which can be estimated from the composition of the final products.

The dependence of the maximum concentration of CuCl(PCD) on the initial hydrochloric acid concentration was shown in Figure 11. The observed maximum concentration decreased almost linearly with increasing hydrochloric acid concentration, up to about 2-3 fold ratio to copper; then, at the higher acid concentration than that, it also reached a minimum.

From the above results, it could be noted that the acid concentration did not have a strong effect on both the rate of $Cu(PCD)_2$ disappearance and the observed maximum concentration of CuCl(PCD), in the whole range of the present acid concentration.

CONCLUSIONS

The above mentioned rate profiles of $Cu(PCD)_2$ can not be explain by the simple succession of reactions which assumed only based on the species appears in the reaction. These findings indicate that the reaction contains some additional competitive processes. To explain such a rate profile, we proposed the probable scheme (see Scheme 1). From the species observed in this system, it was concluded that the original ligand, PCD^- is sequentially substituted by chloride ion [path(I) and (II)]. The free PCD^- ligand reacts with a proton and is decomposed to pyrrolidine and carbon disulfide. Furthermore, it can be assumed that $Cu(PCD)_2$ reacts with copper(II) chloride, which is regarded as the final product; thus CuCl(PCD) is also formed by this reaction [path(III)].



Scheme 1. Estimated scheme of decomposition reaction of $Cu(PCD)_2$ with HCl in DIBK or MIBK

In the CuCl(PCD) formation, it can be assumed that the rate of path(III) is considerably higher than that of path(I), and thus path(III) is dominant rather than path(I), except in the very early stages of the reaction. This is because it can be expected that the rate of CuCl(PCD) formation by path(I) is determined by the decomposition rate of PCD^- ligand dissociated from $Cu(PCD)_2$, and it is much lower than that of path(III). As shown previously, the half-lives of the free ligands in the organic phase are taken as at most about several minutes. On the other hand, it was observed that the reaction of $Cu(PCD)_2$ with $CuCl_2$ almost instantaneously attained the equilibrium immediately after mixing both solutions[6]. Thus, we concluded that the path(III) can be regard as the practical motive force of the decomposition of $Cu(PCD)_2$ extracted from hydrochloric acid solution, although the decomposition of the PCD^- ligand which dissociated from $Cu(PCD)_2$ triggers and cause the series of the above reactions.

Of course, above mentioned kinetic study on the present reaction is insufficient and the above scheme can not give the complete explanation on the mechanism of the present reaction; for example, the saturation of the effect of hydrochloric acid on the reaction rates at higher acid concentrations is not explicable only by this scheme. The concentration - time profiles of both species and the effect of the acid concentration on the rates of disappearance of both species suggest that the both rates become constant at higher acid concentrations, although in the lower acid concentrations they depend on the acid concentration.

Such a rate dependence on the acid concentration is shown in the ligand substitution reaction of some square planar four-coordinate complexes of Pt(II) and Pd(II)[13,14], and it is explained by the mechanism based on an SN_2 reaction mechanism. It can be assumed that similar mechanism to the above is also applied to the ligand substitution steps in path (I) and (II) of the present reaction of $Cu(PCD)_2$, since it is known that copper(II)-dithiocarbamate complexes are a square planar species in solution[15]. To ascertain this, further kinetic studies is required; however, unfortunately, it is difficult because of such an above complicated reaction scheme and of some experimental restrictions (such as medium of the reaction, solubility of the species, and so on).

Therefore, we believe that the above mentioned pathways gave a rough, but reasonable explanation of the decomposition of $Cu(PCD)_2$ extracted from hydrochloric acid media, within the range of possibility.

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