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Perspective

Elementary processes in photocatalysis of methanol and water on rutile $\text{TiO}_2(110)$: A new picture of photocatalysis

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1. Introduction

Photocatalysis has been under intense investigation for decades because of its potential applications in water splitting for efficient hydrogen production, synthesis of molecules from simple precursors, or decomposition of toxic compounds, etc. During the last few decades, significant effort has been devoted to the study of heterogeneous photocatalysis, especially in developing efficient photocatalysts for water splitting. A theoretical picture of heterogeneous photocatalysis has also been gradually developed, based mostly on bulk heterogeneous photocatalysis experiments [1]. Many of the important concepts in this picture of heterogeneous photocatalysis have originated from solid state physics and photoelectrochemistry. The key concept in this commonly used photocatalysis model, which has tremendous influence in this field, is that photocatalytic chemistry is driven by separated electrons and holes upon photoexcitation of electron-hole pairs in the photocatalysis.

The first step of photocatalysis is that excited electrons and holes are created by photoexcitation across the band gap of the semiconductor photocatalyst. In the commonly accepted photocatalysis model (Fig. 1), excited electrons and holes are then separated and transported to surfaces (processes (1) and (3)) where they can induce chemistry, or they are transported to another location where they can recombine either at a bulk (process (2)) or surface (process (4)) site. Thus, electron-hole pair separation, relaxation and charge-transfer processes have been regarded as essential steps for efficient photocatalysis in the traditional photocatalysis model, while electron-hole recombination is viewed as the main inhibitor of photocatalysis.

In the last decade, the photocatalysis model has been reinforced not only by various experimental studies but also by theoretical works. Methanol is widely employed as a hole trap (scavenger) in photocatalytic studies with different types of TiO_2 [2–4]. A series of photooxidation studies of water [5], methoxy [6], formic acid [7], formaldehyde [8], acetic acid [9–11], acetaldehyde [12], acetone [13–16], and other large organic molecules [17–21] on different TiO_2 single crystal surfaces have been also carried out. Although it is hard to identify

the driving force (charge transfer, phonon coupling) for most of these reactions, some of the reactions are believed to be driven by a hole-mediated process [5–7,15,17,20]. Recent density-functional theory (DFT) calculations [22] suggest that the hole transfer (to the adsorbate) and proton transfer (to the surface) are expected to take place concomitantly, leading to photoinduced dissociation of the organic alcohol or acid on anatase $\text{TiO}_2(101)$. However, a significant problem for the hole-mediated process is the energy mismatch between the holes in the valence band and the electronic states of reactants. If the energy mismatch is very large, hole transfer can be effectively inhibited, especially for water and methanol.

Meanwhile, there are several interesting questions proposed as a result of this photocatalysis model. First, the model does not explain how electrons or holes separately and exactly drive chemical reactions at surfaces at the atomic and molecular levels. If the energy is carried by excited electrons, as is implicit in the model, one would assume that a photocatalytic reaction driven by excited electrons should occur on an excited electronic state potential energy surface (or on the conduction

Fig. 1. Important processes in the surface photocatalytic processes: photoexcitation to produce an electron-hole pair, charge transfer processes, bulk and surface recombination processes, electron and charge induced chemistry at surfaces [1].

band). In addition, explanation as to how charged reactants eventually evolve into final neutral products is missing from the conventional model. Further, all surface chemical reactions occur at specific surface sites and surface structure and dynamics have profound effects on the surface reactions. Although such effects have not been investigated extensively, it is difficult to imagine that the surface structure and dynamics would not affect, in a significant way, the surface photocatalytic reaction processes. Previous photocatalysis studies on different surfaces of TiO_2 indicated that surface structure seemed to have a strong effect on photocatalysis [23–27]. However, in this conventional photocatalysis model, no consideration at all has been given to the effects of the surface structure and dynamics on photocatalysis. Finally, most of the electron-hole pairs excited in photocatalysts are recombined through either bulk recombination or surface recombination. It is reasonable to assume that bulk recombination far from surfaces has no role in the photocatalysis. However, it is incongruous to suggest that the large amount of energy ($E = h\nu$) generated via recombination near surface reaction sites would not have any effect on surface chemical reactions. This issue has not been addressed in the conventional photocatalysis model.

