

High Pressure NMR Studies of Homogeneous Catalysts

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Final Seminar

June 4, 1987

In situ studies of transition-metal homogeneous catalysts can be expected to yield significant new understanding of the mechanisms of catalytic reactions. Of the spectroscopic techniques commonly used to study molecules in solution, infrared spectroscopy was the earliest and most widely used method applied to catalyst solutions at high pressures and temperatures. Despite its considerable potential, high pressure nuclear magnetic resonance spectroscopy has not yet been widely used to study homogeneous catalysts, because of its inherent insensitivity and the experimental difficulties involved. However, it is a mature technique that has been used with success on a number of systems [1].

Initial ^{13}C high-pressure NMR experiments on homogeneous catalysts, performed by Heaton and Jonas [2,3], showed that it was feasible to make structural identification of organometallic species formed under extreme conditions. They found that the rhodium cluster $\text{Rh}_{12}(\text{CO})_{30}^{2-}$ was quantitatively converted to $\text{Rh}_5(\text{CO})_{15}^-$ at low pressure (5 bar), and that no further reactions occurred below 298 K up to 1000 bar. These studies also pointed out the need for an NMR probe specifically designed to carry them out, since the sensitivity and resolution were initially only fair and elevated temperatures could not be used because of the possibility of hydrogen embrittlement of the titanium pressure vessel used. Some provision must also be made for mixing catalyst solutions with reactive gases, since this key step is quite slow in the absence of mechanical stirring. A thick wall sapphire tube has recently been shown by Roe to be useful for such studies at pressures up to 1000 psi [4].

The design and testing of an NMR probe based around a pressure vessel and designed for studying homogeneous catalysts from -40°C to 100°C and pressures up to 4000 psi is described [5]. Its significant features are a built-in stirring mechanism to mix the sample under study with reactive gases, and resolution and sensitivity comparable to that obtained in ambient-pressure probes without sample spinning. The rhodium cluster reaction described above was used to demonstrate the probe's capabilities and the amount of improvement obtained in the important areas of its performance.

A rhodium catalyst for converting syngas to oxygenated organic compounds, previously studied by high pressure IR⁶, was chosen for an extended study in order to show the additional information available from the NMR experiment and its usefulness in characterizing complex multicomponent systems. The rhodium catalyst precursor $\text{Rh}(\text{CO})_2\text{acac}$ was dissolved in two solvents, sulfolane/4-methylmorpholine and 1-methyl-2-pyrrolidinone, leading to identification of some of the rhodium carbonyl anionic clusters present at ambient and extreme conditions. In agreement with the results of the IR study, a significant reversible change in the cluster population occurred above 90°C in sulfolane, showing facile cluster rearrangement in this solvent. However, the only identifiable cluster at the more extreme conditions is $\text{Rh}_{15}(\text{CO})_{27}^{3-}$, not the catalytically more interesting $\text{H}_2\text{Rh}_{13}(\text{CO})_{24}^{3-}$, as previously suggested [6]. This same cluster has previously been observed to form by pyrolysis of smaller clusters at the same temperature without application of high pressure [7].

In contrast, the same pressure and temperature produced a wide variety of clusters in 1-methyl-2-pyrrolidinone; only about half could be identified based on literature chemical shifts and coupling constants of known rhodium clusters. Cluster rearrangement in this solvent seems to be slow; no significant changes in the cluster population typically occurred after the initial period of cluster formation, even when the pressure was completely removed. However, a major change did occur in one instance, accompanied by release of oxygenated organic products, including ethylene glycol, and the appearance of an unknown rhodium cluster of very high nuclearity.

High pressure NMR spectroscopy is shown to be useful for studying homogeneous catalysts when intermolecular ligand exchange is slow. The importance of synthetic organometallic chemistry for studying catalysts in situ is also demonstrated, since spectral data for pure compounds is crucial if they are to be later identified in a catalytic system.

References

1. Jonas, J. Science 1982, 216, 1179.
2. Heaton, B. T.; Jonas, J.; Eguchi, T.; Hoffman, G. A. J. Chem. Soc., Chem. Commun. 1981, 331.
3. Heaton, B. T.; Strona, L.; Jonas, J.; Eguchi, T.; Hoffman, G. A. J. Chem. Soc., Dalton Trans. 1982, 1159.
4. Roe, D. C. J. Magn. Reson. 1985, 63, 388; Krusic, P. J.; Jones, D. J.; Roe, D. C. Organometallics 1986, 5, 456.
5. Vander Velde, D. G.; Jonas, J. J. Magn. Reson. 1987, 71, 480.
6. Vidal, J. L.; Walker, W. E. Inorg. Chem. 1980, 19, 896.
7. Vidal, J. L.; Schoening, R. C. J. Organomet. Chem. 1983, 241, 395.