CHROM. 15,510

Note

Liquid chromatography of metal complexes of N-disubstituted dithiocarbamic acids

V. Determination of equilibrium and rate constants for ligand-exchange reactions by high-performance liquid chromatography

J. LEHOTAY*, O. LIŠKA, E. KOLEK and J. GARAJ

Department of Analytical Chemistry, Slovak Technical University, 812 37 Bratislava (Czechoslovakia)

and

G. GUIOCHON

Laboratoire de Chimie Analytique Physique, Ecole Polytechnique, 91 128 Palaiseau Cédex (France)

(First received October 24th, 1982; revised manuscript received November 11th, 1982)

In previous papers[1–4] we described the formation and the identification in non-polar solvents of mixed ligand complexes some dithiocarbamate (DTC) complexes with different N-alkyl substituents according to the equation:

$$L_1-M-L_1 + L_2-M-L_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2\ L_1-M-L_2 \tag{1}$$
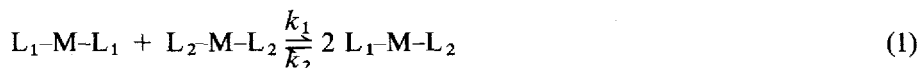
A similar exchange reaction was studied by other authors and the mixed ligand complexes were observed by nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and a.c. voltammetry[5–9]. Moriyasu and Hashimoto[10,11] carried out kinetic and equilibrium high-performance liquid chromatographic (HPLC) studies of mixed ligand complexes formed from some dialkyl-DTC chelates of Ni(II) and Cu(II). Experimentally determined K values were found to be 4.0, the rate constants being in the order of 10^1–10^2 mol^{-1} sec^{-1} for nickel(II) chelates.

The aim of this study was to estimate the influence of polar and non-polar solvents on the equilibrium and rate constants of the ligand exchange reactions of some bis(dialkyldithiocarbomate) complexes of Ni(II) and to consider the reaction mechanism.

EXPERIMENTAL

The experiments were carried out with a high-pressure liquid chromatograph consisting of a high pressure membrane pump equipped with a flow-through Bourdon tube manometer as damping device, a septumless injection port, a separation column (LiChrosorb Si 60, 10 μm) and UV detector. The absorbance of the column effluent

was measured at 254 nm. Standard solutions of the complexes (10^{-3} mol 1^{-1}) in different organic solvents were mixed (1:1) and injected on the column.

RESULTS AND DISCUSSION

HPLC can be applied to the study of equilibria and kinetics of chemical reactions providing: (1) the half-life of the reaction is longer than 5 min; (2) good separability of complexes; and (3) reaction rate $k_2 < k_1$ (see eqn. 1).

The equilibrium constant of the reaction between nickel(II) bis(diethyldithiocarbamate), $Ni(Et_2DTC)_2$ and nickel(II) bis(dibutyldithiocarbamate), $Ni(Bu_2DTC)_2$, is given

$$K = \frac{[Ni(Bu_2DTC)(Et_2DTC)]^2}{[Ni(Bu_2DTC)_2][Ni(Et_2DTC)_2]} \tag{2}$$

The concentrations of the original reactants were calculated according to the peak areas on the chromatograms (Fig. 1). The equilibrium constant values are presented in Table I. It is seen that the solvent has no substantial influence on the equilibrium constant value of reaction 1.
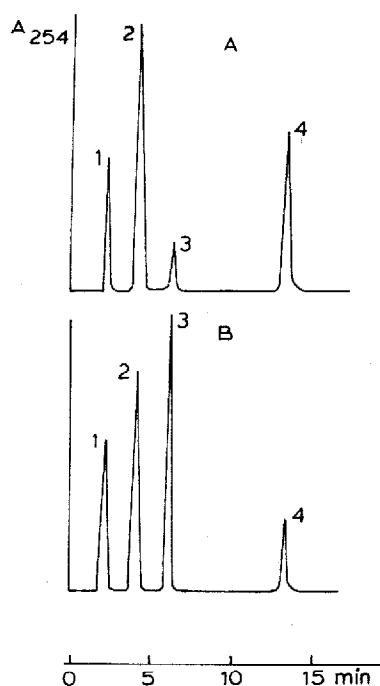