From a basic physical chemistry point of view, there are two key processes in surface photocatalysis: (1) the electronic photoexcitation process of the photocatalyst, and (2) the chemical reactions induced by this electronic excitation. These processes are analogous to molecular photochemical processes in which an individual molecule is first excited to its electronically excited state and subsequently dissociates. In photocatalysis, the electronic excitation typically occurs in a photocatalyst and not in the adsorbed molecules. Therefore, how this electronic excitation drives the reaction of adsorbed molecules is the most important question in photocatalysis. In this perspective, we describe the results of some new experimental studies that address this question directly. These investigations pertain to the photocatalysis of methanol and water on the rutile $\text{TiO}_2(110)$ surface under well controlled conditions. The results obtained are not consistent with the conventional photocatalysis model. Based on these studies, we propose an expanded picture of photocatalysis that involves non-adiabatic conversion processes and ground-state surface reactions. We endeavor to add consideration of the fundamental chemical dynamics to the study of photocatalysis, with the hope of stimulating further studies on fundamental processes in photocatalysis that will further refine the understanding of this important yet poorly understood chemical process.

2. Photocatalysis of methanol and water on TiO_2

2.1. Elementary processes of methanol photocatalytic dissociation

Since the first study of water splitting on TiO_2 in an electrochemical cell by Fujishima and coworkers [28], TiO_2 photocatalysis has been extensively investigated [29–34]. Pure TiO_2 is not an efficient photocatalyst for water splitting [35–37]. However, adding methanol into water can significantly enhance

hydrogen production on TiO_2 [38]. This phenomenon has been explained based on the electron-hole photocatalysis model. In this model, methanol is regarded as a hole trapper, allowing the electron-hole pairs to be separated efficiently so that more electrons can be used for water splitting. However, the elementary reactions involved in the photocatalysis of methanol and water on TiO_2 have not been investigated at the most fundamental level. It is essential to study these elementary steps for methanol photocatalysis if we want to understand the entire photocatalytic process. In the last few years significant advances have been made in the understanding of the elementary steps in the photocatalysis of methanol and water on a single crystal rutile $\text{TiO}_2(110)$ surface, based mainly on newly developed instruments specifically designed for these studies. Photocatalysis of methanol and water on TiO_2 has become a good testing ground for the fundamental photocatalysis mechanisms that have been so widely accepted. The experimental results derived from these studies show that the traditional photocatalysis model does not even qualitatively explain the experimental observations in the study of photocatalysis of methanol and water on rutile $\text{TiO}_2(110)$. A more sophisticated model is needed to explain the elementary processes in the photocatalysis.

We have experimentally studied photocatalytic chemistry of methanol on a single crystal rutile $\text{TiO}_2(110)$ surface using various techniques. A combined two-photon photoemission (2PPE) and scanning tunneling microscopy (STM) study has shown that methanol can be photocatalytically dissociated on the rutile $\text{TiO}_2(110)$ surface by 400-nm laser irradiation [39]. Although STM [39] and 2PPE [40–42] can both be used to study kinetic photocatalytic processes, they cannot be used as a direct probe of the chemical information of the photocatalyzed methanol dissociation products on the surface. Therefore, to study elementary photocatalytic processes we developed an apparatus that combines laser-induced photocatalysis, temperature programmed desorption (TPD), and time-of-flight (TOF) mass spectrometry [43]. The combination of laser-induced photocatalysis with a TPD/TOF mass spectrometer that has extremely low background provides a very sensitive tool to investigate the elementary photocatalytic processes at sub-monolayer levels on single crystal surfaces.

Methanol adsorption on rutile $\text{TiO}_2(110)$ has been carefully investigated previously by Henderson and coworkers [44]. It has been shown that methanol adsorbs on the Ti_{5c} sites, mostly in the molecular form. We have investigated the photo-induced dissociation of partially deuterated methanol (CD_3OH) on rutile $\text{TiO}_2(110)$ using 400 nm laser irradiation [45]. CD_3OH dissociates to formaldehyde (CD_2O) on Ti_{5c} sites in a two-step process, leaving H and D atoms on the bridge-bonded oxygen (BBO) sites:

This experimental result clearly demonstrated that photocatalytic methanol dissociation on rutile $\text{TiO}_2(110)$ occurred on Ti_{5c} sites, not on surface defect sites.

