

DISCOVERY OF METHYLCHLOROSILYLENE (CH₃SiCl) AS A KEY INTERMEDIATE IN THE DIRECT SYNTHESIS OF DIMETHYLDICHLOROSILANE, ((CH₃)₂SiCl₂)

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Twenty years ago, at the onset of the 1980's, prevailing ideas about the mechanism of the Rochow-Müller Direct Synthesis of dimethyldichlorosilane had originated from the research of Voorhoeve and coworkers, and van den Berg and coworkers in The Netherlands, Bazant and coworkers in Czechoslovakia and from Golubtsov, Lobusevich and coworkers in The USSR. Voorhoeve's monograph, *Organohalosilanes: Precursors to Silicones*, was the primary authoritative source of published information. The tenets of the prevailing hypothesis were

1. Cu₃Si (η phase) is the active catalyst leading to selective formation of (CH₃)₂SiCl₂.
2. The polarity of the metal – silicon bond in metal silicides determines or influences product selectivity.
3. The Cu – Si bond energy is greater than the Si – Si bond energy.
4. Promoters, particularly zinc, cadmium and antimony, enhance catalytic activity and selectivity when used in small (< 1 weight percent) amounts.
5. Neither methyl chloride adsorption nor copper diffusion is the rate-limiting step of the reaction.
6. Methyl chloride is dissociatively chemisorbed on the catalytic surface.
7. The reaction follows Langmuir-Hinshelwood kinetics.
8. (CH₃)₂SiCl₂ is formed from a surface intermediate with dimethylsilyl groups.

At the conclusion of his Plenary Lecture at the International Symposium on Organosilicon Chemistry in 1969, Bazant acknowledged the difficulty of doing mechanistic research on a reaction as complex as the Rochow-Müller Direct Synthesis. In 1980, we, then of Union Carbide Corp. at Tarrytown, and Prof. John Falconer's group at the University of Colorado (Boulder) took up the challenge and applied modern surface analytical techniques (AES, XPS, TPD/MS) to learn about

1. The composition of copper-silicon phases under experimental conditions,
 2. The polarity and bond energy of the Cu-Si bond,
 3. The role of promoters (especially zinc and tin) and poisons (mainly lead),
 4. Surface intermediates leading to the formation of the individual methylchlorosilanes.
- We sought to exploit the knowledge in our commercial practice of the Direct Synthesis and to advance the basic science associated with catalytic Direct Reactions of silicon.

This retrospective is a memoir of the events attendant to, the contributors to and the results of our seven year research program. Particular emphasis is given to the discovery of methylchlorosilylene (CH₃SiCl) intermediates as precursors to (CH₃)₂SiCl₂ (See K. M. Lewis and D. G. Rethwisch, Editors, *Catalyzed Direct Reactions of Silicon*, Elsevier, Amsterdam, 1993. pp 333 – 440). Evidence for silylene intermediates has also been published by Clarke, et al., Ono, et al. and Roewer, et al. The state of knowledge of the mechanism of the Direct Synthesis is now defined by their and our ideas.