

High Pressure Nuclear Magnetic Resonance Studies
in Inorganic Chemistry

David G. Vander Velde Literature Seminar

October 18, 1983

The principal application of high pressure nuclear magnetic resonance in inorganic chemistry to date has been studies of solvent exchange on metal ions [1]. These studies have advanced mechanistic understanding of this fundamental process; exchange on most ions was too fast to study with earlier high pressure studies by spectrophotometry or isotopic dilution [2]. The parameter being sought in these studies is the volume of activation, ΔV^\ddagger , which in the expected absence of electrostrictive effects is directly diagnostic of an associative (A or I_a) or dissociative (D or I_d) mode of activation for the exchange. The volume of activation determined by high pressure NMR is frequently simpler to interpret and less subject to systematic error than the entropy of activation determined by variable temperature NMR.

Various hardware configurations have been used for high pressure NMR, but the one most frequently used is a nonspinning sample inside a nonmagnetic pressure vessel, the pressure being applied by a fluid [3,4]. The exchange rates are derived from lineshape analysis by the Swift-Connick equations with correction for possible paramagnetic relaxation contributions to the second and subsequent solvation shells [5].

Mechanistic results obtained with high pressure NMR studies of solvent exchange include the surprising finding of a mechanistic crossover at iron among the divalent first row transition metal ions. This has been confirmed for water exchange [6] and nonaqueous solvent exchange [7], with good agreement between studies conducted using different nuclei [8]. Studies of the trivalent ions show a similar crossover; water exchange from iron (III) was shown to proceed by two mechanisms--I for $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and I_d for $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ [9]. Variations in activation parameters including ΔV^\ddagger were interpreted to indicate a change in the mechanism of dimethylformamide exchange from I_d to D occurring at Er [3].

A significant area of future application for high pressure NMR may be in studies of homogeneous catalysis. A study of the $[\text{Rh}_{12}(\text{CO})_{30}]^{2-}$ cluster (one cluster present in a catalytic system for synthesis of ethylene glycol) showed that it gave $[\text{Rh}_5(\text{CO})_{15}]$ quantitatively when pressurized under CO and H_2 ; no further fragmentation was observed at pressures up to 1 kbar. Also, the exchange of free and bound CO was slow on the NMR timescale [10]. Observation of intermediates formed under reaction conditions may thus be possible for many homogeneous catalysts.

References

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