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Kinetic Studies of Fast Equilibrium by Means of High-performance Liquid Chromatography. III. Ternary Complex Formation between Ni(II) Diethyldithiocarbamate and Other Unlike Ni(II) Chelates

Masataka Moriyasu* and Yohei Hashimoto

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

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The labile ternary complex formation ($MA_2+MB_2 \rightleftharpoons 2MAB$ with $K=[MAB]^2/([MA_2][MB_2])$) between Ni(II) diethyldithiocarbamate(MA_2) and other several Ni(II) chelates(MB_2) was investigated by high-performance liquid chromatography; two solutions of MA_2 and MB_2 were mixed and equilibrated. The tendency to form a ternary complex is summarized as follows: (1) no ternary complex formation takes place (B=dimethylglyoxime and 1-(2-pyridylazo)-2-naphthol), for which high structural stability of binary complex MB_2 is responsible; (2) the ternary complex formation is controlled statistically ($K=4.0$), suggesting the absence of any factor to stabilize or unstabilize the ternary complex (B=*N*,*N*-disubstituted dithiocarbamates and *N*-monosubstituted dithiocarbamates); (3) the ternary complex formation is favored ($K>4.0$) (B=xanthates); and (4) all initial binary complexes are converted into a very stable species which is possibly a ternary complex (B=dithizone). Kinetic characteristics of these ternary complex formations are examined.

Ternary complex formation usually occurs as follows when two solutions of labile binary complexes are mixed:

$$MA_2 + MB_2 \underset{k_-}{\overset{k}{\rightleftharpoons}} 2MAB \tag{1}$$

with

$$K = [MAB]^2/[MA_2][MB_2] = k/k_-. \tag{2}$$

Study of the ternary complex formation has been carried out mainly by the spectroscopic method since many ternary complexes have characteristic absorption bands. However, this method cannot be applied if the ternary complex gives rise to no characteristic absorption. Our previous studies[1,2] made use of the high-performance liquid chromatography (HPLC) to investigate the ternary complex formation between two different *N*,*N*-disubstituted dithiocarbamate chelates of Ni(II) or Cu(II). In this method two solutions of MA_2 and MB_2 are mixed, kept standing to reach the equilibrium state for the ternary complex formation, and a portion of the mixture is subjected to the HPLC. The separation speed of HPLC is so high that labile ternary complexes are allowed to be eluted out without undergoing any disproportionation. Thus, considerably fast equilibria can be traced by the HPLC based on the conventional principle. Rate constants k and k_- can be determined as follows: when two very dilute solutions of MA_2 and MB_2 are mixed, the ternary complex will gradually be produced until the equilibrium shown in Eq. 1 is attained. During the progress of ternary complex formation, portions of the mixed solution are taken out to be subjected to HPLC. The progress of the reaction is caused to stop immediately after the solution is injected into the column. Thus, concentrations of each species can be determined as a function of time, allowing the determination of k and k_-.

It was confirmed in our previous report[2] that labile ternary complex formations between two different *N*,*N*-disubstituted dithiocarbamate chelates are controlled statistically with a factor of $K=4.0$ in the case of Ni(II) and Cu(II); different factors are expected in cases where two binary complexes whose coordinated ligands are different in property from each other are mixed, depending on the nature of the ligands. The purpose of the present study is to clarify to what extent the HPLC is applicable to the investigation of labile ternary complex formation. We selected Ni(II) chelates since they provide ternary complex formations of such a moderately high rate as to allow kinetic studies to be carried out easily.

