

GDCh- und Chemisches Kolloquium

Der GDCh-Ortsverband Oldenburg und das Institut für Reine und Angewandte Chemie der Carl von Ossietzky Universität Oldenburg laden zu einem Vortrag

von Prof. Herbert Mayr, LMU München

zum Thema **Mythologie in der Organischen Chemie: Eine kinetische Analyse**

herzlich ein.

Termin: **Donnerstag, den 27.01.2011, 17 Uhr c.t.**
Großer Hörsaal der Naturwissenschaften, W3-1-161,
Carl-von-Ossietzky-Straße 9-11

Einladender Prof. Dr. J. Christoffers, Prof. Dr. S. Doye

Mythology in Organic Chemistry: A Kinetic Analysis

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Several concepts in organic chemistry persist, though their inconsistency has repeatedly been demonstrated in the past. This lecture will report on recent developments in the author's laboratory on three different topics

- 1) **Reactivity selectivity principle:**¹ In activation-controlled reactions, selectivity may decrease, increase, or remain constant as reactivity increases. Only when the diffusion limit is approached, is an increase of reactivity generally associated with a decrease of selectivity.
- 2) **Kornblum's rule and Salem-Klopman concept of charge and orbital controlled reactions:**² The ambident reactivities of some prototype nucleophiles, thiocyanate, cyanide, nitrite, cyanate, and nitronate anions, cannot be described by these rules. Changes from kinetic to thermodynamic control, and from activation to diffusion control have to be considered when interpreting the ambident reactivities of these nucleophiles. A novel approach to ambident reactivity based on Marcus theory will be presented.
- 3) **Free energy profiles of S_N1 solvolyses.**³ Rate constants for the reactions of benzhydrylium ions with halide ions and with solvents are combined with solvolysis rate constants to construct quantitative free energy profiles of S_N1 solvolyses. It will be demonstrated that the Gibbs energy profile presented in most organic chemistry texts, with formation of a carbocation over a high barrier followed by reaction with the solvent over a smaller barrier, is almost never realized. We can now use absolute rate constants for summarizing many experimental results reported in the 1940s to 1960s.

(1) H. Mayr, A. R. Ofial, *Angew. Chem. Int. Ed. Engl.* **2006**, 45, 1844-1854.

(2) a) R. Loos, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2003**, 125, 14126-14132. b) A. A. Tishkov, H. Mayr, *Angew. Chem. Int. Ed.* **2005**, 44, 142-145. c) A. A. Tishkov, U. Schmidhammer, S. Roth, E. Riedle, H. Mayr, *Angew. Chem.* **2005**, 117, 4699-4703; *Angew. Chem. Int. Ed.* **2005**, 44, 4623-4626. e) H. F. Schaller, U. Schmidhammer, E. Riedle, H. Mayr, *Chem. Eur. J.* **2008**, 14, 3866-3868.

(3) a) S. Minegishi, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2004**, 126, 5174-5181. b) S. Minegishi, R. Loos, S. Kobayashi, H. Mayr, *J. Am. Chem. Soc.* **2005**, 127, 2641-2649.

GDCh-Ortsverband Oldenburg
Der Vorsitzende
Prof. Dr. Mathias Wickleder

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Prof. Dr. Gunther Wittstock



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