Porphyrin Metalation

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Activation Energy for the Self-Metalation Reaction of 2H-Tetraphenylporphyrin on Cu(111)**

*Stefanie Ditze, Michael Stark, Martin Drost, Florian Buchner, Hans-Peter Steinrück, and Hubertus Marbach**

Metalloporphyrins adsorbed on solid surfaces have received particular attention recently.[1] This high interest is due to their omnipresence in nature and in state-of-the art technology: The iron porphyrin in heme is responsible for oxygen transport in the bloodstream of mammals, and the magnesium porphyrin in chlorophyll is the key to photosynthesis;[2] in colorimetric sensors light-emitting properties of metalloporphyrins are utilized to identify chemical species adsorbed at the central metal atom.[3] The potential of porphyrins for the fabrication of tailor-made functional molecular architectures on well-defined substrates has stimulated significant activity in fundamental research.[4] One important observation was that metalloporphyrin layers can not only be prepared by direct deposition from the gas phase, but can also be synthesized in situ on the surface on demand by pre- or postdeposition of the respective metal atoms. This in situ metalation readily proceeds at room temperature (RT) or after moderate annealing.[5] It was studied in detail for 2H-tetraphenylporphyrin (2HTPP) complexes with Co,[5a,6] Fe,[5b,c,7] Ni,[8] Cu,[9] Zn,[6,10] and Ce[1c,11] on Ag(111) and Au(111). The surface-mediated reaction follows Equation (1),

$$\mathrm{M(ads) + 2HTPP(ads) \rightarrow MTPP(ads) + H_2(g)} \quad (1)$$

where M is the corresponding metal. The relevant elementary steps are: a) coordination of the metal atom by the intact free-base porphyrin, 2HTPP, b) successive transfer of the two hydrogen atoms from the respective nitrogen atoms to the metal atom, and c) formation and release of H_2. Based on DFT calculations in the gas phase, the transfer of the first hydrogen to the metal was identified as the rate-limiting step and thus determines the activation energy for the metalation.[6,12]

[*] S. Ditze, M. Stark, M. Drost, Dr. F. Buchner, Prof. Dr. H.-P. Steinrück, Dr. H. Marbach
Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials
Universität Erlangen-Nürnberg
Egerlandstrasse 3, 91058 Erlangen (Germany)
E-mail: marbach@chemie.uni-erlangen.de

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The experimental determination of the reaction kinetics and the activation barrier for in situ metalation on a surface, however, still presents a great challenge. In the liquid phase this is typically performed by isothermal studies at various temperatures, but to the best of our knowledge no such investigations are available for larger organic molecules adsorbed on surfaces. The only value for the activation energy of a metalation reaction reported so far was derived not from isothermal data, but from a temperature-programmed desorption (TPD) measurement of deuterium during the metalation of 2DTPP (deuterated analogue of 2HTPP) with Zn on Ag(111).[6] Redhead's equation[13] was used to deduce the activation energy. The deduced value is in good agreement with the value obtained from DFT calculations for the free molecule, that is, neglecting the surface; this indicates that the influence of the surface is small.[6] The major weakness of the Redhead approximation is the fact that the prefactor k_0 cannot be determined but must be assumed; usually a value of $10^{-13}\,s^{-1}$ is used in the corresponding analysis.

Herein, we present a direct approach to study the kinetics and to determine the activation energy for the metalation of 2HTPP with Cu substrate atoms on a Cu(111) surface, by scanning tunneling microscopy (STM) under isothermal conditions. For this purpose, we exploit the very different adsorption behavior of 2HTPP and MTPP on Cu(111) as indicated in Figure 1.[9,14]

