Inorganica Chimica Acta, 23 (1977) L13–L14

Mechanism of Ligand Substitution in Five-Coordinate Square-Pyramidal Nickel(II) Complexes

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Received March 24, 1977

Very few kinetic studies of ligand substitution in five-coordinate transition metal complexes have been reported. The limited data available suggest that five-coordinate d^8 metal complexes follow dissociate mechanisms [1–8], while other five-coordinate systems sometimes react via associative pathways [9, 10]. Before the generality of these results can be ascertained, it is necessary that more reactions be investigated.

Two kinetic studies of five-coordinate low-spin nickel(II) have appeared. Grimes and Pearson [2] studied phosphine exchange in trigonal-bipyramidal $[Ni(CN)_2(PR_3)_3]$ complexes. Sweigart and Heidtmann [1] reported the kinetics of the replacement of tri-n-butylphosphine by various nucleophiles in the square-pyramidal complexes $[Ni(S_2P_2(OR)_2)_2\text{-}PBu_3]$ (R = Et, $PhCH_2CH_2$, C_6H_{11}). A dissociative mechanism for ligand substitution was found in both of these studies.

In order to expand the knowledge in this area, we have initiated a detailed kinetic study of ligand substitution in the complexes $[M(diars)_2X]^+$ (M = Ni, Pd, Pt; diars = *o*-phenylenebisdimethylarsine; X = Cl^-, Br^-, I^-, SCN^-, $SeCN^-$, *etc.*). A preliminary report of the results for reaction (1) is presented herein.

$$[Ni(diars)_2Br]^+SCN^- \rightleftharpoons [Ni(diars)_2SCN]^+ + Br^- \qquad (1)$$

The $[M(diars)_2X]^+$ complexes were first prepared by Nyholm and coworkers [11] and have been the subject of a number of spectroscopic [12] and thermodynamic [13] studies. The complexes have a square-pyramidal geometry [12].

A Durrum stopped-flow apparatus was used to study reaction (1) in methanol solvent at 20.5 °C. The ionic strength was maintained at 0.1 *M* with $NaNO_3$. The metal complex concentration was 2 X 10^{-4} *M* and the NaBr and NaSCN concentrations were in pseudo-first order excess. The reaction was followed at 490 nm. The results are represented in Table I.

The rate constants for reaction (1) measure the rate of approach to equilibrium. The results are compatible with a dissociative mechanism:

$$M{-}Br \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M + Br^-$$

$$M + SCN^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M{-}SCN$$

$$k_{obs} = \frac{k_1k_3[SCN^-] + k_2k_4[Br^-]}{k_3[SCN^-] + k_2[Br^-]} \qquad (2)$$

TABLE I. Kinetic Data for Reaction (1).[a]

$10^3[Br^-]$, *M*	$10^3[SCN^-]$, *M*	k_{obs}, s^{-1}
3.0	2.0	4.3
3.0	5.0	5.8
3.0	15.0	8.4
6.0	2.0	3.2
6.0	5.0	4.6
6.0	15.0	7.1
12.0	2.0	2.6
12.0	5.0	3.7
12.0	15.0	6.0

[a] Methanol solvent; 20.5 °C; ionic strength 0.1 *M* ($NaNO_3$).

The best fit of the data to equation (2) yields k_1 = 10 s^{-1}, k_4 = 1.2 s^{-1}, and k_3/k_2 = 0.9. From this the equilibrium constant for reaction (1) is calculated to be 7.5, which is similar to the value reported [13] in water as solvent.

The data in Table I are clearly inconsistent with an associative mechanism:

$$M{-}Br + SCN^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Br{-}M{-}SCN \underset{k_4}{\overset{k_3}{\rightleftharpoons}} M{-}SCN + Br^-$$

$$k_{obs} = \frac{k_1k_3[SCN^-] + k_3k_4[Br^-]}{k_2 + k_3}$$

Although this work is only the third report of ligand substitution at low-spin five-coordinate nickel(II), we believe that all such reactions will prove to be dissociative and that associative pathways will be found only for metal complexes having less than eight *d* electrons.

Acknowledgment

We wish to thank Research Corporation for support of this work.

References

1 D. A. Sweigart and P. Heidtmann, *Chem. Commun.*, 556 (1973); *J. Chem. Soc. Dalton*, 1686 (1975).
2 C. G. Grimes and R. G. Pearson, *Inorg. Chem.*, *13*, 970 (1974); P. Meier, A. E. Merbach, M. Dartiguenave and Y. Dartiguenave, *J. Am. Chem. Soc.*, *98*, 6902 (1976).

3 T. D. B. Morgan and M. L. Tobe, *Inorg. Chim. Acta, 5,* 563 (1971).
4 P. Meakin and J. P. Jesson, *J. Am. Chem. Soc., 96,* 5751 (1974).
5 R. F. Heck, *J. Am. Chem. Soc., 85,* 651, 657 (1963).
6 F. Basolo, A. T. Brault and A. S. Poe, *J. Chem. Soc.,* 676 (1964).
7 P. M. Enriquez and S. S. Zumdahl, *Inorg. Chem., 12,* 2475 (1973).
8 B. F. G. Johnson, J. Lewis and M. V. Twigg, *J. Chem. Soc. Dalton,* 1876 (1975).
9 D. A. Sweigart, D. E. Cooper and J. M. Millican, *Inorg. Chem., 13,* 1272 (1974); D. A. Sweigart, *Inorg. Chim. Acta, 18,* 179 (1976).
10 R. V. Snyder and G. N. LaMar, *J. Am. Chem. Soc., 98,* 4419 (1976).
11 C. M. Harris, R. S. Nyholm and D. J. Phillips, *J. Chem. Soc.,* 4379 (1960).
12 J. R. Preer and H. B. Gray, *J. Am. Chem. Soc., 92,* 7306 (1970).
13 R. Ettorre, G. Dolcetti and A. Peloso, *Gazz. Chim. Ital., 97,* 1681 (1967).