DFT calculations on the ground-state potential energy sur-

face indicate that the first step (O–H dissociation) has a small barrier, while the second step (C–D dissociation) has a considerably larger barrier (Fig. 2). This ground state picture seems to be able to explain the experimentally observed two-step process. The key reason that methanol photocatalysis is efficient on rutile $\text{TiO}_2(110)$ is that the reverse barrier in the second step is high, thus preventing the recombination of formaldehyde and an H-atom on BBO to form methoxy. In addition, the desorption energy of formaldehyde on Ti_{5c} is also relatively small, so desorption of formaldehyde competes with recombination of formaldehyde + H_{BBO} to form methoxy. This ground state reaction picture provides a clear picture for photocatalytic dissociation of methanol to form formaldehyde plus two H_{BBO} on the surface, whereas the conventional electron-hole photocatalysis model via the excited state pathway seems not to be able to explain clearly how the elementary reactions proceed in methanol photocatalysis.

In addition to the formation of formaldehyde from methanol photocatalysis on rutile $\text{TiO}_2(110)$, we have also observed further photocatalytic oxidation to form methyl formate (HCOOCH_3) through cross coupling of formaldehyde and methoxy [46]:

We concluded from this study that this reaction could also occur through direct coupling of formaldehyde and methoxy and did not have to go through a hole-mediated process involving an HCO intermediate, as had been suggested [47]. Instead, the cross coupling reaction might simply occur on the ground electronic state, promoted by localized surface heating from photon irradiation.

From these experimental studies, it is quite clear that methanol dissociation on rutile $\text{TiO}_2(110)$ occurs in multiple

elementary oxidation steps. After methanol dissociation, BBO sites become covered with H-atoms, prompting the question of how molecular hydrogen might be formed during methanol photocatalysis. Recent experimental results on the photocatalysis of fully deuterated methanol on $\text{TiO}_2(110)$ indicate that molecular hydrogen (D_2) is formed from thermal recombination of D-atoms, not photoinduced recombination of D-atoms [48].

Thus, we now understand that while methanol dissociation is photocatalytically driven, the formation of molecular hydrogen is clearly a thermally driven process. Studies of these elementary photocatalytic processes allow us to build a detailed picture of the hydrogen production from methanol photocatalysis on rutile $\text{TiO}_2(110)$. Implicit in this picture is the assumption that elementary steps occur on the ground-state potential energy surface. Ground-state reactions are clearly at odds with the widely used model of electron-hole-driven chemistry in photocatalysis. Note also that the electron-hole photocatalysis model cannot provide a clear picture of the elementary processes involved in methanol photocatalysis.

2.2. Strong photon energy dependence of methanol photocatalysis

As pointed out above, based on the electron-hole photocatalysis model, photocatalytic dissociation is driven by separated electrons or holes that are on the band edges. According to this picture, as long as the photon energy is above the band gap energy, photocatalysis should occur with the same efficiency regardless of the photon energy. We have tested this idea by measuring the initial dissociation rate of methanol on rutile $\text{TiO}_2(110)$ with two irradiation wavelengths: 355 nm and 266 nm [49]. The initial rate was found to be strongly dependent on photon energy, with the initial quantum yield being about two orders of magnitude higher at 266 nm than at 355 nm. This result is consistent with the picture that reactions occur on the ground electronic state, where increased photon energy should be more efficient in driving chemical reactions. This striking result is clearly in contradiction with the traditional electron-hole photocatalysis model that charge carriers in TiO_2 rapidly thermalize to their respective band edges via strong coupling with phonon modes first, which predicts that photocatalysis should only depend on the numbers of electron-hole pairs and should not depend strongly on the photon energy. The strong wavelength dependent photocatalytic rate for methanol photocatalysis suggests that unconditional application of the traditional electron-hole photocatalysis model may lead to wrong conclusions being drawn.