Experimental

Reagents. The chelating reagents used are sodium diethyldithiocarbamate (NaDEDTC), sidum ethyldithiocarbamate (NaEDTC), sodium propyldithiocarbamate (NaPDTC), pottasium ethylxanthate (KEXAN), pottasium propylxanthate (KPXAN), 1-(2-pyridylazo)-2-naphthol (HPAN), dimethylglyoxime (HDMG), dithizone (H_2Dz), oxine, salicylaldehyde oxime, 1-nitroso-2-naphthol, and (*E*)-benzoin oxime. NaEDTC and NaPDTC were prepared by the usual procedure[3] from alkylamine, carbon disulfide, and sodium hydroxide. KPXAN was prepared from 1-propanol, carbon disulfide, and pottasium hydroxide.[4] These salts were recrystallized from chloroform–methanol. The other chelating reagents were obtained commercially and purified when necessary. NaDEDTC, NaEDTC, NaPDTC, KEXAN, and KPXAN were dissolved in water. H_2Dz was dissolved in chloroform and the content was determined by measuring the absorption at 606 nm ($\varepsilon=4.06\times10^4$).[5,6] The other chelating reagents which are sparingly soluble in water were dissolved in suitable organic solvents such as chloroform and methanol. The standard solution of Ni(II) was prepared by dissolving $NiCl_2\cdot6H_2O$ in water. The content of Ni(II) was determined by colorimetry on its diethyldithiocarbamate. Before use all solvents used for HPLC were saturated with water.

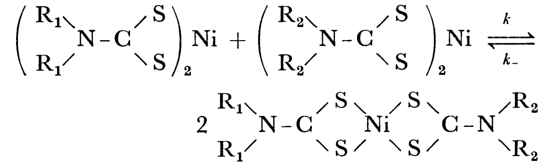
Apparatus. The HPLC apparatus used in this study is similar to the one described previously.[1,7] Absorption spectra of each metal chelate were measured by a Model-124 Hitachi double-beam spectrometer.

Procedure. The Ni(II) chelates of DEDTC, EDTC, PDTC, EXAN, and PXAN were prepared by mixing the Ni(II) standard solution and the corresponding chelating reagent in water. The metal chelates prepared were extracted with chloroform under the condition for complete extraction. In order to remove residual free ligands in chloroform, the extract was washed with water four times. The Ni(II) chelate of dithizone was prepared in the following way: To the Ni(II) aqueous standard solution, a slight excess of dithizone in chloroform was added. Since in acidic media the rates of formation and extraction of Ni(II) dithizonate are slow,[8] a small amount of dilute aqueous ammonia (0.5 vol%) was added and the mixture was shaken vigorously for 30 min. Then, the chloroform layer was washed three times with 0.2 vol% aqueous ammonia to remove the residual free dithizone in chloroform. The solutions of the other Ni(II) chelates were prepared by mixing the Ni(II) standard solution and the corresponding chelating reagent in an organic solvent, and diluting the resulting solution with chloroform to a proper concentration.

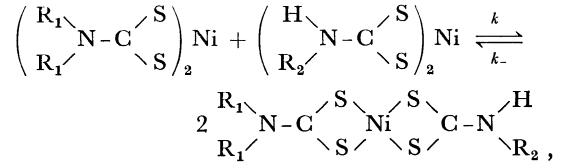
Results and Discussion

HPLC of Various Ni(II) Chelates. Chromatographic behavior of various Ni(II) chelates was examined on silica gel packings. Among them, Ni$(DEDTC)_2$, Ni$(EDTC)_2$, Ni$(PDTC)_2$, Ni$(EXAN)_2$, Ni$(PXAN)_2$, Ni$(DMG)_2$, Ni$(PAN)_2$, and Ni$(HDz)_2$ gave good chromatograms. Calibration curves of these metal chelates are linear over a wide range of sample amounts. Contrary to this, the Ni(II) chelates of oxine, salicylaldehyde oxime, 1-nitroso-2-naphthol, and (*E*)-benzoin oxime gave no quantitative results because partial or complete decomposition takes place in the course of chromgatography. Silica gel seems too active for these chelates of relatively low stability and other less active packings are expected to give satisfactory results. In the present research these Ni(II) chelates which failed to give quantitative results on silica gel packings were left omitted from further examination.

