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An NMR Method for Determining Outer Sphere Complex Stability Constants Involving Neutral Ligands

JACK R. VRIESENGA and GEORGE H. FAIRCHILD*

Department of Chemistry, Syracuse University, Syracuse, N.Y. 13210, USA

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It is commonly accepted that outer sphere complexes are precursors to ligand substitution reactions of transition metal complexes [1–4]. Direct measurement of outer sphere complex stability constants, K_{os}, has been limited to 'ion-pairs'. Of equal importance are the interactions between metal ions and incoming neutral ligands. At present, no direct method of measuring K_{os} for these 'ion-neutral' outer sphere complexes has been reported. In the absence of direct experimental techniques, investigators [3–6] have resorted to calculating K_{os} for such species using the Eigen–Fuoss equation [7]; however, the validity of using this equation to calculate ion-neutral K_{os} values has been questioned [3, 8–10]. In other cases, K_{os} was indirectly determined from various reaction rate constants only after making an untested assumption regarding the value of the Eigen–Wilkins statistical factor, f [11, 12]. In this paper, we report an NMR method for measuring K_{os} for ion-neutral outer sphere complexes, apply the method to measure K_{os} for the outer sphere complex formed between pyridine and the $[Co(CD_3OD)_6]^{2+}$ ion in d_4-methanol, and evaluate the limitations of this method.

The equilibrium studied and its associated equilibrium constant are defined in eqn. 1 and eqn. 2, respectively:

$$\underset{(1)}{[Co(CD_3OD)_6]^{2+}} + \underset{(2)}{py} \overset{K_{os}}{\rightleftharpoons} \underset{(3)}{[Co(CD_3OD)_6\cdots py]^{2+}} \qquad (1)$$

$$K_{os} = \frac{[3]}{[1][2]} \qquad (2)$$

In eqn. 1, species (*3*) represents a pyridine molecule within the first solvation sphere of the $[Co(CD_3OD)_6]^{2+}$ ion, forming an 'ion-neutral' outer sphere complex. Experimental conditions were chosen to ensure that the equilibrium depicted in eqn. 1 was the predominant process in solution, that is, $[CO^{2+}]_{total} \gg [py]_{total} = 0.050$ *M*. K_{os} was determined by measuring the proton NMR spin–lattice relaxation time, $(T_1)_{obs}$ (using inversion-recovery techniques), of the bulk α-H resonance of pyridine as a function of total Co^{2+} concentration. The temperature range for this study was chosen such that the pyridine exchange by species such as $[Co(CD_3OD)_5py]^{2+}$ did not affect $(T_1)_{obs}$ of bulk pyridine (*i.e.* pyridine exchange was slow on the NMR time scale), and the equilibrium depicted in eqn. 1 was facile on the NMR time scale. Under these conditions, $(1/T_1)_{obs}$ for the bulk α-H resonance of pyridine can be expressed as a simple weighted average:

$$(1/T_1)_{obs} = f_3(1/T_1(3)) + f_2(1/T_1(2)) \qquad (3)$$

where

$$f_3 = \frac{[3]}{[2] + [3]} \qquad (4)$$

and

$$f_2 = \frac{[2]}{[2] + [3]} = 1 - f_3 \qquad (5)$$

$T_1(2)$ is the α-H spin-lattice relaxation time of a pyridine molecule in the non-outer sphere complex environment, *i.e.* outside the first solvation sphere of $[Co(CD_3OD)_6]^{2+}$. $T_1(2)$ will be influenced by long range dipolar interactions with the paramagnetic cobalt(II) ions and is therefore dependent on the cobalt(II) concentration. Because $T_1(2)$ cannot be directly measured, an estimate of the concentration dependent effects on $T_1(2)$ could be made based on the T_1 data for the methyl proton resonance of t-butanol. It was assumed that this species does not effectively form an outer sphere complex with the cobalt(II) ion. Therefore, variations in T_1 for this resonance are due solely to the previously mentioned long range dipolar interactions, with $1/T_1$ being directly proportional to cobalt(II) concentration. We concluded that in the presence of cobalt(II), variations in $1/T_1(2)$ can be approximated by measuring the corresponding variations in $1/T_1$ for the methyl proton resonance of t-butanol, and applying a 'correction factor' to the $1/T_1(2)$ data. The resulting $T_1(2)$ values are summarized in Table I.

We also limited the quantitative interpretation of the T_1 data to the α-H of pyridine, where it was found that $T_1(3) \ll T_1(2)$. The end result was that uncertainties in $T_1(2)$ had very little effect on the analysis of the α-H T_1 data.