Fig. 1. Chromatograms of the reaction of $Ni(Et_2DTC)_2$ and $Ni(Bu_2DTC)_2$ in chloroform: A, after 60 min; B, after 24 h (at equilibrium). Conditions: column 245 × 0.4 cm I.D., packed with 10-μm LiChrosorb Si 60; mobile phase, 10% chloroform in cyclohexane, flow-rate 0.21 cm sec^{-1}. Peaks: 1 = vacancy peak; 2 = $Ni(Bu_2DTC)_2$; 3 = $Ni(Bu_2DTC)(Et_2DTC)$; 4 = $Ni(Et_2DTC)_2$.

TABLE I

EQUILIBRIUM CONSTANTS OF REACTION 1 IN DIFFERENT ORGANIC SOLVENTS

Solvent	K
Carbon disulphide	2.91 ± 0.05
Tetrachloromethane	3.84 ± 0.05
Chloroform	2.86 ± 0.14
Methylene chloride	2.81 ± 0.07
Dioxan	3.11 ± 0.09
Pyridine	2.98 ± 0.10
Dimethylformamide	2.79 ± 0.12

The rate constants were calculated by means of a computer according to the second order equation

$$k_1 = \frac{x_r}{c_0(2c_0 - x_r)t} \cdot \log \frac{x_r}{x_r - x} - \log \frac{c_0 x_r (x_r - c_0) - x}{c_0 x_r (x_r - c_0)} \qquad (3)$$

where c_0 is the initial concentration of original complex, x_r is the equilibrium concentration and x is the concentration at time t. The time t was measured from the mixing of the original complexes to the injection on the column. The results obtained are presented in Table II. It is obvious that the reaction rate is dependent on the

TABLE II

RATE CONSTANTS OF REACTION 1 IN DIFFERENT ORGANIC SOLVENTS

Solvent	$k_1 (l\ mol^{-1}\ min^{-1})$
Carbon disulphide	325.9 ± 18.6
Tetrachloromethane	85.2 ± 2.3
Chloroform	4.3 ± 0.1
Methylene chloride	3.7 ± 0.1
Dioxan	80.8 ± 4.0
Pyridine	15.1 ± 0.3
Dimethylformamide	16.2 ± 0.8

solvent and its polarity, but it is difficult to explain why for instance the ligand-exchange reaction proceeds at a higher rate in carbon disulphide than in the more polar pyridine. It is necessary, therefore, to take into account the interactions between the molecules of the solvent and the complex.

One of the effects which could have a significant influence on the course of the reaction is the steric effect. In the presence of some base the formation of a new adduct occurs due to the reaction

$$Ni(II)L_4 + 2 B \rightarrow trans\text{-}Ni(II)L_4B_2 \qquad (4)$$

and the original planar complex of Ni(II) is transformed to an octahedral form[12]. This may account for the lower reaction rate in pyridine. The formation of octahedral complexes in pyridine was confirmed by ^{1}H NMR spectrometry[13,14]. Dimethylformamide could also form an octahedral complex with nickel(II) dithiocarbamates because both solvents can be coordinated by the free nitrogen electron pair to the central metal atom. Since the difference in polarity between these solvents is not very high, the ligand exchange reaction should proceed in both media at approximately equal rates. This assumption is confirmed by the results presented in Table II.

Steric effects due to hydrogen bonding could have a significant rôle in the cases of chloroform and dichloromethane. ^{1}H NMR spectra of some DTC complexes show that a strong solvent–complex interaction exists in these solvents[15] and the formation of solvates in the solid state was observed[16]. The formation of relatively strong hydrogen bonds between the proton from chloroform and the sulphur atoms from DTC ligands can be presumed according to X-ray analysis[17]. It follows from Table II that the course of reaction 1 in chloroform and dichloromethane is very slow.

