Kinetic Studies of Fast Equilibrium by Means of High-performance Liquid Chromatography. IV. Separation of Rotamers of Palladium(II) Dithiocarbamates

Masataka Moriyasu,* Yohei Hashimoto, and Masaru Endo†

Kobe Women's College of Pharmacy, Motoyamakita-machi, Higashinada-ku, Kobe 658

†*Kinki District Narcotic Control Office, Uchikyuhoji-machi, Higashi-ku, Osaka 540*

(Received October 28, 1982)

The restricted rotation about carbon-nitrogen bonds of unsymmetrical palladium(II) dithiocarbamate chelates has been investigated by high-performance liquid chromatography. At higher temperatures, the rotation is so rapid that two rotamers have not been distinguished, and a single sharp peak has appeared on chromatograms, whereas at lower temperatures, they have been separated. The activation energy of the rotation of palladium(II) dithiocarbamate ($\Delta H^{*}=83\pm5$ kJ mol^{-1} for $Pd(C_6H_5CH_2CH_2NHCSS)_2$) is smaller than usual values of the energy barrier to rotate double bonds, but larger than those to rotate single bonds.

In our previous reports[1-3] it was shown that fast equilibrium including ternary complex formation between two different dithiocarbamate chelates of nickel(II) or copper(II) ($MA_2+MB_2\rightleftharpoons 2MAB$) could be traced by high-performance liquid chromatography (HPLC), while the labile ternary complex MAB was eluted without disproportionation. When kinetically unstable species are chromatographed, they are transformed gradually into other species in the column. The chromatogram patterns vary whether or not the separation is faster than the transformation. When the separation is much faster, the transformation during chromatography will be negligible, and kinetically unstable species will be eluted without any change in the column. On the other hand, when the separation is much slower, unstable species is not detected. Between these two extremes, the separation and the transformation will compete and complicated chromatograms will be obtained. Therefore, in order to trace fast reactions in solution by HPLC, kinetically unstable species should be stabilized in the column by some ways, and the following methods are suggested. (1) Temperature control: Since the rate of reaction decreases with decreasing temperature, kinetically unstable species will be stabilized when HPLC is performed at low temperatures. (2) Flow rate control: Since the residence time of each species in the column decreases with increasing flow rate of the eluent, this brings a similar result to temperature decrease. (3) Sample amount: The effect of sample amount on chromatograms should differ whether the reaction proceeds according to the first-order or the second-order rate law. The progress of second-order reactions is slow, when low initial concentrations of reactants are chosen. Thus, different chromatogram patterns will be obtained, when samples of different initial concentrations with the same sample volume are supplied to HPLC. Contrary to this, when a reaction proceeds according to the first-order rate law, the progress of the reaction should be indifferent to sample amounts, giving unchanged chromatogram patterns. Thus the change of sample concentrations might give a useful information on the reaction mechanism.

In this report equilibria between various kinetically unstable species present in the solution of palladium(II) dithiocarbamate chelates have been scrutinized by means of HPLC.

Experimental

Reagents. Sodium or ammonium salts of various *N,N*-disubstituted and *N*-monosubstituted dithiocarbonic acids were prepared by mixing corresponding aliphatic amine, carbon disulfide, and sodium hydroxide (or aqueous ammonia).[4] The following amines were used: symmetrical secondary amines (dimethylamine, diethylamine, dipropylamine, dibutylamine, pyrrolidine, piperidine, perhydroazepine, morpholine, and dibenzylamine), unsymmetrical secondary amines (*N*-methylbenzylamine, *dl*-2-methylpiperidine, and *l*-ephedrine), and primary amines (methylamine, ethylamine, propylamine, butylamine, benzylamine, and phenethylamine). Standard solutions of palladium(II) and nickel(II) (0.1 mol dm^{-3}) were prepared by dissolving $PdCl_2$ and $NiCl\cdot 6H_2O$ in dilute hydrochloric acid.

