Angewandte International Edition Chemie

Surface Chemistry

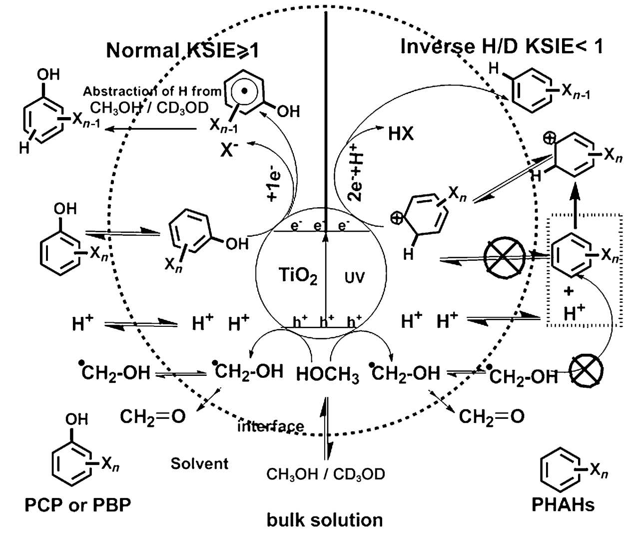
DOI: 10.1002/anie.201409392

Inverse Kinetic Solvent Isotope Effect in TiO_2 Photocatalytic Dehalogenation of Non-adsorbable Aromatic Halides: A Proton-Induced Pathway**

Wei Chang, Chunyan Sun, Xibin Pang, Hua Sheng, Yue Li, Hongwei Ji, Wenjing Song, Chuncheng Chen, Wanhong Ma, and Jincai Zhao**

Abstract: *An efficient redox reaction between organic substrates in solution and photoinduced h^+_{vb}/e^-_{cb} on the surface of photocatalysts requires the substrates or solvent to be adsorbed onto the surface, and is consequentially marked by a normal kinetic solvent isotope effect (KSIE ≥ 1). Reported herein is a universal inverse KSIE (0.6–0.8 at 298 K) for the reductive dehalogenation of aromatic halides which cannot adsorb onto TiO_2 in a [D_0]methanol/[D_4]methanol solution. Combined with in situ ATR-FTIR spectroscopy investigations, a previously unknown pathway for the transformation of these aromatic halides in TiO_2 photocatalysis was identified: a proton adduct intermediate, induced by released H^+/D^+ from solvent oxidation, accompanies a change in hybridization from sp^2 to sp^3 at a carbon atom of the aromatic halides. The protonation event leads these aromatic halides to adsorb onto the TiO_2 surface and an ET reaction to form dehalogenated products follows.*

Despite the widespread use of TiO_2 photocatalysis to generate H_2 through sacrificial organics,[1] degrade organic pollutants in air or water,[2] and synthesize important organic compounds,[3] the known reaction pathways of organic substrates remain limited to interfacial single-electron transfer (SET) followed by free-radical ion or free-radical chemical reactions.[2c,4–6] Because the photoinduced h^+_{vb}/e^-_{cb} is not capable of diffusing from a catalytic surface into bulk solution, the dissolved substrate must typically be adsorbed onto the TiO_2 surface to facilitate efficient ET. However, the successful photocatalytic transformation of dissolved substrates which have difficulty approaching the surface of the solid catalyst always requires a relay reagent or an additional indirect reaction route. In general, solvent serves this role to firstly react with h^+_{vb} or e^-_{cb} to form a diffusing solvent radical, and then leads to reactions between substrates and these radicals. Typically, these types of reactions, which are performed in a solvent and its deuterated congener, should show a normal kinetic solvent isotope effect (i.e., KSIE ⩾ 1) if the solvent bond (i.e., the H−OH bond or the H−CH_2OH bond) is cleaved in the rate-determining step (RDS), or a KSIE = 1 if the cleavage does not occur in the RDS.[7] In TiO_2 photocatalysis, examples of well-known dehalogenation reactions are the degradation of polychlorinated phenols (PCP) and polybrominated phenols (PBP),[8] which adsorb easily onto TiO_2 in alcohol solutions. Under anaerobic conditions, substrates directly accept e^-_{cb} used for debromination through an inner-sphere ET, while the solvent alcohol acts as an electron donor to capture h^+_{vb} and is thereby oxidized into an aldehyde (Scheme 1, left). Accordingly, the dehalogenation reactions of PCP and PBP show normal KSIEs in either [D_0]alcohol/[D_n]alcohol or H_2O/D_2O. However, for the extremely hydrophobic aryl halides such as



Scheme 1. Mechanisms of TiO_2 photocatalysis: well-established ET-induced free-radical reaction for adsorbable substrates (left) and a proton-induced pathway presented in this study for non-adsorbable substrates (right).

[*] Dr. W. Chang, Dr. C. Sun, Dr. X. Pang, Dr. H. Sheng, Dr. Y. Li, Prof. H. Ji, Prof. W. Song, Prof. C. Chen, Prof. W. Ma, Prof. J. Zhao
Key Laboratory of Photochemistry, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry
Chinese Academy of Sciences, Beijing 100190 (China)
E-mail: whma@iccas.ac.cn
jczhao@iccas.ac.cn
Dr. C. Sun
Department of Chemistry, Shaoxing University
Zhejiang Shaoxing 312000 (China)

[**] We thank the National Basic Research Program of China (973 program No. 2013CB632405), the National Science Foundation of China (Grant No. 21137004, 21221002, 21277147 and 21377134), the "Strategic Priority Research Program" of the Chinese Academy of Sciences (No. XDA09030200), and the Chinese Academy of Sciences for financial support. We also wish to thank Dr. Yun Shen and Dr. Minyang Zhuang for helpful advice.

