CONTROLLED HYDROLYSIS OF $AlMe_3$ TO TETRAMETHYLALUMOXANE

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Alumoxanes belong to the family of organometallics comprising an Al-O-Al unit with pendant organic substituents.[1,2] They have attracted attention as highly active catalysts in the polymerisation of a wide range of organic monomers.[3,4] In particular, methylaumoxane (MAO), the Me_3Al and H_2O condensation product, is a very effective co-catalyst in olefin polymerisation by group 4 metallocenes.[5-7] Despite being used on an industrial scale, MAO is one of the least understood co-catalysts and the limited knowledge about its molecular structure hampers efforts to tailor its co-catalytic effectivity. Over the last two decades, many experimental and theoretical studies have been conducted to understand both the subtle pathways of synthesis and properties of alumoxane species.[8,9]

The hydrolytic approach seems conceptually the simplest way to alumoxanes. However, all attempts for the initial three decades focused on hydrolysis reactions involving homoleptic low-alkyl aluminates. Although various methods of introducing water have been used to lower the hydrolysis reaction rate, the low stability of diverse resulting species has prevented their detailed structural investigations. Therefore, further studies based on structurally well-defined molecular alkylalumoxanes' controlled transformations are highly desired and may lead to the accelerated development of alumoxane-based catalysts.

In the course of our group's extensive studies on the factors controlling hydrolysis of various organometallics compounds, herein, I present an efficient stoichiometric route to well-defined tetramethylalumoxane, $[Me_2(py)Al(\mu_3\text{-}O)AlMe_2]_2$, by the hydrolysis of $AlMe_3$ in the presence of pyridine as a strong Lewis base. Strikingly, the seemingly simple compound reported herein is the first tetramethylalumoxane characterised structurally in a crystal form. To better understand the mechanism of the alumoxanes formation and the intermediates' nature, we extended our investigations on kinetic measurements using variable-temperature ^{1}H NMR spectroscopy. In summary, our studies bring us closer to the rational synthesis of methylalumoxanes, and simultaneously provide a new insight into the complex process of organoaluminium compounds' hydrolysis.

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