Apparatus. The HPLC apparatus is of our own construction. A two-plunger reciprocal pump (Model KHD-W-294, Kyowa Seimitsu Co. Ltd.), a variable sample injector (Model KHP-U1-130, Kyowa Seimitsu Co. Ltd.), a silica-gel column, and a variable wavelength UV-visible detector (Model SPD-1, Shimadzu) were combined. Silica-gel packings (LiChrosorb SI 100, 5 μm, E. Merck Darmstadt; Polygosil 50-5, 5 μm, M. Nagel, Duren; Wako-gel LC 10 H, 10 μm, Wako Pure Chemicals Co. Ltd.) were slurry-packed into stainless steel columns (diameter 4 mm, length 25 cm). Absorbance of palladium(II) dithiocarbamate chelates was measured by a double-beam spectrometer (Model 124, Hitachi).

Procedure. In order to carry out HPLC at low temperatures, column and solvent reservoir were immersed into refrigerant composed of water-methanol in a bath (Model Cryocool CC-80f, Neslab Instruement Inc.). When sillica-gel packings and mixed solvent sysrems of hexane-isopropyl acetate were combined, HPLC was made possible even at −70 °C, though column efficiency was reduced below −40 °C. For the determiantion of rate constants, the HPLC apparentus was modified as depicted in Fig. 1. The procedure was as follows. An equilibrated solution composed of two isomers (X⇌Y) was supplied to HPLC through injector I and the portion corresponding to X (or Y) was collected into a reservoir thermostated in the bath. The collected solution was stirred and then stood for a few minutes. After the flow path was changed by the six-way valve, the solution in the reservoir was sucked in from injector II. The injection was repeated for a definite interval. Since the reaction X→Y (or Y→X) proceeded gradually in the thermostated solution, peak of Y (or X) grew while that of X (or Y) fell with each injection. Thus the progress of the

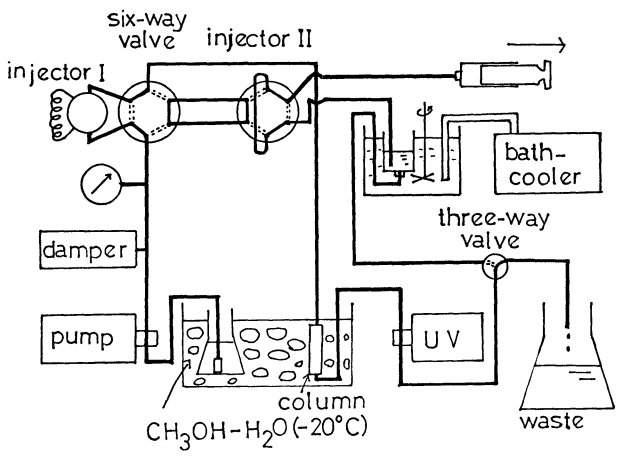


Fig. 1. Block diagram of HPLC apparatus.

reaction was traced by HPLC. All the measurements were repeated three times.

Theoretical

HPLC of Two Isomers in the Equilibrium State. Two different species (X and Y) exist in the equilibrated state in solution, fast interconversion of two isomers being an example.

$$X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Y , \quad (1)$$

$$K_1 = y_e/x_e = k_1/k_{-1}. \quad (2)$$

Here, x_e and y_e are concentrations of X and Y in the equilibrium state, respectively. Possible chromatogram patterns will be considered first. It is assumed that intrinsic retention time of X is smaller than that of Y, and K_1 is close to 1.0. (1) When k_1 and k_{-1} are very small and separation is achieved promptly, two species X and Y will be eluted separately without interconversion. In this case the obtained chromatograms will be similar to those of the separation of two stable species (Fig. 2(a)). (2) With the increase of k_1, partial interconversion will commence to occur during the course of chromatography. When a part of species X with smaller retention time is converted into Y, its linear velocity passing through the column is reduced, and the peak of X tends to cause tailing (Fig. 2(b)). Similarly the peak of Y will cause leading. (3) When the rate of interconversion is moderately fast, and separation and interconversion occur competitively in the column, complicated chromatograms will be obtained (Figs. 2(c) and 2(d)). (4) When the interconversion is much faster than the separation and consequently the equilibrium in Eq. 1 is maintained throughout the HPLC process, a single peak will appear on chromatograms, and the retention time is the mean of the intrinsic retention times of X and Y (Fig. 2(e)). A fall of column temperature and an increase of flow rate will bring the change of chromatogram patterns, Fig. 2(e)→Fig. 2(d)→Fig. 2(c)→Fig. 2(b)→Fig. 2(a), because interconversion will be retarded by these procedures. The decrease of initial concentration of the sample will bring a similar result provided that the interconversion proceeds according to the second-order rate law.