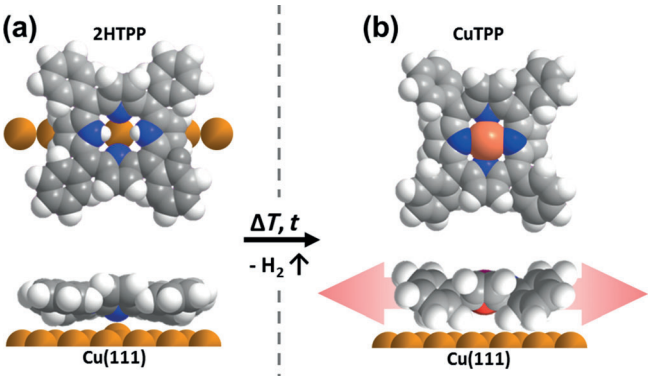

Figure 1. Illustration of the adsorption behavior of 2HTPP and CuTPP on Cu(111). a) Owing to the strong interaction of the iminic nitrogen atoms of the 2HTPP porphyrin macrocycle with the underlying Cu substrate, the molecule is literally pulled towards the surface; thus it exhibits a flat conformation and is rather immobile at RT. b) For CuTPP all four nitrogen atoms are coordinated equally to the Cu center. As a result the interaction with the surface is reduced and the molecule is very mobile at RT.

The ability of free-base porphyrins to "pick up" predeposited metals (e.g.: Fe,[15] Cu,[9] Zn[16]) and react with them has been shown on Ag(111) and Au(111). Depending on the metal, this metalation reaction either occurred at RT or upon heating to temperatures as high as 550 K. The reaction was always found to be selective, meaning that no metalation with Ag or Au substrate atoms occurred, presumably because of the noble-metal character of the materials. However, on Cu substrates the metalation of free-base porphyrins with substrate atoms has recently been reported in STM, TPD, XPS, and NEXAFS studies.[9,12,17] For 2HTPP on Cu(111), self-metalation was reported to start about 400 K; that is, at RT no CuTPP is formed.[9,17c] Along with the metalation, a drastic change of the adsorption behavior was observed in STM: In contrast to 2HTPP on Ag(111)[18] and to CuTPP on Cu(111),[9,14a] 2HTPP does not form supramolecular aggregates on Cu(111), but adsorbs as individual molecules with a well-defined orientation relative to the densely packed substrate rows;[9] furthermore, it diffuses comparably slowly along these directions.[14b] Owing to the slow diffusion it is possible to observe isolated, individual molecules at RT (see Figure 2a).

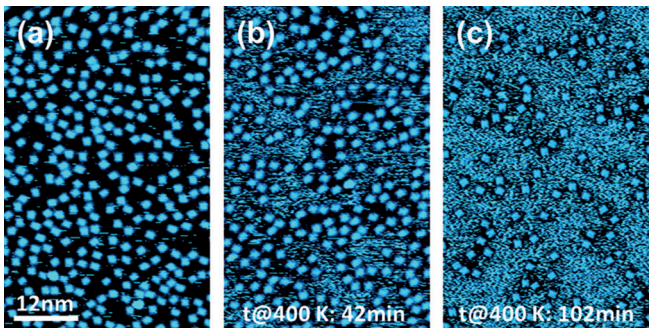

Figure 2. Constant-current STM images of 2HTPP as prepared on Cu(111) at a) room temperature and b,c) after annealing at 400 K for the indicated times. The estimated molecular densities of 2HTPP and the corresponding tunneling parameters are:
a) $\rho_0 = 0.135$ molecules nm^{-2} $U_{bias} = -1.07$ V, $I_{tunnel} = 200$ pA;
b) $\rho_{42\ min,400\ K} = 0.094$ molecules nm^{-2}, $U_{bias} = -1.20$ V, $I_{tunnel} = 231$ pA;
(c) $\rho_{102\ min,400\ K} = 0.042$ molecules nm^{-2}, $U_{bias} = -1.20$ V, $I_{tunnel} = 230$ pA.

