CHEMISTRY LETTERS, pp. 117-120, 1980.

KINETIC STUDIES ON THE LABILE TERNARY NICKEL(II) CHELATES OF N-DISUBSTITUTED DITHIOCARBAMIC ACIDS BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Masataka MORIYASU and Yohei HASHIMOTO
Kobe Women's College of Pharmacy, Higashinada-ku, Kobe 658

The labile ternary complex formed by mixing two solutions of nickel(II) dialkyldithiocarbamate solutions was separated by high-performance liquid chromatography. The equilibrium constant and rate constants of formation and disproportionation of the ternary complex were obtained.

From the first report by Huber et al.,[1)] a number of reports on the separation of metal chelates by high-performance liquid chromatography(HPLC) have been appeared. Concerning HPLC of metal chelates of N-disubstituted dithiocarbamic acids, several reports[2-8)] have been published including our previous one.[9)] Liska et al.[10,11)] have pointed out in their recent report that owing to ligand exchange, when two nickel(II) chelates of different dialkyldithiocarbamic acids were injected simultaneously on the column, three peaks appeared on chromatogram. In this report the method is described to determine kinetic characteristics of the formation and disproportionation of the ternary complex by HPLC.

Sodium salts of N-disubstituted dithiocarbamic acid of $-CH_3$, $-C_2H_5$, $-nC_3H_7$, $-isoC_3H_7$, $-nC_4H_9$, $-isoC_4H_9$, $-(CH_2)_4-$, $-(CH_2)_5-$ and $-(CH_2)_6-$ were prepared by usual procedure from dialkylamine, carbon disulfide and sodium hydroxide. These salts were recrystalized from chloroform-methanol or chloroform-hexane. An HPLC apparatus of our own construction was used.[9)] The two plunger reciprocal pump(Model KHD-W-294, Kyowa Seimitsu Co. Ltd.), damper, sample injector(3 μl or 100 μl) and column were combined. A single-beamed spectrometer(Model Specta 20, Toshiba Beckmann Co. Ltd., 210-700 nm) equipped with a flow cell was used as a detector.

By a well deactivated silica gel column[12)] N,N-dialkyldithiocarbamic acid chelates of Hg(II), Cu(II), Ni(II) and Co(III) etc. gave good chromatograms without dissociation of the chelates during chromatography. These metal chelates gave linear calibration graphs from a few ng(detection limit) to 1000 ng. Fig. 1(a) and (b) show chromatograms of nickel chelates of N,N-di-n-propyldithiocarbamic acid(MA_2) and N,N-tetramethylenedithiocarbamic acid(MB_2), respectively. After these two solutions were mixed, the resulting solution was allowed to stand for some minutes at room temperature(25 °C) and then supplied to HPLC. As shown in Fig. 1(c), the third peak, which is attributed to a ternary complex(MAB), appeared on chromatogram. It follows that different chelates exist in the following equilibrium were separated.

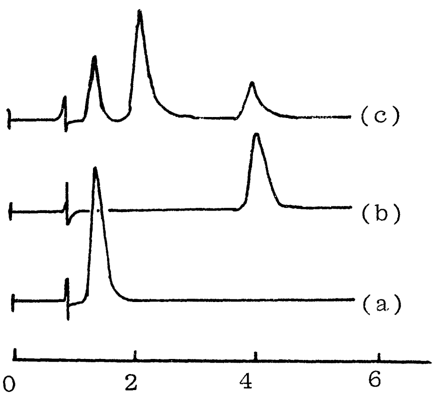

Fig. 1 Separation of Labile Nickel(II) Ternary Chelate by HPLC

(a) 1.0 mM Ni(II) chelate of N,N-di-n-propyldithicarbamic acid(MA_2) (b) 1.0 mM Ni(II) chelate of N,N-tetramethylenedithiocarbamic acid(MB_2) (c) 1.0 mM MA_2 + 1.0 mM MB_2