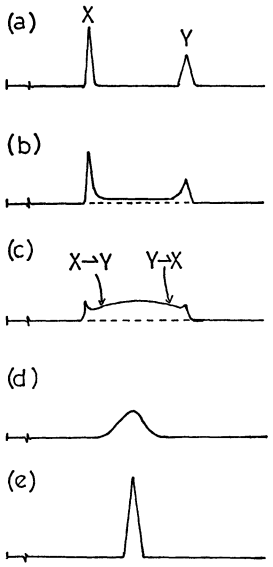


Fig. 2. Possible chromatogram patterns of the system of two kinetically unstable species in equilibrium state.

Determination of Equilibrium and Rate Constants. There exists some difficulty in the determination of the equilibrium and the rate constants, since species X and Y are hardly obtained in a pure state. The measurement of two peak areas in Fig. 2(a) does not give K_1 values directly due to the difference of absorption coefficients of X and Y. The determination of K_1 should thus be carried out by the following procedure, if a chromatogram pattern shown in Fig. 2(a) is obtained. The equilibrated solution is supplied to HPLC, and two fractions corresponding to X and Y are collected. These two solutions are diluted to a definite volume with an HPLC solvent. After standing enough time to attain the equilibrium ($X \rightleftharpoons Y$), K_1 can be determined by one of the following alternative methods. (1) The measurement of absorbance of these two solutions gives K_1 values. (2) When a portion of these two solutions is rechromatographed, chromatogram patterns shown in Fig. 2(a) will be obtained again. The measurements of peak heights (or peak areas) of these two solutions give K_1 values. The calibration curves of X and Y are obtained when K_1 values are determined.

The determination of k_1 and k_{-1} will be carried out as follows. If X (or Y) can be obtained in a pure state, k_1 and k_{-1} are determined easily. This assumption, though being hardly attained in case of a fast equilibrium, will be useful to extend the discussion. Therefore, we consider first using this assumption. In this case, rate constants are determined by dissolving pure X (or Y) and after standing for a definite time a portion of the solution is supplied to HPLC. When the injection is repeated at a definite interval, the peak of Y (or X) will grow while that of X (or Y) will fall. The rate constants are expressed by the following alternative equations whether the reaction proceeds according to the first-order (3) or the second-order (4) rate law.[5]

$$k_1 = (y_e/x_0t)\ln\{y_e/(y_e-y)\}, \quad (3)$$

$$k_1 = [y_e/\{2x_0t(x_0-y_e)\}] \times \ln[\{y(x_0-2y_e)+x_0y_e\}/\{x_0(y_e-y)\}]. \quad (4)$$

Here, x_0, y, and y_e denote initial concentration of X, concentration of Y at t and at equilibrium state, respectively.

Since the aforementioned premise is not satisfied actually, some modification of the formulation is required. The fraction of X (or Y) is collected by HPLC and then the solution is kept in the thermostated bath. After standing for some minutes, a portion of the thermostated solution is rechromatographed. At this time t', the reaction X→Y (or Y→X) already proceeds partially, and we denote the concentrations of X and Y at t' as x' and y', respectively. After a definite interval Δt, a portion of the solution is injected repeatedly. Eqs. 3 and 4 are modified as follows.

$$k_1 = \{y_e/x_0(t'+\Delta t)\}\ln\{y_e/(y_e-y'-\Delta y)\}, \quad (3')$$

$$k_1 = [y_e/\{2x_0(t'+\Delta t)(x_0-y_e)\}] \times \ln[\{(y'+\Delta y)(x_0-2y_e)+x_0y_e\}/\{x_0(y_e-y'-\Delta y)\}]. \quad (4')$$

Here, $y'+\Delta y$ is the concentration of Y at $t'+\Delta t$.

