

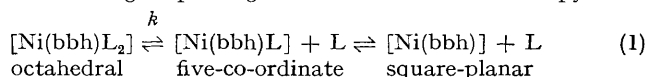
Ligand Exchange at Octahedral Nickel(II). Direct Evidence for a Dissociative Transition State

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Summary The comparison of kinetic parameters for ligand exchange with those for the octahedral to square-planar structural interconversion of a complex of nickel(II) provides direct evidence for a five-co-ordinate transition state for the ligand exchange process.

CUSUMANO¹ has recently reported a kinetic study of the fast octahedral to square-planar interconversion of bis-pyridine adducts of [biacetyl bis- α -hydroxybenzylidenehydrazone-(2-)- $N^1N^1'OO'$]nickel(II), [Ni(bbh)], in chlorobenzene. The relaxation data were consistent with the mechanism in reaction (1), where L is a substituted pyridine, the rate-determining step being the loss of a co-ordinated pyridine



molecule from the octahedral adduct, with rate constant k . As Cusumano pointed out, this rate-determining step is identical with that proposed for ligand exchange at an octahedral centre.² We show here that the two processes do indeed have very similar rates; this observation provides the most direct evidence yet available for the dissociative nature of ligand exchange at a labile octahedral metal complex.

We have measured by the ¹⁴N n.m.r. line-broadening technique the rate of exchange of pyridine (py) and 2-methylpyridine (2-Mepy) with [Ni(bbh)]. Measurements were made in the pure base and in the pyridine diluted to 20% by volume with chlorobenzene. For reasons of sensitivity, lower concentrations could not be used. Spectra were recorded on a Jeol PS-100 Fourier-transform spectrometer at 7.23 MHz. A pulse width of 40 μ s and a repetition

TABLE. Rate constants and activation parameters for ligand exchange on $[\text{Ni}(\text{bbh})\text{L}_2]$ where L is py or 2-Mepy.

Solvent	$\log k$ (25 °C)	ΔH^\ddagger kJ mol ⁻¹	ΔS^\ddagger J mol ⁻¹ K ⁻¹	$10^{-6}A/h$ Hz
100% py	4.75 ± 0.03	52 ± 2	22 ± 6	11.9 ± 0.5
20% py in PhCl	4.54 ± 0.03	62 ± 3	50 ± 10	11.3 ± 0.5
ca. 5×10^{-3} mol dm ⁻³ py in PhCl ^a	4.51	65.8 ± 0.8	63 ± 17	
100% 2-Mepy	5.93 ± 0.04	48 ± 3	30 ± 10	9.4 ± 0.6
20% 2-Mepy in PhCl	5.95 ± 0.05	55 ± 4	56 ± 10	9.6 ± 0.6
ca. 0.1 mol dm ⁻³ 2-Mepy in PhCl ^a	5.58	43 ± 3	8 ± 13	

^a Values refer to the dissociation of L from $[\text{Ni}(\text{bbh})\text{L}_2]$ and are taken from ref. 1.

rate of about 200 s⁻¹ were used to accumulate up to 10,000 transients. Spectra were phase-corrected and digitized in the absorption mode with the on-line computer and the digitized spectra were fitted by a least-square procedure to a Lorentzian function to obtain line widths at half-maximum height. Line widths for pure pyridine were similar to, but somewhat narrower than, those reported by Marianelli.³ Temperatures were recorded by a calibrated thermocouple and are believed correct to ± 1 °C.

Rate constants, activation parameters, and ¹⁴N scalar coupling constants, A/h , were evaluated from the line-broadening data by the method due to Swift and Connick.⁴ As Lincoln has also found in a ¹⁴N n.m.r. study of a similar system,⁵ the line-broadening data were consistent with a ' $\Delta\omega$ ' nuclear relaxation mechanism⁴ in the temperature range (-10 to 100 °C) studied. Chemical shifts of the bulk-pyridine signal were also measured; because of the broad spectra they were of low precision but within experimental error consistent with the assumed relaxation mechanism.

Results are summarised in the Table. Quoted errors are estimates derived from least-squares analysis of the line-broadening data over an 80 K temperature range. In order to make possible a direct comparison with Cusumano's results, the n.m.r. exchange rate has been multiplied by a factor of two to allow for the fact that k (equation 1) refers to the dissociation of one pyridine molecule while the n.m.r. experiment gives the average rate of exchange of two

pyridine molecules. The value of ΔS^\ddagger has also been increased by $R \ln 2$.

Comparison of the values of $\log k$ in the Table shows clearly that the rates of ligand exchange and dissociation are very similar. The solvents used in this work are not the same as that used by Cusumano but our data indicate that the change in solvent from pure ligand to a 20% chlorobenzene solution produces only minor effects on the rates and activation parameters. Our kinetic data in 20% pyridine-chlorobenzene are almost identical to those reported¹ for ligand dissociation in chlorobenzene.

The agreement for the 2-methylpyridine system is not so good. While the rates agree within a factor of 2.5 there is a significant difference in activation parameters for the two processes which is difficult to explain. The increased rate of exchange of 2-methylpyridine compared to pyridine is primarily associated with the enthalpy term, which is consistent with the smaller values of A/h for 2-methylpyridine and reflects the weaker bonding of this sterically hindered ligand. Cusumano's data indicate a compensation between a much lower ΔH^\ddagger value and a less positive ΔS^\ddagger value which he explains in terms of different solvation effects for the sterically hindered ligands.

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