Column: LiChrosorb SI 100 (4 mm x 25 cm) Eluent: hexane:cyclohexane:isopropylacetate = 50:50:15 (water saturated) Detector: UV 323 nm Flow rate: 1.8 cm^3/min. Pressure: 100 kg/cm^2

$$2MAB \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} MA_2 + MB_2 \qquad (1)$$

$$K = [MA_2][MB_2]/[MAB]^2 \qquad (2)$$

Since these chelates are labile, as soon as they are separated to each other, ternary complex should begin to disproportionate into MA_2 and MB_2 with the rate constant k_{-1}. The amount of ternary complex, therefore, should decrease when it passes through the column. It is debatable whether chromatograms obtained still maintain the information in the equilibrium state before chromatography. If disproportionation during chromatography really occurs, it will be detected either (A) by changing the column length with a definite flow rate, or (B) by changing the flow rate with a definite column length. With a definite column length(25 cm), flow rate rate was changed from 1.8 to 0.4 cm^3/min. The peak heights of each chelate remained unchanged within this range, which suggests that disproportionation can be neglected under the present condition. This might be rationalized by the fact that during chromatography prompt dilution of each component occurs and, therefore, disproportionation which is anticipated to occur by a bimolecular process caused by collision of the ternary complex, will be retarded effectively.[13)]

Concentrations of MA_2 and MB_2 in Fig. 1(c) were both 0.5 mM, which indicates that just half of these chelates were converted into the ternary complex in equilibrium state. Then it follows that "disproportionation constant K" in Eq.(2) is equal to 0.25. Other ternary complex systems formed by nickel(II) ion and disubstituted dithiocarbamic acids gave similar results. From this fact it could be concluded that formation of the ternary complex is controlled exclusively by a statistical factor. This might be reasonable because there seems to be no factor such as steric hindrance either to stabilize or unstabilize the ternary complex.[14)]

The rate constants k_1 and k_{-1}, are determined by the following way. When two solutions of MA_2 and MB_2 are mixed, the rate of formation of the ternary complex is expressed as

$$\frac{d[MAB]}{dt} = k_1[MA_2][MB_2] - k_{-1}[MAB]^2. \quad (3)$$

Considering $k_{-1}/k_1 = K = 0.25$ and taking the initial concentrations of MA_2 and MB_2 to be the same and equal to a_0, it follows

$$\frac{d[MAB]}{dt} = k_1 a_0^2 - k_1 a_0 [MAB], \quad (4)$$

which, on integration, considering initial concentration of the ternary complex is zero, gives

$$[MAB] = a_0(1 - e^{-k_1 a_0 t}), \quad (5)$$

and therefore

$$\ln\{1/(1 - [MAB]/a_0)\} = k_1 a_0 t. \quad (6)$$

The plot of Eq.(6) for the system mentioned above is indicated in Fig. 2.

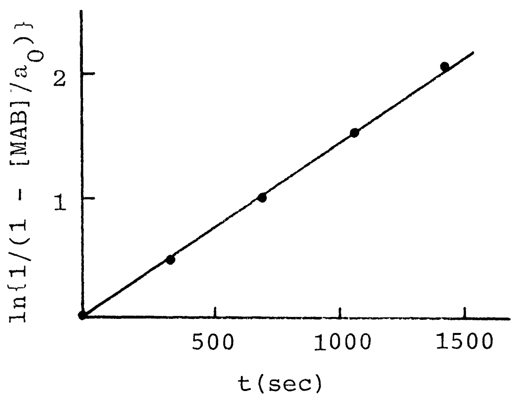

Fig. 2 The Rate of Formation of Ternary Complex

Very dilute solution of MA_2 and MB_2 were mixed. After standing for a definite time, the resulting solution was supplied to HPLC. The concentration of ternary complex was determined by direct measurement of peak height of MAB appeared on chromatogram.