Results and Discussion

Comparison of HPLC of Palladium(II) and Nickel(II) Dithiocabamate Chelates. Chromatographic behavior of various palladium(II) dithiocarbamate chelates was compared with that of nickel(II) dithiocarbamate chelates. As mentioned in our previous report,[6] retention times of each palladium(II) dithiocarbamate were very close to those of corresponding nickel(II) dithiocarbamate when silica gel packings and mixed solvent systems of hexane–isopropyl acetate were used. The characteristic feature of the chromatograms of palladium(II) chelates is an appearance of very broad peaks in some cases, as exemplified in Fig. 3. When

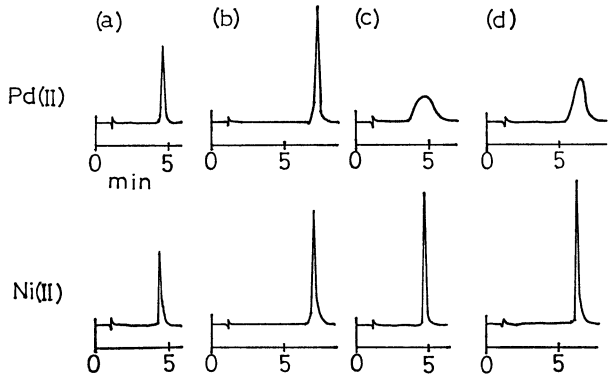
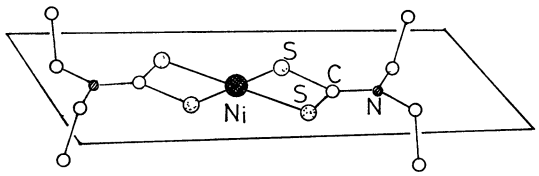


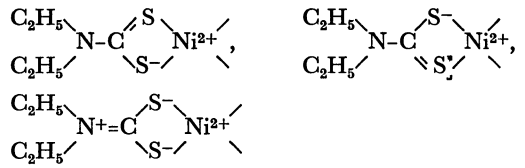
Fig. 3. Comparison of HPLC of dithiocarbamate chelates of Pd(II) and Ni(II).
Column: Polygosil 50-5 (4 mm×25 cm). Eluent: hexane:isopropyl acetate=100:15 (water saturated). Flow rate: 1.5 cm³/min. Detector: 305 nm (Pd), 325 nm (Ni). Sample size: 0.01 cm³. Sample: MA_2 A= (a) $(CH_3)_2NCSS^-$, (b) $O(CH_2CH_2)_2NCSS^-$, (c) $(C_6H_5CH_2CH_2)HNCSS^-$, (d) $(CH_3CH_2)HNCSS^-$.

palladium(II) chelates were derived from symmetrical secondary amines such as diethylamine and piperidine, peaks were always sharp. However, *N*-monosubstituted dithiocarbamate chelates derived from primary amines gave broad peaks. This seems to be attributable to the decomposition of the chelates since *N*-monosubstituted dithiocarbamate chelates of some metal ions are less stable chemically than *N,N*-disubstituted dithiocarbamate chelates.[7] This explanation, however, is not valid because solutions of *N*-monosubstituted dithiocarbamate chelates of palladium(II) did not give any change in absorption spectra after 10 d. Furthermore, dithiocarbamate chelates derived from unsymmetrical secondary amines such as *N*-methylbenzylamine also gave broad peaks. The characteristic feature of the chromatograms is summarized that peaks are broadened when unsymmetrical palladium(II) dithiocarbamates are chromatographed.