Ni(DEDTC)$_2$–Ni(EDTC)$_2$. These two binary chelates were mixed at 25 °C and after kept standing long enough to attain the equilibrium, the mixture was supplied for HPLC. Three peaks corresponding to Ni$(DEDTC)_2$, Ni$(EDTC)_2$, and Ni(DEDTC)(EDTC) appeared on chromatograms (Fig. 1). The heights of each peak were independent of flow rate, suggesting that no disproportionation of the ternary complex occurs in course of chromatography. Similar to the system composed of two different Ni(II) *N,N*-disubstituted dithiocarbamate chelates,[1,2] the equilibrium constant K was 4.0. The system Ni$(DEDTC)_2$–Ni$(PDTC)_2$ gave similar results. From these results it can be concluded that the ternary complex formation according to the following equations is controlled statistically, *i.e.*, there exists no factor in operation which makes the ternary complex stable or unstable:



(3)



(4)

where R_1 and R_2 denote alkyl groups.

Rate constants k and k_- were determined by the following equation with a procedure similar to the one described in our previous report:[2)]

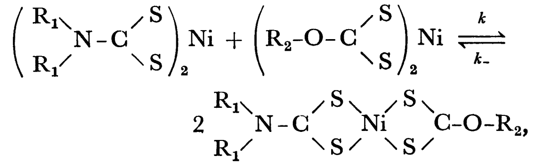
$$k = -(1/a_0t)\ln(1-y/a_0) \tag{5}$$

with

$$k_- = k/4, \tag{6}$$

where the initial concentrations of two binary complexes MA_2 and MB_2 are designed to be the same $(=a_0)$ with each other and y is the concentration of ternary complex MAB at a reaction time t after mixing. Thus, rate constants k and k_- were determined to be $(1.6\pm0.25)\times10^2\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$ and $(4.0\pm0.6)\times10^1\ \mathrm{mol^{-1}\,dm^3\,s^{-1}}$, respectively, for the system Ni$(DEDTC)_2$–Ni$(EDTC)_2$ (in chloroform: ethyl acetate: hexane=1:1:3) at 25 °C. These values are similar to those reported in our previous report[2)] for corresponding complex formations between Ni$(DEDTC)_2$ and other various Ni(II) *N,N*-disubstituted dithiocarbamate chelates.

Ni(DEDTC)$_2$–Ni(EXAN)$_2$. Both dithiocarbamates and xanthates are *S,S*-coordinates chelating reagents and their chemical structures are similar to one another. When solutions of two binary complexes of Ni(II) dithiocarbamate and xanthate are mixed, the following ternary complex formation occurs:



(7)

as evidenced by Fig. 2. Unlike the system composed

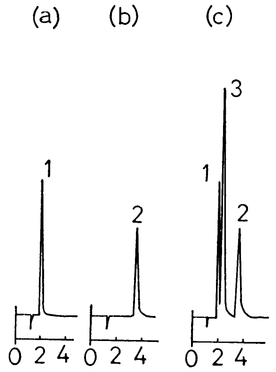


Fig. 1. Ternary complex formation between Ni$(DEDTC)_2$ and Ni$(EDTC)_2$.
Column: Shodex silipak (4 mm × 15 cm). Eluent: (hexane:ethyl acetate=100:15 (water saturated). Flow rate: 3.2 cm³/min. Detector: 325 nm. Sample size: 50 µl.
Sample: (a) 2.5×10^{-4} mol dm^{-3} Ni$(DEDTC)_2$, (b) 2.5×10^{-4} mol dm^{-3} Ni$(EDTC)_2$, (c) 2.5×10^{-4} mol dm^{-3} Ni$(DEDTC)_2$+2.5×10^{-4} mol dm^{-3} Ni$(EDTC)_2$. These samples are solutions in hexane:chloroform: ethyl acetate=3:1:1 at 25 °C.
1: Ni$(DEDTC)_2$, 2: Ni$(EDTC)_2$, 3: Ni(DEDTC)(EDTC).