The value of the rate constant in dioxan is substantially higher than in the above solvents. The nucleophility of dioxan is lower than that of pyridine and dimethylformamide[18], suggesting a lower probability for the formation of an octahedral compound in dioxan. Instead, the high rate of ligand exchange indicates bond weakening between the central metal atom and the sulphur of the DTC ligand due to the higher polarity of dioxan. This is confirmed by the fact that in polar solvents the S_E mechanism of ligand exchange was evident while in low polarity solvents these reactions exhibit the S_F mechanism[19].

Interesting results were obtained in carbon disulphide and tetrachloromethane. The rate of ligand exchange in these solvents was surprisingly high (Table II). In the case of carbon disulphide this fact cannot be explained only on the basis of dispersion forces. It can be assumed that in carbon disulphide another effect based on the chemical similarity between the DTC ligand and the molecule of carbon disulphide occurs. According to the S_F substitution mechanism, the initial interaction occurs between the central metal atom of the DTC complex and the sulphur atom of the other DTC ligand. Splitting of the metal–sulphur bond in the complex and the rearrangement of ligands follows. Considering the similarity of the DTC ligand and carbon disulphide, there is a possibility that the molecules of solvent interact with the DTC complex in a way similar to the interaction between two molecules of DTC complexes. Consequently, the metal–sulphur bond is weakened, explaining the high rate of ligand exchange. In the case of tetrachloromethane it is difficult to explain the high rate of ligand exchange. Due to the fact that the stability of the metal–sulphur bond is the decisive factor on the ligand-exchange rate, it is probable that tetrachloromethane will affect this bond. However, on the basis of the available information it was not possible to determine the actual type of interaction involved.

In conclusion, the equilibrium constant of the ligand exchange reaction was not significantly dependent on the solvents used. The values of K presented in Table I are in a very good agreement with published data[11]. On the contrary, the rate constant is strongly dependent on the nature of solvent, which indicates different reaction mechanisms.

The results demonstrate that HPLC can be used for solving equilibrium and kinetic problems. The values of the equilibrium and the rate constants for ligand

exchange between molecules of DTC metal complexes estimated by means of HPLC confirm some previously published assumptions.

REFERENCES

1 O. Liška, G. Guiochon and H. Colin, *J. Chromatogr.*, 171 (1979) 145.
2 O. Liška, J. Lehotay, E. Brandšteterová and G. Guiochon, *J. Chromatogr.*, 171 (1979) 153.
3 J. Lehotay, O. Liška, E. Brandšteterová and G. Guiochon, *J. Chromatogr.*, 172 (1979) 379.
4 O. Liška and H. Colin, *13th International Symposium on Chromatography, Cannes, 1980,* Abstract K19.
5 K. Bernauer, S. Fallab and H. Erlenmeyer, *Helv. Chim. Acta,* 39 (1956) 1993.
6 M. L. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que and L. H. Pignolet, *J. Amer. Chem. Soc.,* 95 (1973) 4537.
7 L. Que and L. H. Pignolet, *Inorg. Chem.,* 13 (1974) 351.
8 E. Beinrohr and J. Garaj, *Collect. Czech. Chem. Commun.,* 45 (1980) 1785.
9 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry,* Interscience, New York, 3rd ed., 1972.
10 M. Moriyasu and Y. Hashimoto, *Chem. Lett.,* (1980) 117.
11 M. Moriyasu and Y. Hashimoto, *Bull. Chem. Soc. Jap.,* 53 (1980) 3590.
12 R. Chant, A. R. Hendrickson, R. L. Martin and N. M. Rohde, *Inorg. Chem.,* 14 (1975) 1895.
13 C. S. Vigee and C. L. Watkins, *J. Inorg. Nucl. Chem.,* 34 (1972) 3936.
14 C. S. Vigee and C. L. Watkins, *J. Inorg. Nucl. Chem.,* 37 (1975) 1793.
15 R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn and A. H. White, *Inorg. Chem.,* 11 (1972) 2435.
16 E. Sinn, *Inorg. Chem.,* 15 (1976) 369.
17 V. Kettmann and J. Garaj, *Collect. Czech. Chem. Commun.,* 46 (1981) 6.
18 I. H. Hildebrand and R. L. Scott, *The Solubility of Non-electrolytes,* Dover, New York, 3rd ed., 1964.
19 F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions,* Wiley, New York, 2nd ed., 1967.