The reason for this rather unusual behavior is the strong interaction of the imine nitrogen atoms with Cu substrate atoms, which leads to a very specific adsorption geometry that is regarded as a precursor for metalation.[14b,c,17c] This strong interaction induces a pronounced intramolecular deformation, as represented in Figure 1a. In the resulting flat conformation the phenyl substituents are oriented almost parallel to the plane of the macrocycle. In contrast, the behavior of the metalated reaction product, CuTPP, is quite different: Since all four nitrogen atoms are coordinated to the central Cu atom, there is no site-specific interaction to the substrate. Consequently, the mobility of CuTPP is so high that isolated molecules cannot be imaged with STM at RT.[9] The mobile species can be regarded as a 2D gas and are imaged as noisy streaks or areas in the micrograph as can be seen in Figure 2b,c.[9,19] In addition, the reduced interaction with the Cu(111) surface results in a different porphyrin conformation, in which the phenyl substituents are considerably rotated relative to the plane of the macrocycle (Figure 1b).[17c] The changed conformation allows for attractive T-type intermolecular interactions between neighboring CuTPP molecules; at higher CuTPP coverage this leads to the formation of supramolecular assemblies in the form of long-range-ordered quadratic islands (see Figure S1 in Supporting Information).[9]

The different appearance of 2HTPP and CuTPP in STM makes it possible to investigate the progress of the metalation reaction on Cu(111): In Figure 2a an STM image of a 2HTPP layer is shown after adsorption at RT. Figures 2b and 2c show the same layer after annealing to 400 K for 42 and 102 min, respectively, and subsequent cooling to RT. At temperatures around 400 K the metalation reaction is apparently slow enough to be followed on the time scale of minutes. It is evident in Figure 2a–c that individual 2HTPP molecules can be clearly distinguished; this makes it possible to determine their molecular density and thus to quantitatively follow the isothermal reaction as a function of time. The formed CuTPP molecules are observed as the streaky features and thus cannot be quantified.

In order to determine the reaction kinetics, we systematically investigated the decrease of the number of 2HTPP molecules (i.e. the decrease of the 2HTPP density) as a function of the annealing time at different (constant) temperatures, namely, 390, 395, 400, and 410 K. The starting coverage of 2HTPP, expressed in terms of molecular density ρ_0, varied between 0.135 and 0.174 molecules nm^{-2} (this corresponds roughly to 23–30% of a saturated monolayer of CuTPP on Cu(111) in a well-ordered quadratic adsorbate lattice). For each temperature, the 2HTPP density was determined by analyzing more than 25 independent images (size 61×61 nm^2) of different surface regions (see Figures S2 and S3 in the Supporting Information; in total more than 250000 2HTPP molecules were counted).

In Figure 3a the decrease of the normalized densities (ρ_t/ρ_0) of 2HTPP with increasing annealing time is depicted for the four temperatures studied. As expected, the reaction occurs faster at higher temperatures. In all cases, an exponential decrease is found. This is even more evident from Figure 3b, where the plot of $\ln(\rho_t/\rho_0)$ versus time yields linear behavior for all temperatures. The linear decrease in this type of plot is strong evidence for a pseudo-first-order reaction, following the equation $\rho_t/\rho_0 = \exp(-k_T t)$. This behavior is not unexpected, since the concentration of one reaction partner, namely the Cu atoms, remains unchanged because of the infinite reservoir in the Cu(111) crystal. The slopes of the fitted lines in Figure 3b represent the rate constants k_T of the metalation reaction at the corresponding temperatures.

Using the Arrhenius equation, $k_T = A \cdot \exp(-E_a/k_B T)$, we can now determine the activation energy and the prefactor by plotting $\ln(k_T)$ versus T^{-1} (Figure 3c). Linear regression yields $E_a = (1.48 \pm 0.12)$ eV and $A = 10^{(15\pm1.6)}$ s^{-1}. DFT calculations of the activation energy for the metalation of the bare free-base porphyrin macrocycle with Cu in the gas phase resulted in values ranging from 1.03 to 1.60 eV, depending on the level of theory and applied basis sets.[6,12] Overall, our experimen-