2.3. Water cannot be dissociated on rutile $\text{TiO}_2(110)$ at 400 nm

We have shown that methanol can be photocatalytically dissociated on rutile $\text{TiO}_2(110)$ with 400 nm light, and we have not been able to detect photocatalytic dissociation of methanol at wavelengths longer than 400 nm. Methanol dissociation on rutile $\text{TiO}_2(110)$ thus appears to be limited by the band gap

Fig. 2. Schematics for the ground and excited state reaction pathways for photocatalytic dissociation of methanol on the rutile $\text{TiO}_2(110)$ surface. Calculated energetics of the two-step dissociation of CD_3OH on rutile $\text{TiO}_2(110)$ on the ground electronic state are also shown here [45].

excitation energy (~ 3 eV, 400 nm). We have further investigated photocatalytic dissociation of water on rutile $\text{TiO}_2(110)$ under exactly the same conditions used for our studies of methanol photocatalysis [23]. Surprisingly, no dissociation of water on rutile $\text{TiO}_2(110)$ at 400 nm was observed at either 0.5 ML or 1.0 ML. This observation is also not explainable by the electron-hole model. According to this model, as soon as electron-hole pairs are created, photocatalysis of water on TiO_2 should take place, as in the case of methanol. Therefore, other important factors must be governing methanol and water photocatalysis on rutile $\text{TiO}_2(110)$ that are not accounted for by the conventional model. We have also calculated the ground-state energy landscape for water dissociation on rutile $\text{TiO}_2(110)$, which reveals a low reverse barrier of the second O–H dissociation step. This low barrier suggests that dissociated H atoms are more likely to recombine with adsorbed O than to recombine with each other to form H_2 . Thus, the low reverse barrier for the second dissociation step may inhibit water splitting. Similar to the results on methanol photocatalysis, the experimental and theoretical results for water on rutile $\text{TiO}_2(110)$ point to dynamics on the electronic ground-state potential energy surface being important in photocatalysis. From this result, it suggests that water photocatalysis on rutile $\text{TiO}_2(110)$ is not limited by the band gap excitation, whereas methanol photocatalysis on the same surface is clearly limited by the band gap excitation. Instead, water photocatalysis is limited by the energetics and dynamics of the reactions on rutile $\text{TiO}_2(110)$. Recent experimental results in our laboratory indicate that water photodissociation on rutile $\text{TiO}_2(110)$ also does not occur at 355 nm, implying that much higher photon energy than the band gap energy is required to drive the water splitting process.

Further, we have carried out further experiments with methanol and water co-adsorbed on rutile $\text{TiO}_2(110)$ with laser irradiation at 400 nm [50]. With different mixed ratios of co-adsorption of water and methanol on rutile $\text{TiO}_2(110)$, no net dissociation of water was observed, while methanol was still dissociated. These observations show clearly that methanol cannot enhance water splitting on rutile $\text{TiO}_2(110)$, which is contradictory to the previous assumption that methanol acts as a hole trapper so that water splitting can be enhanced on TiO_2 powder in solution conditions. This result is also inconsistent with the conventional electron-hole pair photocatalysis model.

3. Revised picture of photocatalysis

In the series of experiments summarized above, we have found many inconsistencies with the conventional model of photocatalysis. First, the lack of water photocatalysis under the same conditions where methanol photocatalysis was observed to be efficient may be explained with a ground-state reaction picture. Second, the initial rate of the methanol dissociation is strongly dependent on the photon energy, which could be mostly explained by a ground-state reaction. Third, the cross-coupling reaction of formaldehyde and methoxy to produce methyl formate is apparently direct and is therefore consistent with a ground-state process. Fourth, the conventional

electron-hole model cannot explain all the elementary steps in the photocatalyzed decomposition of methanol. Fifth, it is clear that methanol does not necessarily act as a hole trapper to facilitate water splitting in water/methanol mixtures, as has been widely assumed. Ground-state reactions would be expected to lead to the observed result that water and methanol dissociate with about the same efficiency whether they are individually or co-adsorbed. Finally, the fact that methanol and water on rutile $\text{TiO}_2(110)$ behave very differently when irradiated at 400 nm shows that band-gap excitation is not sufficient to drive all photocatalytic reactions. Again, this result could be easily explained by the different dynamics of methanol and water dissociation on their respective ground-state potential energy surfaces. A unifying explanation of these phenomena must go beyond a simple model based on electron- or hole-mediated processes and take into account chemical dynamics.