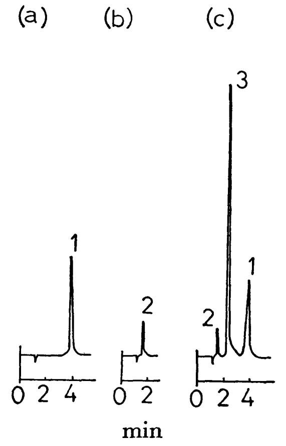


Fig. 2. Ternary complex formation between Ni(DEDTC)$_2$ and Ni(EXAN)$_2$
Column: Shodex silipak (4 mm × 15 cm). Eluent: hexane:ethyl acetate = 100:8 (water saturated). Flow rate: 3.2 cm^3/min. Detector: 315 nm. Sample size: 50 μl.
Sample: (a) 2.5×10^{-4} mol dm^{-3} Ni(DEDTC)$_2$, (b) 2.5×10^{-4} mol dm^{-3} Ni(EXAN)$_2$, (c) 2.5×10^{-4} mol dm^{-3} Ni(DEDTC)$_2$+2.5×10^{-4} mol dm^{-3} Ni(EXAN)$_2$. These samples are solutions in hexane:chloroform: ethyl acetate = 3:1:1 at 25 °C.
1: Ni(DEDTC)$_2$, 2: Ni(EXAN)$_2$, 3: Ni(DEDTC)(EXAN).

of two Ni(II) dithiocarbamate chelates, this system gave an equilibrium constant K larger than 4.0 (8.3± 1.2, in chloroform:ethyl acetate:hexane = 1:1:3) at 25 °C, and about 60% of the initial binary complexes was converted into the ternary complex. This result suggests the presence of some factor to stabilize the ternary complex, even though there seem to exist none of apparent driving factors in favor of the ternary complex formation, such as steric factors, π-bond formation, hydrogen bond formation, and neutralization of the charge.[9)]

When K is not equal to 4.0, rate constants k and k_- should be determined from the following rather complicated equation[10)] derived on the assumption that a bimolecular collisional process is operating in the ternary complex formation:

$$k = (2/m_0t)\left[\ln\frac{\left(\dfrac{2a_0+m_0}{1-4/K}-y\right)}{\left(\dfrac{2a_0-m_0}{1-4/K}-y\right)}+\ln\left(\frac{2a_0-m_0}{2a_0+m_0}\right)\right], \tag{8}$$

where

$$m_0 = 4a_0\sqrt{1/K}. \tag{9}$$

Two solutions of MA$_2$ and MB$_2$ were mixed at 25 °C and after a measured time a portion of the mixed solution was supplied for HPLC. With the lapse of time the peak of the ternary complex rose while those of the binary complexes fell, the results being plotted in Fig. 3. The validity of the bimolecular collisional process was confirmed by changing the initial concentration a_0. Rate constants k and k_- were determined to be $(1.3\pm0.1)\times10^2$ mol^{-1} dm^3 s^{-1} and $(1.6\pm0.2)\times10^1$ mol^{-1} dm^3 s^{-1}, respectively, (in chloroform: ethyl acetate:hexane = 1:1:3) at 25 °C.

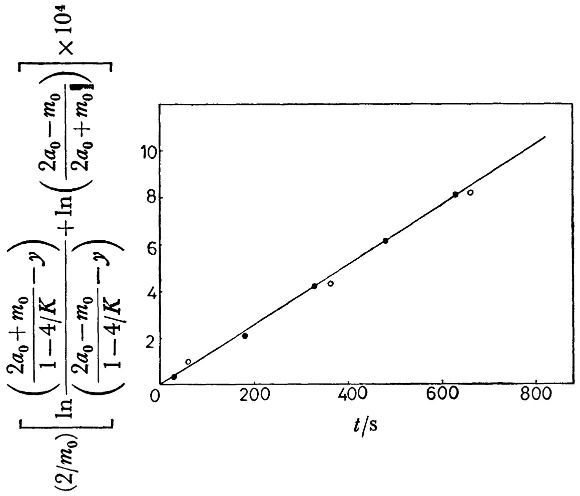


Fig. 3. Plot of Eq. 8.
Chromatographic conditions were similar to those shown in Fig. 2.