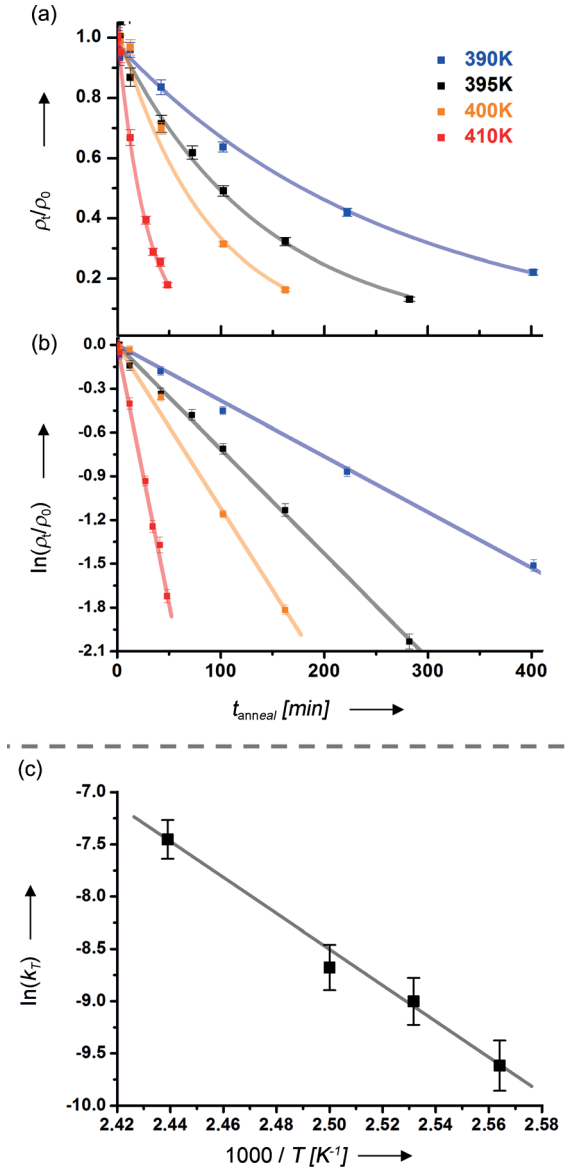

Figure 3. a) Plot of the normalized molecular density (ρ_t/ρ_0) of 2HTPP on Cu(111) versus then annealing time at the indicated constant temperatures. b) Logarithmic plot of the data in (a). c) Arrhenius plot of the rate constants, k_T, derived from the corresponding line slopes in (b).

tally determined result thus is in very good agreement with the theoretically predicted values.

In conclusion, we have determined the reaction kinetics and the activation energy of the self-metalation reaction of 2HTPP on a Cu(111) surface by isothermal STM experiments. The obtained value of (1.48 ± 0.12) eV for the rate-limiting step falls well within the range predicted by density functional theory for the gas-phase reaction. This agreement could indicate that the rate-limiting step is the same on the surface and in the gas phase or that a possible surface-related step has a comparable magnitude. To the best of our knowledge, our study represents the first direct determination of the activation energy for a metalation reaction (or a comparably complex reaction) on a surface. Our novel approach to determine the kinetics of surface reactions of large organic molecules is based on the counting of individual molecules (here the starting compound, 2HTPP) in STM images as a function of time at different temperatures. Possible extensions for future studies include investigating the role of the surface coverage or the crystallographic orientation of the surface (e.g. stepped surfaces) to obtain more information on the rate-limiting step. Also, calculations including the Cu surface are highly desired. The expansion to other suitable systems of interest is a promising perspective. Automated image-processing routines currently under development will speed up the analysis significantly. We believe that our approach will play an important role in gaining detailed quantitative insight into complex surface reactions.

Experimental Section

All experiments and sample preparation were performed in a two-chamber ultrahigh-vacuum (UHV) system at a background pressure in the low 10^{-10} mbar regime. The microscope is an RHK UHV VT STM 300 with RHK SPM 100 electronics. All voltages given refer to the sample and the images have been recorded in constant-current mode at RT. Besides background subtraction no further processing of the STM data was performed. The Cu(111) single crystal was purchased from MaTeck and 2HTPP (98% purity) from Porphyrin Systems. The substrate surface was cleaned and prepared by repeated cycles of Ar^+ ion sputtering (500 eV) and annealing up to 850 K. The porphyrin layers were prepared by thermal sublimation with a home-built Knudsen cell onto the substrate held at RT. Details on the sample temperature measurement and regulation, as well as on the error estimation, are given in the Supporting Information.

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