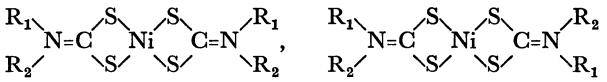
Separation of Two Rotamers of Palladium(II) Dithiocarbamates. The X-ray conformational study of nickel(II) diethyldithiocarbamate has shown[8] that this chelate has a structure as shown below. All the atoms except terminal methyl groups lie in the same plane.



The carbon-nitrogen bond length is 1.33 Å (1 Å= 10^{-10} m), which is much shorter than that of the usual carbon–nitrogen single bond (1.47 Å), but slightly longer than that of the carbon-nitrogen double bond (1.30 Å). The bond lengths of two carbon-sulfur bonds are identical (1.71 Å) within the experimental error. These results suggest that the contribution of the following three canonical forms is possible and that of the last form is largest.



It is well known that the carbon-nitrogen double bonds are rigidly fixed, similarly to the carbon-carbon double bonds. On the other hand, the carbon-nitrogen single bonds rotate freely at room temperature. When two different substituents (R_1 and R_2) are linked to each nitrogen atom, two geometric isomers shown below might be separated, provided that the carbon-nitrogen bond has a double bond character.



A similar explanation is valid for palladium(II) chelates because palladium(II) has been well known to form square-planer complexes. We chromatographed several unsymmetrical palladium(II) dithiocarbamates at various temperatures. An example of chromatograms of palladium(II) dithiocarbamate derived from

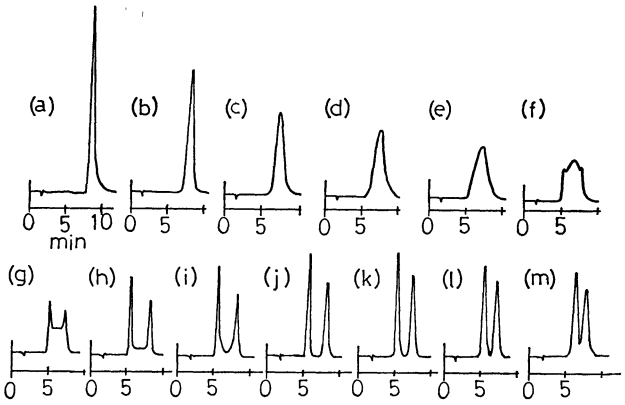


Fig. 4. Chromatograms of Pd(II) dithiocarbamate derived from phenethylamine at various temperatures. Column: Wakogel LC-10H (4 mm×25 cm). Eluent: hexane:isopropyl acetate=100:15 (water saturated). Flow rate: 1.5 cm³/min. Detector: 305 nm. Sample size: 0.01 cm³. Sample: 1.0×10^{-3} mol dm^{-3} Pd-[$(C_6H_5CH_2CH_2)HNCSS]_2$ (a) 50 °C, (b) 40 °C, (c) 30 °C, (d) 25 °C, (e) 20 °C, (f) 15 °C, (g) 10 °C, (h) 0 °C, (i) −10 °C, (j) −20 °C, (k) −30 °C, (l) −40 °C, (m) −50 °C.