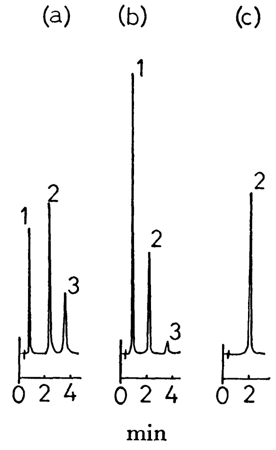
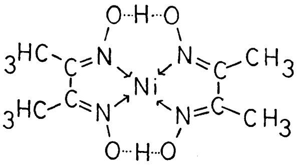
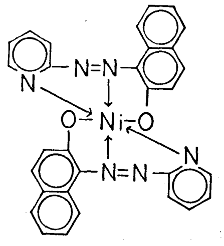


Fig. 4. Chromatograms of a mixture of Ni(DEDTC)$_2$, Ni(PAN)$_2$, and Ni(DMG)$_2$.
Column: Shodex silipak (4 mm × 15 cm). Eluent: hexane : ethyl acetate = 100:25 (water saturated). Flow rate: 3.2 cm^3/min. Detector: (a) 254 nm, (b) 325 nm, (c) 530 nm. Sample sizes: 5 μl.
1: Ni(DEDTC)$_2$, 2: Ni(PAN)$_2$, 3: Ni(DMG)$_2$.

Similar results were obtained for the system Ni(DEDTC)$_2$–Ni(PXAN)$_2$. Equilibrium constant K and rate constants k and k_- for the ternary complex formation were also determined (K=7.6±1.4, $k=(1.0\pm0.1)\times10^2$ mol^{-1} dm^3 s^{-1}, and $k_-=(1.3\pm0.25)\times10^1$ mol^{-1} dm^3 s^{-1}, in chloroform:ethyl acetate:hexane = 1:1:3) at 25 °C.

Ni(DEDTC)$_2$–Ni(PAN)$_2$–Ni(DMG)$_2$. When these two or three binary metal chelates were mixed, the peaks of the initial binary chelates alone appeared on chromatograms (Fig. 4). Then, an attempt was made to cause ternary complexes to be formed in the following way: Two or three free chelating reagents in methanol were mixed and then the Ni(II) aqueous solution was added to form metal chelates. The metal chelates were extracted with chloroform and then supplied for HPLC. The chromatogram patterns were similar to those shown in Fig. 4, excluding the possibility of the formation of any stable ternary complexes. Thus, the following alternative explanations are plausible: (1) no ternary complex formation occurs because initial binary complexes have very stable structures; and (2) a very labile ternary complex is formed. In this case, the ternary complex formed should undergo disproportionation into two binary complexes almost instantaneously in the column, resulting in the appearance of only the peaks of binary complexes on chromatograms. The present authors regard the former explanation as the more plausible for the following reasons: as shown below, Ni(DMG)$_2$ has a very stable structure by dint of hydrogen bond formation[11] and Ni(PAN)$_2$ has a stable six-coordinated structure.[12] When a ternary complex is to be formed, either the hydrogen bond should be broken or the five-coordinated ternary chelate formed. These ternary chelates will be rather unstable energetically. The chromatogram patterns shown in Fig. 4 were independent of experimental conditions such as flow rate, column temperature, and initial concentrations of binary complexes, which is in favor of the former explanation.[2] If the latter explanation is correct, the Ni(II) ternary complex formed should be extraordinarily labile in comparison with other various Ni(II) chelates.





