Kinetics of Redistribution of some Tetrahedral Nickel(II) Chelates

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Summary Scrambling of *N*-t-butylsalicylaldiminonickel(II) or *N*-isopropyltrifluoroacetyliminonickel(II) with *N*-isopropylacetyliminonickel(II) has been shown to follow a rate law for second-order reversible reactions in tetrachloroethylene solvent, activation entropies and energies being consistent with a bimolecular associative mechanism.

WE report a study of slow redistribution kinetics on nickel(II) and a determination of the kinetic order in both forward and reverse reactions, equation (1).

$$\mathrm{NiL^1_2 + NiL^2_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2NiL^1L^2} \qquad (1)$$

We have measured kinetics of equation (1) with the ligands L^1 and L^2 = (**1**) or (**2**), using the characteristic contact shift n.m.r. spectra of the complexes.[1] The peaks for closely similar groups of nuclei (*e.g.* $\mathrm{Bu^t}$ hydrogen)† were resolved on a curve-analyser and related to concentration. The slow appearance and decay of such peaks were measured by integration of peak areas. Reactions were reversible and second order in both forward and reverse directions; some kinetic data are shown in Table 1. The second reaction was also conveniently run with a large excess of (**2a**) over (**2b**) to give kinetics pseudo-first-order in (**2b**), and to drive the reaction to completion. Equilibrium constants obtained for some of these reactions (Table 2) are close to the statistical figure suggested by Holm *et al.* from qualitative observation.[1,2]

TABLE 1

Rate data for Equation (1) *in tetrachloroethylene at* 298K

L^1	L^2	k(l mol^{-1}s^{-1})	$\Delta E\ddagger$ (kJmol^{-1})	$\Delta S\ddagger$ (JK^{-1})
(**1a**)	(**2a**)	$k_2 = 2{\cdot}9 \times 10^{-4}$	64	−150
		$k_{-2} = 2{\cdot}3 \times 10^{-5}$	89	−80
(**2a**)	(**2b**)	$k_2 = 10{\cdot}8 \times 10^{-4}$	68	−119

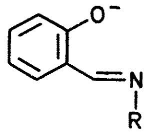
TABLE 2

Typical thermodynamic data for equation (1) *in tetrachloroethylene*

L^1	L^2	K^a (Temp. K)	ΔH (kJ mol^{-1})
(**1b**)	(**2a**)	0·53 (298)	19
(**1e**)	(**2a**)	0·65 (301)	—
(**1a**)	(**2a**)	13^b (298)	25
(**2b**)	(**2a**)	4·0 (321)	—

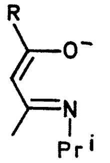
[a] Statistical value = 4. [b] Extrapolated value.

The large negative entropies for both directions of the reversible second-order reaction are consistent with an associative mechanism in which $\mathrm{NiL^1_2}$ and $\mathrm{NiL^2_2}$ are each present in the activated complex although other mechanisms could be found to fit the data.[3] However, mechanisms based on a preliminary dissociation of either complex are unlikely in this non-polar solvent, and associated species, with octahedral stereochemistry at nickel, are known at lower temperatures for some of these systems.[1,2] These may approximate to the bonding in an associative intermediate.



(1)

	R
(a)	$\mathrm{Bu^t}$
(b)	$\mathrm{Pr^i}$
(c)	$\mathrm{Pr^n}$
(d)	$\mathrm{Bu^n}$
(e)	$\mathrm{3\text{-}C_5H_{11}}$



(2)

	R
(a)	Me
(b)	$\mathrm{CF_3}$
(c)	Ph

Scrambling reactions with almost random behaviour have previously been observed in systems like equation (1) where $L^1 \neq L^2$ = (**1**).[2] Chakravorty and Holm's[2] preliminary findings were that reaction was fast if the complexes existed substantially in tetrahedral form ($t_{\frac{1}{2}} < 3$ min), but that negligible exchange occurred if either $\mathrm{NiL^1_2}$ or $\mathrm{NiL^1L^2}$ is square planar. We have extended these observations to other ligands and find slow reactions with half-lives of hours or more where L^1 = (**1**) and L^2 = (**2**) or $L^1 \neq L^2$ = (**2**) even where these complexes are substantially tetrahedral.[1,2,4] However, the slow reaction of the complex of salicylaldimine (**1a**) with the complex of (**2a**) probably depends on the presence of the bulky $\mathrm{Bu^t}$ group, since the compound (**1b**) reacts much faster. We also found that the scrambling reaction, equation (1), for substantially diamagnetic square planar $\mathrm{NiL^1_2}$ with L^1 = (**1c** or **d**) did in fact occur, simply by mixing the solids [*e.g.* L^1 = (**1a**), L^2 = (**1d**)] and running the mass spectrum which always showed the parent ion expected for the scrambled compound $\mathrm{NiL^1L^2}$. No reaction was observed by contact-shift methods even after several days. This does not contradict the work of Holm *et al.*[1,2,4] which was not exactly comparable.

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† Signals for $\mathrm{Bu^t}$ hydrogen on (**1a**) and the mixed complex from (**1a**) and (**2a**) are separated by 120 Hz at 90 MHz (303K) but overlap slightly because of a linewidth of *ca.* 40 Hz. Shifts are temperature dependent.

[1] R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, 1964, **86**, 379.

[2] A. Chakravorty and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 3999.

[3] K. Moedritzer, *Adv. Organometallic Chem.*, 1968, **6**, 171; J. C. Lockhart, *Chem. Rev.*, 1965, **65**, 131; J. C. Lockhart "Redistribution Reactions," Academic Press, New York, 1970.

[4] G. W. Everett, jun., and R. H. Holm, *J. Amer. Chem. Soc.*, 1965, **87**, 2117.