All the observations above, taken together, are consistent with each other if we assume that photocatalysis occurs on the ground-state potential energy surface, as opposed to an electronically excited surface. Here, we will develop this idea further. As discussed in the introduction, in the first step of photocatalysis the photon energy is converted to electronic energy in the system when electrons are excited from the valence band (VB) to the conduction band (CB) of the photocatalyst. For an elementary reaction step or set of steps to occur on the ground state, this electronic energy must be converted to energy of nuclear motion (vibration or phonon), and then this energy may drive chemical processes.

An analogous process is found in the photochemistry of isolated molecules where dissociation follows initial electronic excitation. In the example illustrated in Fig. 3, the first step in molecular photochemistry is the excitation of the molecule from the ground electronic state (S_0) to a bound excited state (S_1) or a repulsive state. When a molecule is excited to a repulsive state, direct dissociation of the molecule (process 1) would occur on an electronically excited potential energy surface. When a molecule is excited to a bound electronic state, several pathways are possible: (1) the excited molecule may fluoresce to the ground state; (2) the excited molecule may jump to a dissociative state via non-adiabatic coupling (process 2, predissociation); (3) the excited molecule may go through a non-adiabatic process (process 3, internal conversion) to the ground electronic state and then dissociate on the ground-state surface. In large molecular systems such non-adiabatic conversion processes from excited states to the ground state often govern the photochemical dynamics. For larger systems, such as large clusters or catalysts, photochemistry via nonadiabatic processes is expected to be even more important. In these large molecular systems, the nonadiabatic process from the excited electronic state to the ground state is usually referred to as electron-hole recombination.

Certainly, not all recombination would be useful in driving surface chemical reactions in photocatalysis; thus, we divide electron-hole recombination into two categories: surface recombination (SR) and bulk recombination (BR), as shown in Fig. 4. When electron-hole recombination near the surface (SR) relaxes to vibrational or phonon energy, this energy—now on

Fig. 3. Fundamental photochemical processes in molecular photochemistry: (1) direct dissociation via a repulsive electronic states, (2) predissociation via nonadiabatic coupling to a dissociative state, and (3) dissociation via nonadiabatic conversion from the excited state to the ground state.

the ground-state potential energy surface—may be localized near the surface and couple to adsorbed molecules on a time scale that competes with energy dissipation throughout the surface. Energy from recombination at sites far away from the adsorbed molecules (BR) would not be expected to be available to adsorbed molecules before being dissipated. With this simple concept, we can now define a quantum efficiency for photocatalysis, which should be the number of surface recombinations that can drive adsorbate reactions divided by the total number of recombinations,

$$\eta_{\text{pc}} = N_{\text{SR}} / (N_{\text{SR}} + N_{\text{BR}}) \quad (5)$$

This new photocatalysis picture can provide a qualitative explanation for all the observations discussed in Section 2, whereas the conventional electron-hole model falls short. If ground-state reactions dominate or at least play an important role in photocatalytic reactions at surfaces, then new approaches to the development of superior photocatalysts are warranted. For example, given a model based on the dynamics of surface non-adiabatic processes and ground-state surface chemical reactions, it would be possible to build quantitative theoretical pictures for specific surfaces and reactions for comparison with well-defined photocatalysis experiments. In addition, design criteria for photocatalysts would need to highlight photocatalysts with proper chemical structures and favorable adsorbate-surface dynamics for efficient reactions to take place.

These experiments suggest that photocatalysis might not be very different from thermal catalysis, as both photocatalysis and thermal catalysis may proceed on ground electronic state potential energy surfaces. This suggestion should be welcome news to those who wish to carry out theoretical calculations of photocatalytic reactions because current theory can make relatively accurate predictions for ground-state reactions whereas

Fig. 4. Conceptual illustration of a new photocatalysis model in which energy from electron-hole recombination drives chemical processes in surface adsorbates. In this qualitative picture, the energy from surface recombination may be coupled to the reaction coordinate efficiently, while the energy generated bulk recombination is dissipated into the bulk.

no accurate theories for excited-state surface reactions are yet on the horizon. Of course, there are still significant differences between photocatalysis and thermal catalysis within the proposed model. Thermal catalytic reactions occur on thermally equilibrated surfaces, which can be treated statistically, whereas photocatalytic reactions that are driven by localized vibrational or phonon excitation are not in thermal equilibrium and may be non-statistically relevant. In addition, energy dissipation from the locally excited sites would likely reduce the energy available for the reaction of an adsorbate. Electron-hole recombination near the surface is central to the proposed model. Thus, bulk materials may not make good photocatalysts. Smaller sized photocatalysts with a high surface to volume ratio should be more efficient, because they would allow more energy to be localized near the surface reaction sites.