Under conditions of a large excess of Co^{2+} relative to pyridine (*i.e.* $[1] \gg [3]$) the following relationship can be derived:

$$f_3 = \frac{K_{os}[Co^{2+}]}{K_{os}[Co^{2+}] + 1} \qquad (6)$$

where $[Co^{2+}]$ represents the total concentration of $[Co(CD_3OD)_6]^{2+}$ (*i.e.* $[1] + [3]$). For the sake of clarity, the following quantities are defined:

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*Present address: Department of Chemistry, State University of New York, College at Oswego, Oswego, N.Y. 13126.

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TABLE I. $(T_1)_{obs}$ of the α-H of Pyridine as a Function of $[Co(CD_3OD)_6]^{2+}$ Concentration; temp = −44.0 °C; $[py]_{total}$ = 0.0480–0.0496 *M*.

$[Co^{2+}]$ *M*	$(T_1)_{obs}$ msec	$T_1(2)$ msec	$\Delta(T_1)_{obs}$ msec
0.265 ± 0.002	51.0 ± 1.1	130 ± 11	84.0 ± 7.1
0.362 ± 0.002	40.8 ± 0.4	113 ± 8	64.1 ± 3.3
0.530 ± 0.002	31.2 ± 0.6	86.4 ± 5.3	49.0 ± 3.1
0.596 ± 0.002	28.9 ± 0.3	84.7 ± 5.3	43.8 ± 1.9
0.679 ± 0.002	26.4 ± 0.6	80.6 ± 5.2	39.2 ± 2.3

$$\Delta(1/T_1)_{obs} = (1/T_1)_{obs} - (1/T_1(2)) \qquad (7)$$

$$\Delta(1/T_1(3)) = (1/T_1(3)) = (1/T_1(2)) \qquad (8)$$

Therefore, eqn. 3 simplifies to

$$\Delta(1/T_1)_{obs} = f_3(1/T_1(3)) \qquad (9)$$

By substituting eqn. 6 for f_3, the above equation becomes

$$\Delta(1/T)_{obs} = \frac{K_{os}[Co^{2+}]\Delta(1/T_1(3))}{K_{os}[Co^{2+}] + 1} \qquad (10)$$

Inversion of eqn. 10 results in the relationship

$$\Delta(T_1)_{obs} = \frac{\Delta(T_1(3))}{K_{os}[Co^{2+}]} + \Delta(T_1(3)) \qquad (11)$$

where $\Delta(T_1)_{obs} = 1/\Delta(1/T_1)_{obs}$ and $\Delta(T_1(3)) = 1/\Delta(1/T_1(3))$.

The $\Delta(T_1)_{obs}$ data for the bulk α-H of pyridine at −44.0 °C, as given in Table I, are plotted in accordance with eqn. 11 (Fig. 1). An analysis of this data resulted in a $T_1(3)$ value of 11 ± 2 msec and a K_{os} value of 0.60 ± 0.16 M^{-1}. This experimentally measured K_{os} value is larger than the approximate value of 0.1 M^{-1} obtained by the Eigen–Fuoss equation.

As with any method, there are certain limitations which must be addressed in assessing its general applicability. First, the method is limited to studies involving paramagnetic metal centers; this ensures the existence of two magnetically distinct environments (*i.e.* outer sphere and non-outer sphere environments) needed to monitor the equilibrium by T_1 relaxation time measurements. Second, appropriate concentrations of metal and ligand must be chosen such that a measurable amount of bulk ligand exists in solution (*e.g.* in this study, $[py]_{total}$ = 50 m*M* and $[Co^{2+}]_{total}$ = 0.3–0.7 *M*, causing the amount of bulk pyridine to range from 3 to 7 m*M*). Finally, the study must be carried out at temperatures where bound ligand dissociation does not significantly contribute to bulk ligand $(T_1)_{obs}$ values.

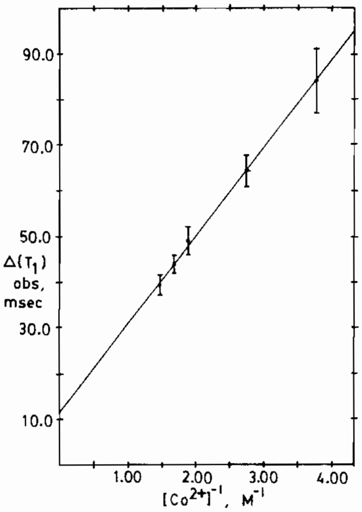

Fig. 1. Plot of $\Delta(T_1)_{obs}$ *versus* $1/[Co^{2+}]$; bulk α-H of pyridine (temp. = −44.0 °C).

We have demonstrated that this method can be used to determine K_{os} for ion-neutral outer sphere complexes and that, in this case, K_{os} is larger than anticipated. The mechanistic implications of these results will be the subject of future work.

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