Fakultät für Naturwissenschaften
Institut für Chemie

lädt ein

gemeinsam mit der Gesellschaft Deutscher Chemiker zum

Vortrag
von Herrn

Prof. Herbert Mayr

***Department of Chemistry
Ludwig-Maximilians-Universität***

GDCh

GESELLSCHAFT
DEUTSCHER CHEMIKER

"Stepwise or Concerted? One-Bond-Nucleophilicity and -Electrophilicity Parameters for the Mechanistic Analysis of 1,3-Dipolar Cycloadditions"

am:	07. November 2024
um:	16:00 Uhr
wo:	im Raum 1/232

Die kleine Kaffeerunde vor dem Vortrag beginnt um 15:30 Uhr im Raum 1/232.
Das Mitbringen von eigenen Trinkgefäßen ist erwünscht.
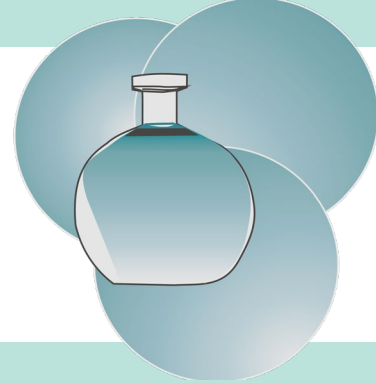
Gäste sind herzlich willkommen!

TECHNISCHE UNIVERSITÄT
IN DER KULTURHAUPTSTADT EUROPAS
CHEMNITZ

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Equation (1) governs rate constants for reactions of electrophiles with nucleophiles when no σ-bond is broken and only one new bond is formed in the rate-determining step.[1] We measured rates of the reactions of diazoalkanes with one-bond electrophiles (Ar_2CH^+) of known electrophilicity E and used Eq. (1) to calculate their nucleophilicity parameters N and s_N. The electrophilicity parameters E of diazoalkanes were calculated analogously from the rate constants of their reactions with one-bond nucleophiles of known N and s_N parameters.
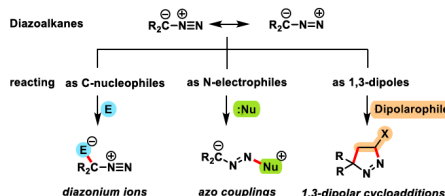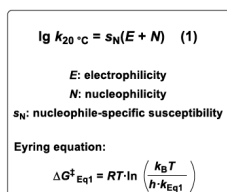

Figure 1. Diazoalkanes reacting as one-bond nucleophiles, one-bond electrophiles, or 1,3-dipoles.

If the cycloadditions of diazoalkanes with dipolarophiles proceed stepwise via zwitterionic intermediates, which undergo fast subsequent cyclizations, the rate constants can be predicted by Eq. (1). For concerted cycloadditions, the comparison of the observed rate constants with the ones calculated by Eq. (1) can be used to calculate the energy of concert $\Delta G^{\ddagger}_{concert}$ (Fig. 2).[2]

In contrast to earlier reports, the cycloadditions *of* ethyl diazoacetate and diethyl diazomalonate with enamines proceed stepwise via initial azo couplings. They involve attack of the enamines at $\pi^*_{(N=N)}$ of the diazoalkanes, which is perpendicular to the 3-center 4-electron π-system commonly considered in PMO treatments. Given the prior neglect of $\pi^*_{(N=N)}$, it is necessary to revise the classical PMO approach to reactions of 1,3-dipoles of the propargyl anion-type.[3]
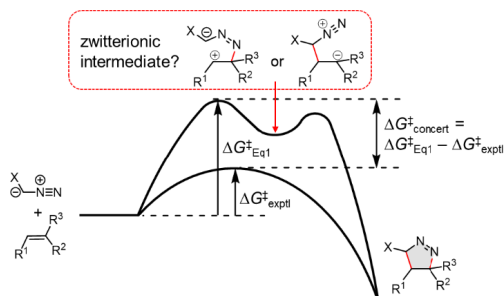

Figure 2. Energy of concert $\Delta G^{\ddagger}_{concert}$ as derived from the difference of the experimentally observed Gibbs activation energy ($\Delta G^{\ddagger}_{exptl}$) to the one calculated by Eq. (1), $\Delta G^{\ddagger}_{Eq1}$.

1) H. Mayr, M. Patz, Angew. Chem. Int. Ed. Engl. 1994, 33, 938–957.
2) L. Li, R. J. Mayer, A. R. Ofial, H. Mayr, J. Am. Chem. Soc. 2023, 145, 7416–7434.
3) L. Li, P. Mayer, D. S. Stephenson, A. R. Ofial, R. J. Mayer, H. Mayr, Angew. Chem. Int. Ed. 2022, 61, e202117047.

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