4. Future issues and challenges

We have presented a series of experimental results on the photoinduced decomposition of methanol and water on rutile $\text{TiO}_2(110)$ that are not consistent with the widely accepted model of photocatalysis, which is based on the concept that separated electrons or holes supply the driving force for chemical reactions of surface adsorbates (i.e., the reactions occur in an excited electronic state). We have proposed a new photocatalysis model that is based on nonadiabatic dynamics and reaction on the ground-state potential energy surface. This model assumes that photons promote electrons from the valence band to the conduction band and that adsorbate reactions are driven by the energy released in a localized region when electrons and holes recombine near the surface. This simple picture of photocatalysis qualitatively explains all of the new experimental results from our laboratory. Experimental tests of this model with other photocatalytic systems under well-controlled conditions will determine how broadly applicable it is. Nevertheless, within the context of the proposed model, the design of an effi-

cient photocatalyst should focus on enhancing electron-hole recombinations near surfaces, instead of separating electrons and holes as the currently accepted model has suggested. In addition, designing a proper chemical surface structure is also expected to be crucial.

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Graphical Abstract

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Conceptual illustration of a new photocatalysis model in which energy from direct electron-hole recombination or electron-hole recombination initiated by charge transfer to adsorbates drives chemical processes in surface adsorbates.

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甲醇和水在金红石TiO₂(110)表面光催化基元过程研究: 表面光催化新的物理图像的探讨

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摘要: 作为在能源和环境领域有着重要应用前景的绿色技术, 光催化发展受到了广泛的关注. 然而, 光催化反应机理和动力学方面的研究却远远落后于光催化剂的发展. 一系列的研究结果表明, TiO₂表面光催化反应起始于光的吸收. TiO₂吸收大于其带隙的光子后, 则会产生电子空穴对, 而电子, 空穴分离后, 会在百飞秒量级时间范围内弛豫到导带或者是价带边上, 多余的能量则会激发声子振动. 而分离的电子或者是空穴会在皮秒或者是更长时间范围内与反应物相互作用, 来驱动反应发生. 因此, 在这种前提下, 反应速率和激发光的波长就没有直接联系了. 相反, 反应速率和TiO₂对不同光波长的光吸收系数有很大关系.

本文总结了本课题组最近在金红石TiO₂(110)表面开展的甲醇和水的光解离基元过程的研究结果. 首先, 我们发现在金红石TiO₂(110)表面, 利用400 nm去照射甲醇或者水覆盖的金红石TiO₂(110)表面, 甲醇能够高效的发生解离, 而水却没有观察到的解离. 通过基于基态反应的理论计算, 发现水两步解离的低能垒是反应不能有效发生的关键. 另外, 我们也研究了甲醇在355和266 nm光照下在金红石TiO₂(110)表面的解离, 结果发现, 甲醇在266 nm照射下的解离速率比355 nm快了100倍, 而TiO₂对266 nm光的吸收系数比355 nm也就高了2–4倍. 这充分说明了光子能量对反应有非常显著的贡献, 现有的光催化模型已经不能很好地解释我们观察的实验现象. 在此基础上, 我们提出了一个基于非绝热过程和基态反应的模型来解释这些新的实验现象. 这个模型不仅能解释我们的实验结果, 还能为增进光催化的理解打开一扇新的大门. 为了能让这个模型应用到一般的光催化过程中, 需要着重开展表面附近电子-空穴复合导致的基态光催化反应的研究, 来验证和完善这个新的模型.

关键词: 二氧化钛; 光催化; 电子-空穴分离; 非绝热过程; 基态势能面

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