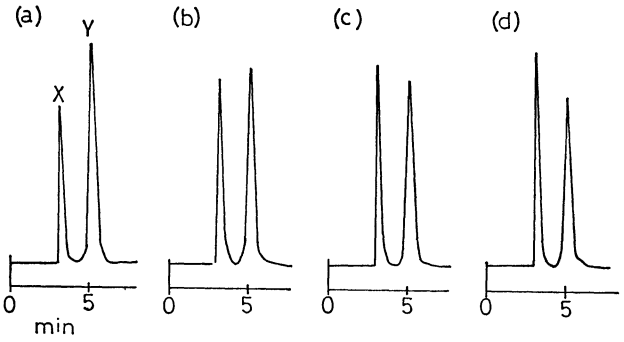


Fig. 5. Change of chromatogram patterns during the course of interconversion of two rotamers of Pd(II) dithiocarbamate derived from phenethylamine. Column: LiChrosorb SI 100 (5 μm, 4 mm×25 cm). Eluent : hexane : isopropyl acetate=100:15 (water saturated). Flow rate: 2.5 cm³/min. Detector: 305 nm. Sample size: 0.2 cm³. Sample: A 0.025 cm³ solution of 2×10^{-3} mol dm^{-3} Pd[$(C_6H_5CH_2CH_2)$-NHCSS]$_2$ was supplied to HPLC and the fraction corresponding to the latter peak was collected. After thermostated at 0 °C for a few minutes, a 0.2 cm³ portion of the solution was supplied to HPLC. The initial concentration of Y ($=y_0$) was determined to be 2.0×10^{-5} mol dm^{-3}. (a) at t_0, (b) at $t_0+5.0$ min, (c) at $t_0+10.0$ min, (d) at t_0+30 min(equilibrium). The value k_1 ($=k_{-1}$) was determined to be 1.1×10^{-3} s^{-1} in this case.

phenethylamine is shown in Fig. 4, which gave the broadest peak at room temperature. These chromatograms suggest that partial rotation around the carbon-nitrogen bond does occur during chromatography at intermediate temperatures. At lower temperatures (<−20 °C), the rotation is negligible because neither tailing nor leading was observed. When the temperature was lowered down to −40 °C, two peaks gradually overlapped due to the decrease of column efficiency. At higher temperatures (>50 °C), the rotation is so rapid that two isomers cannot be distinguished by HPLC. Other palladium(II) chelates derived from unsymmetrical amines such as ethylamine and *N*-methylbenzylamine gave similar results. Contrary to palladium(II) chelates, unsymmetrical nickel(II) chelates always gave single peaks at any temperatures. From these results, it can be concluded that palladium(II) chelates undergo relatively slow intramolecular carbon-nitrogen bond rotation, while for nickel(II) chelates the rotation is rapid even at lower temperature. This suggests that a lone-pair electron on the nitrogen atom is withdrawn by palladium(II) ion more strongly than by nickel(II) ion.

Reaction Mechanism of the Rotation. In order to elucidate whether the rotation proceeds according to the first- or second-order rate law, HPLC conditions such as flow rate and initial concentration of the sample were varied. When the flow rate was doubled at 15 °C, the chromatogram was found to be similar to that shown in Fig. 4(g) (at 10 °C), suggesting that the reaction is approximately doubled with 5 °C rise in temperature. Then the sample solution was diluted various times, and 0.01 cm³ each of the solution was supplied to HPLC at 15 °C. The chromatogram pattern was independent of initial concentration, suggesting the first-order reaction mechanism.

Determination of K_1 and k_1. The equilibrium constants K_1 and the rate constants k_1 of palladium(II) chelate derived from phenethylamine were determined at various temperatures according to the procedure described in the previous theoretical section. The K_1 values were always equal to 1.0 within the experimental error. Two peak areas in Figs. 4(i)—4(l) were also the same, suggesting that two rotamers have almost the same absorption coefficients. These results seem to be in good agreement with the fact that no steric hindrance exists for these two rotamers. Since $K_1=1.0$, Eq. 3′ will be simplified to

$$k_1 = k_{-1} = \{0.5/(t'+\Delta t)\} \ln \{x_0/(x_0-2y'-2\Delta y)\}. \quad (5)$$

An example of the change of chromatogram patterns at 0 °C is shown in Fig. 5. Here X and Y denote the former and the latter peaks, respectively, because it is not always possible to conclude which rotamer is eluted faster. The k_1 value at 0 °C was thus determined to be $(1.1\pm0.1)\times10^{-3}$ s^{-1}. The energy barrier of rotation ΔH^* was obtained by measuring k_1 at different temperatures, and the results are plotted in Fig. 6. Since the rotation is so rapid at higher temperatures that the determination of k_1 was impossible above 10 °C. The energy barrier ΔH^* was determined to be 83 ± 7 kJ mol^{-1}. This value is much larger than that to rotate usual single bonds, but smaller than that to rotate double bonds. For example, the activation energy to rotate carbon–carbon single and double bonds are well known to be about 12 and 260 kJ mol^{-1}, respectively.[9] Since the upper limit of the thermal energy of molecules in solution is 63—85 kJ mol^{-1},[9] a value of 83 kJ mol^{-1} seems to be near the limit that the reaction proceeds promptly at room temperature. The k_1 value at room temperature is extraporated to be 3.6×10^{-2} s^{-1} (at 25

