



## University of Groningen

# Million-fold acceleration of a Diels-Alder reaction due to combined Lewis acid and micellar catalysis in water

Otto, S.; Engberts, J.B.F.N.; Kwak, J.C.T.

Published in: Journal of the American Chemical Society

DOI:

10.1021/ja9816537

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date: 1998

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Otto, S., Engberts, J. B. F. N., & Kwak, J. C. T. (1998). Million-fold acceleration of a Diels-Alder reaction due to combined Lewis acid and micellar catalysis in water. *Journal of the American Chemical Society*, 120(37), 9517 - 9525. https://doi.org/10.1021/ja9816537

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

# SUPPORTING INFORMATION

## **Supporting Information**

Sijbren Otto, Jan B.F.N. Engberts\* and Jan C.T. Kwak

# Million-Fold Acceleration of a Diels-Alder Reaction due to Combined Lewis-Acid and Micellar Catalysis in Water

## **Derivation of equation (1)**

Assuming complete binding of the dienophile to the micelle and making use of the pseudophase model, one can derive an expression relating the observed pseudo-first-order rate constant  $k_{obs}$  to the concentration of surfactant, [S]. Assuming a negligible contribution of the reaction in the aqueous phase to the overall rate, the second-order rate constant in the micellar pseudophase  $k_m$  is now given by the following equation:

$$\mathbf{k}_{m} = \frac{\mathbf{k}_{obs}}{[2]_{m}}$$

Next we express  $[2]_m$  as a function of the partition coefficient  $P_2$  and the concentration of surfactant in the equation:

$$P_2 = \frac{[2]_m}{[2]_w}$$
 A2

$$[2]_{w} = \frac{n_{2,w}}{V_{w}} = \frac{n_{2,t} - n_{2,m}}{V_{w}} = \frac{n_{2,t} - [2]_{m} \cdot V_{m}}{V_{w}}$$
A3

Where  $n_{2,w}$ ,  $n_{2,m}$  and  $n_{2,t}$  are, respectively, the number of moles of 2 in the aqueous phase, the micellar phase and the total of the two.  $V_w$  and  $V_m$  are the volumes of the aqueous phase and the micellar pseudophase<sup>1</sup>.

Substitution of A2 in A3 and solving for  $[2]_m$  gives:

$$\frac{1}{[2]_m} = \frac{V_w}{P_2 \cdot n_{2,t}} + \frac{V_m}{n_{2,t}}$$
A4

The volume of the micellar pseudophase can be estimated from the molar volume of the micellized surfactant  $V_{mol,S}$ :

$$V_m = ([S] - cmc) \cdot V_t \cdot V_{mol.S}$$
 A5

Substituting A5 in A4 and substituting  $n_{2,t}$  with  $[2]_t \cdot V_t$  yields:

$$\frac{1}{[2]_m} = \frac{V_w}{P_2 \cdot [2]_t \cdot V_t} + \frac{([S] - cmc) \cdot V_{mol,S}}{[2]_t}$$
 A6

Combining A6 and A1 gives the final equation with which  $k_m$  and  $P_2$  can be obtained by plotting [2],/ $k_{obs}$  versus [S].

$$\frac{[\mathbf{2}]_{t}}{\mathbf{k}_{obs}} = \frac{V_{mol,S}}{\mathbf{k}_{m}} \cdot [\mathbf{S}] + \frac{\mathbf{V}_{w}}{\mathbf{P}_{2} \cdot \mathbf{V}_{t} \cdot \mathbf{k}_{m}} + \frac{cmc \cdot V_{mol,S}}{\mathbf{k}_{m}}$$

$$A7$$

## Note

1) Inevitably, the estimate of a molar volume of the micellized surfactant that is available for solubilization is somewhat arbitrary.