1.0×10^{-4}M MA_2 + 1.0×10^{-4}M MB_2 (in chloroform, 25 °C)

When a_0 was chosen to be small, chromatogram immediately after mixing did not give the peak of ternary complex. With the increase of t, the peak height of MAB increased, while those of MA_2 and MB_2 decreased. The concentration of the ternary complex can be determined either (A) from the decrease of the peak heights of MA_2 and MB_2, or (B) as is the present case in which disproportionation during chromatography can be neglected, from the direct measurement of the peak height of the ternary complex. Thus, k_1 and k_{-1} shown in Fig. 2 were calculated to be 1.4×10^1 $M^{-1}s^{-1}$ and 3.5×10^0 $M^{-1}s^{-1}$, respectively(in chloroform, 25 °C).

Similar experiments were carried out for N-disubstituted dithiocarbamic acid chelates of other metal ions. Though Liska et al. have claimed that formation of mixed ligand complex does not occur for Cu(II) and Co(III),[8] in our research formation of ternary complex was observed for Cu(II) chelates. Since Cu(II) chelates are more labile than Ni(II) chelates, during chromatography disproportionation did occur. Therefore peak of ternary complex appeared on chromatogram only when a_0 was chosen to be low and flow rate was relatively high. With the decrease of flow rate, the peak of ternary complex decreased and finally disappeared. The rate of disproportionation in column was sensitive to the activity of the column and temperature. The peak height of ternary complex was high when well deactivated column was used and temperature was low. Since the rate of disproportionation was so high as to compete with the separation process by HPLC, precise determination of K was difficult. It colud safely be concluded at present for the system of Cu(II) chelates of N,N-diethyldithiocarbamic acid and N,N-di-n-propyldithiocarbamic acid, more than 47 % of the initial chelates were converted into the ternary complex. It seems likely that ternary complex formation of Cu(II) chelates is also controlled by a statistical factor. Because the rate of ligand exchange of Co(III) is slow, the formation of mixed ligand complex was observed only when complex formation was carried out by adding aqueous mixed solution of two different sodium salts of N-disubstituted dithiocarbamic acid. Thus treated four peaks, which will be attributed to MA_3, MA_2B, MAB_2 and MB_3, appeared on chromatogram.

As shown in the present report, HPLC will be a powerful tool for the investigation of equilibrium with considerably large rate constant. The results of systematic study will be published in a successive report.

References and Notes

1) J.F.K.Huber and J.C.Kraak, Anal. Chem., 44, 1554 (1972).
2) P.Heizmann and K.Ballschmiter, J. Chromatogr., 137, 153 (1977).
3) P.C.Uden and I.E.Bigley, Anal. Chim. Acta, 94, 29 (1977).
4) J.W.O'Laughlin and T.P.O'Brien, Anal. Lett., A11, 829 (1978).
5) G.Schwedt, Chromatographia, 11, 145 (1978).
6) G.Schwedt, Chromatographia, 12, 289 (1979).
7) O.Liska, J.Lehotay, E.Brandstererova, G.Guichon and H.Colin, J. Chromatogr., 172, 384 (1979).
8) J.Lehotay, E.Brandstererova, O.Liska and G.Guichon, J. Chromatogr., 172, 379 (1979).
9) M.Moriyasu and Y.Hashimoto, Anal. Lett., A11, 593 (1978).
10) O.Liska, G.Guichon and H.Colin, J. Chromatogr., 171, 145 (1979).
11) O.Liska, J.Lehotay and E.Brandstererova, J. Chromatogr., 171, 153 (1979).
12) Deactivation of silica gel column was essential to obtain reproducible data. After 100 cm^3 of water containing(2-3 %) acetone was pumped through the column, 300 cm^3 of water saturated eluent was flowed. After this procedure reproducibility was good and experimental error was less than 5 %.
13) From the peak height and width shown in Fig. 1(c), when ternary complex was eluted out, it was diluted at least to 1/150 of the initial concentration.
14) H.Sioge, Angew. Chem. Internat. Edit., 14, 397 (1975).

(Received November 21, 1979)