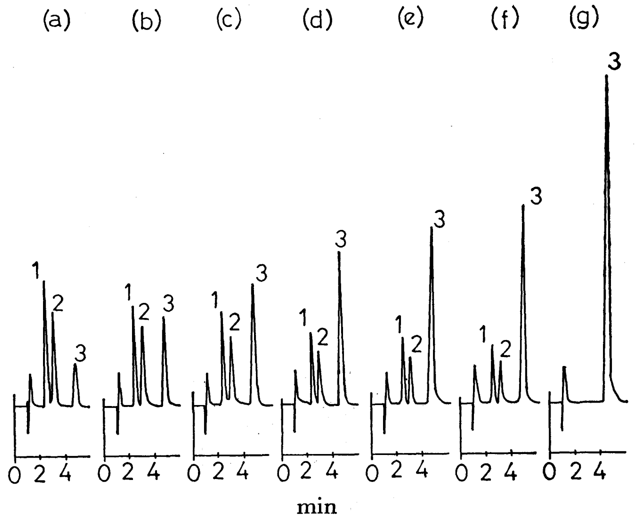


Fig. 5. Change of chromatogram patterns of the mixture of Ni(DEDTC)$_2$ and Ni(HDz)$_2$.
Column: LiChrosorb SI 100 (4 mm × 25 cm). Eluent: hexane:ethyl acetate = 100:10 (water saturated). Flow rate: 3.2 cm^3/min. Detector: 312 nm. Sample size: 50 μl. Sample: 2.5×10^{-5} mol dm^{-3} Ni(DEDTC)$_2$+2.5×10^{-5} mol dm^{-3} Ni(HDz)$_2$ (a); after mixing 1 min, (b); 3.5 min (c); 6 min, (d); 8.5 min, (e); 11 min, (f); 13.5 min, (g); 1 d. These samples are solutions in chloroform:ethyl acetate: hexane = 1:1:3 at 50 °C.
1: Ni(DEDTC)$_2$, 2: Ni(HDz)$_2$, 3: a new species (see text).

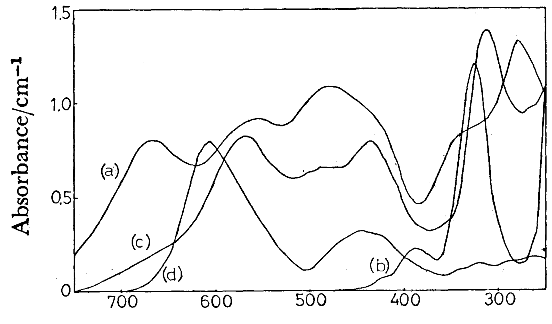
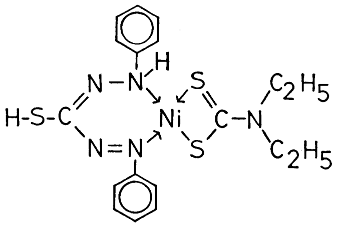


Fig. 6. Absorption spectra of various species in the system Ni(DEDTC)$_2$–Ni(HDz)$_2$.
(a): 4.0×10^{-5} mol dm^{-3} Ni(HDz)$_2$, (b): 4.0×10^{-5} mol Ni(DEDTC)$_2$, (c): the reaction product between 4.0×10^{-5} mol dm^{-3} Ni(HDz)$_2$ and 4.0×10^{-5} mol dm^{-3} Ni(DEDTC)$_2$, (d): 2.0×10^{-5} mol dm^{-3} H$_2$Dz. These samples are solutions in chloroform.