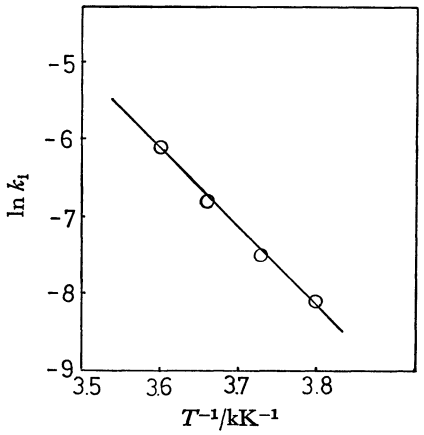


Fig. 6. Activation energy of the carbon-nitrogen bond rotation. Chromatographic conditions were similar to those shown in Fig. 5. The values of k_1 were determined at various temperatures with the similar procedure shown in Fig. 5. The value ΔH^* was determined from the following equation: $k_1 = A_0 \exp(-\Delta H^*/RT)$.

°C) from Fig. 6. From this result it is calculated that the interconversion reaction X→Y proceeds to 50% within 10 s at 25 °C.

Ternary Complex Formation. When chloroform solutions of two different dithiocarbamate chelates of palladium(II) (MA_2 and MB_2) were mixed, ternary complex formation was found to occur similarly to the cases of nickel(II) and copper(II).[1]

$$MA_2 + MB_2 \underset{k_-}{\overset{k}{\rightleftharpoons}} 2MAB, \quad (6)$$

$$K = [MAB]^2/[MA_2][MB_2]. \quad (7)$$

An example of chromatograms of ternary complex formation is shown in Fig. 7. The equilibrium constant K is 4.0, which suggests that similarly to copper(II) and nickel(II) ternary complex formation is controlled by a statistical factor. Rate constants k were measureed for several systems, and the results were tabulated in Table 1 together with the data on nickel(II) and copper(II) complexes described in our previous reports.[1,3] The values of palladium(II) complexes are much smaller than those of nickel(II), which is in agreement with the fact that palladium(II) forms more inert complexes than nickel(II).

Ternary complex formation, which was found to proceed according to the second-order rate law, should

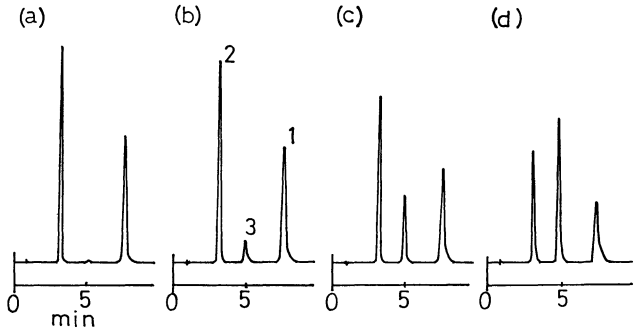
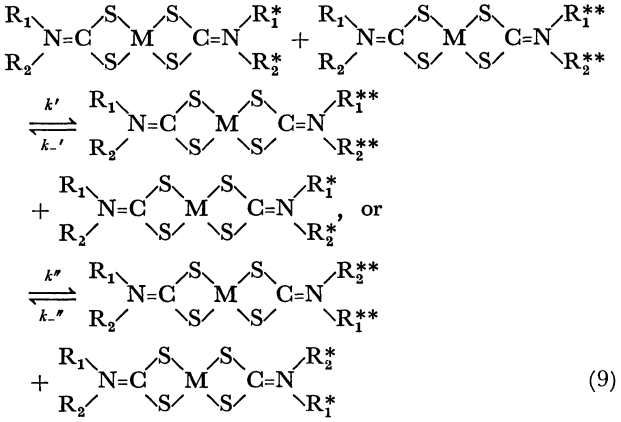