Ni(DEDTC)$_2$–Ni(HDz)$_2$. When these two binary complexes were mixed, characteristic chromatograms different from those for the other systems were obtained. As ashown in Fig. 5, with the lapse of time, the peaks of binary complexes fell while a new peak appeared and grew gradually. The progress of the reaction was slow at room temperature. After 1-d standing, the peaks of the binary complexes disappeared completely when the initial concentrations of two binary complexes had been chosen the same ($=a_0$). There seems to remain some debatable points on what reaction occurred in the mixed solution. To the solution given in Fig. 5(g), in which the reaction had been completed, dilute aqueous ammonia (0.5 vol%) was added and the mixture was shaken vigorously for about 30 s. No free dithizone was extracted out into the aqueous layer, excluding the possibility of free dithizone being liberated in the reaction. It is reported[8] that Ni(II) dithizonate may exist in two forms, *i.e.*, as the keto-form complex Ni(HDz)$_2$ and enol-form complex NiDz. The Ni(II) chelates used in the present research was spectroscopically confirmed to be the keto-form complex. The absorption spectrum of the species produced, shown in Fig. 6(c), is different from those of such species as the initial binary complexes and free dithizone. It is different also from the one of the enol-form complex NiDz.[13] These results suggest that a new species was produced in the reaction. The absorption spectrum of the new species resembles the one of Ni(HDz)$_2$ in the visible range, with weaker absorption; in the UV range the absorption maximum (=312 nm) appeared between those of Ni(DEDTC)$_2$ (=325 nm) and Ni(HDz)$_2$ (=280 nm). These phenomena may be interpreted well in terms of the ternary complex formation. The possibility of the formation of higher-order complexes such as polynuclear complex, however, cannot completely be ruled out for the following reason: It should be noted that Ni(HDz)$_2$ has the *N*,*N*-coordinated structure,[14] though most of other metal dithizonates have the *N*,*S*-coordinated structure. Some intramolecular structural rearrangement which stabilizes the ternary complex might occur during the course of ternary complex formation. The structure of the possible ternary complex will be as follows, provided that no structural rearrangement occurs.



The following chemical equation will hold for the possible ternary complex formation since the reverse reaction can be neglected:

$$\mathrm{Ni(DEDTC)_2 + Ni(HDz)_2 \xrightarrow{k} 2Ni(DEDTC)(HDz)}. \tag{10}$$

Rate constant k of this reaction will be obtained from the following equations based on the bimoelcular collisional process:

$$1/x = 1/a_0 + kt \tag{11}$$

$$1/(a_0 - y/2) = 1/a_0 + kt, \tag{12}$$

where x and y are concentrations of Ni(DEDTC)$_2$ (=Ni(HDz)$_2$) and Ni(DEDTC)(HDz), respectively, at a reaction time t after mixing. Figure 7 shows plots for Eq. 12. The validity of the bimolecular process was confirmed by changing the initial concentration a_0. Rate constant k was thus determined to be $(1.8 \pm 0.2) \times 10^1\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ and $(7.4 \pm 0.4) \times 10^1\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ at 25 °C and 50 °C, recepectively (in chloroform: ethyl acetate:hexane=1:1:3).

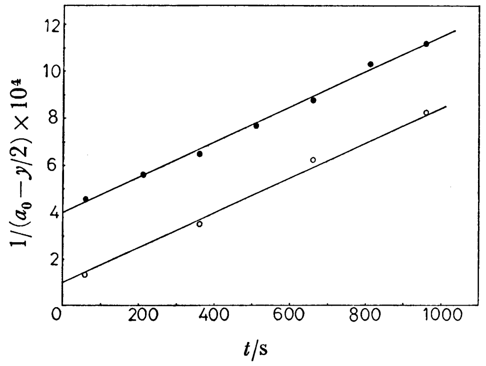


Fig. 7. Plot of Eq. 12.
Chromatographic conditions were similar to those shown in Fig. 5.
○: $a_0 = 1.0 \times 10^{-4}\ \mathrm{mol\ dm^{-3}}$, ●: $a_0 = 2.5 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$.
These samples are solutions in chloroform:ethyl acetate: hexane=1:1:3 at 50 °C.

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