Fig. 7. Ternary complex formation of two Pd(II) dithiocarbamates.
Column: Polygosil 50-5 (4 mm×25 cm). Eluent: hexane:isopropyl acetate=100:3 (water saturated). Flow rate: 2.0 cm³/min. Detector: 305 nm. Sample size: 0.01 cm³. Sample: 5×10^{-4} mol dm^{-3} PdA_2+ 5×10^{-4} mol dm^{-3} PdB_2 in $CHCl_3$, A=Pd[$(CH_3CH_2)_2$-NCSS]$_2$, B=Pd[$(CH_3CH_2CH_2)_2$NCSS]$_2$. 1) PdA_2, 2) PdB_2, 3) PdAB. (a) After mixing 1.0 min, (b) 10 min, (c) 290 min, (d) 3 d (equilibrium). The mixed solution was thermostated at 25 °C.

be accompanied by cleavage of metal–sulfur bond and the exchange of ligand, dithiocarbamates. A similar reaction occurs when B=A in Eq. 6.

$$MA_2 + MA_2^* \rightleftharpoons 2MAA^*. \quad (8)$$

Here * is added to distinguish two MA_2. When A is a symmetrical dithiocarbamate, no net reaction will occur and the reaction cannot be traced by HPLC. On the other hand, when A is an unsymmetrical dithiocarbamate, the reaction shown in Eq. 9 should occur.



(9)

Table 1. Summary of rate constants of ternary complex formation

$$MA_2 + MB_2 \underset{k_-}{\overset{k}{\rightleftharpoons}} 2MAB, \quad K=[MAB]^2/[MA_2][MB_2]=4.0$$

B	k/mol^{-1} dm^3 s^{-1}		
	M=Cu(II)	M=Ni(II)	M=Pd(II)
$(CH_3CH_2CH_2)_2NCSS^-$	$(6.4\pm0.3)\times10^3$ a)	$(2.4\pm0.2)\times10^2$ a)	$(4.0\pm0.3)\times10^{-2}$ c)
$(C_6H_5CH_2)_2NCSS^-$	$(3.4\pm0.8)\times10^3$ a)	$(1.9\pm0.2)\times10^2$ a)	$(7.2\pm0.5)\times10^{-3}$ c)
$(CH_3CH_2)HNCSS^-$	——	$(1.6\pm0.3)\times10^2$ b)	$(1.2\pm0.2)\times10^{-2}$ c)
$(C_6H_5CH_2CH_2)HNCSS^-$	——	——	$(1.9\pm0.2)\times10^{-2}$ c)

A: $(CH_3CH_2)_2NCSS^-$ a) Ref. 1, b) Ref. 3, c) this work. For experimental conditions of a) and b), see Refs. 1 and 3. Experimental conditions of c) are described in Fig. 7.

The latter pathway in Eq. 9 should be accompanied by the isomerization reaction, while the former does not bring any reaction. Thus, the presence of another path of the isomerization reaction is suggested. Since the reactions shown in Eqs. 6 and 8 are essentially similar, it will reasonably be concluded that $k'+k''$ is close to k shown in Table 1. Both k_1 and k'' of palladium(II) dithiocarbamates will be of the order 10^{-2} on the assumption that $k' \approx k''$. There exists, however, an essential difference between k_1 and k'' that k_1 is a first-order rate constant, while k'' second-order. Therefore, at higher concentrations such as 1 mol dm^{-3}, the isomerization will occur according to two competitive pathways (Eqs. 1 and 9). On the other hand, at lower concentrations such as 10^{-3} mol dm^{-3} at which the major parts of the present experiments were carried out, bond rotation will be a predominant process.

References

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