Supporting information for this article (details for preparation of the experiments and analytical methods) is available on the WWW under http://dx.doi.org/10.1002/anie.201409392.

decabromodiphenyl ether (deca-BDE), they are incapable of adsorbing onto the TiO_2 surface and do not have either hydrogen atoms available for abstraction or sufficiently high electron density for oxidation by an alcohol free-radical. Although the dehalogenation of them has been well evidenced in the photocatalytic experiments,[9] questions still remain to be solved: how do they undergo dehalogenation while alcohol is used as both solvent and hole capture? What is the KSIE for the dehalogenation of them in [D_0]alcohol/[D_n]alcohol?

In this study, we show that photocatalytic reactions for these highly hydrophobic polyhalogenated aromatics proceed through a protonation mechanism which induces subsequent dehalogenation reactions, thus resulting in an inverse KSIE in [D_0]methanol/[D_4]methanol solutions (Scheme 1, right). The reaction of this substrate type for TiO_2 photocatalysis does not involve direct ET or a diffusive solvent free-radical mechanism, but processes along a previously unknown pathway. The reaction path for organic substrates in solution mainly depends on the adsorption property of the substrate onto the TiO_2 surface.

We chose deca-BDE, which is a widely used nonpolar, and extremely hydrophobic model compound ($\log K_{o/w} \approx 14$) for photocatalytic dehalogenation,[9a] to observe the KSIE during TiO_2 photocatalysis ($\lambda > 360$ nm UV light) in anaerobic [D_0]methanol and [D_4]methanol at 298 K (Figure 1 a).

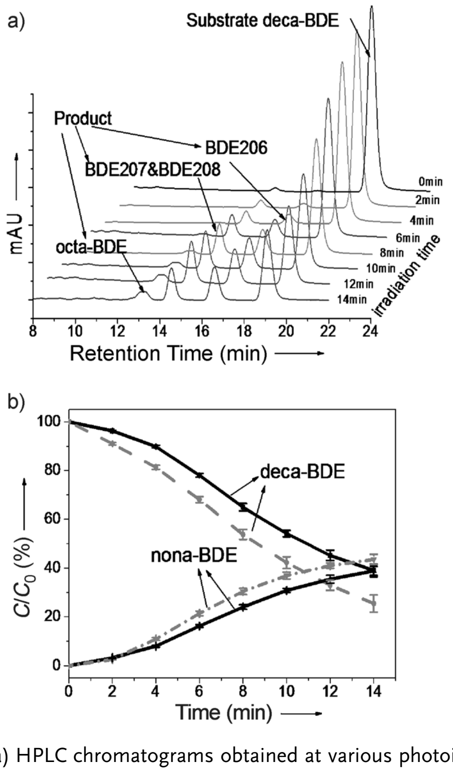
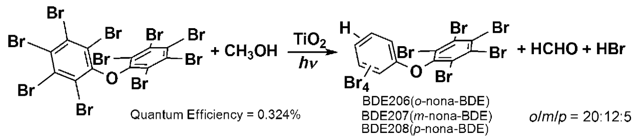


Figure 1. a) HPLC chromatograms obtained at various photoirradiation times for the TiO_2 photocatalytic dehalogenation of decabromodiphenyl ether (deca-BDE) in anaerobic methanol. b) Time-resolved evolution of the photocatalytic dehalogenation of deca-BDE and formation of nonabromodiphenyl ether (nona-BDE) in [D_0]methanol/[D_4]methanol. Solid lines and dashed lines indicate that the reaction was performed in [D_0]methanol and [D_4]methanol, respectively. Each data point shown represents the average value of three experiments, all of which were within a 5% uncertainty.

Indeed, the conversion rate of deca-BDE in [D_0]methanol was slower than in [D_4]methanol (Figure 1 b), and the observed H/D KSIE was significantly smaller than 1. In this case, the alcohol functioned as both a solvent and a reactant, with the latter donating both electrons and hydrogen atoms to react with h^+_{vb} for formation of an aldehyde and protons. The inverse KSIE differed from the normal KSIE of which the general prediction is the exponential decay with an increasing proton mass for the homogenous cleavage of the C–H/D bond.[10] Furthermore, we quantitatively detected the corresponding dehalogenation products of nonabromodiphenyl ether (nona-BDE), including BDE-206, DBE-207, and BDE-208 (Scheme 2), using HPLC and MS (see Figure S1 in the



Scheme 2. TiO_2 photocatalytic dehalogenation of deca-BDE in methanol.

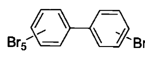
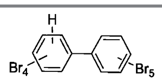
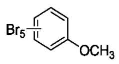
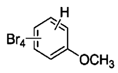
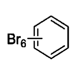
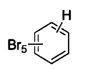
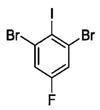
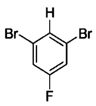
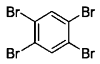
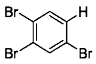
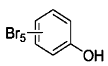
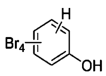
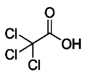
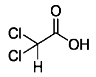
Supporting Information). Moreover, the kinetics of the formation of nona-BDE were similar to those for the dehalogenation of deca-BDE (i.e., the reaction proceeded faster in [D_4]methanol; Figure 1 b), although further debromination was inevitable (octa-BDE was also formed for prolonged photoirradiation). The formation of bromide ions was detected by IC (see Figure S2), and the approximate stoichiometric yield also confirmed that the inverse KSIE was about 0.7 and resulted from the reaction depicted in Scheme 2. The h_{vb}^+-induced oxidation of an alcohol solvent to form an aldehyde and protons never gives an inverse KSIE.[11] Therefore, the inverse KSIE phenomenon was attributed to the reduction of deca-BDE by e^-_{cb}.

Table S1 shows that the kinetics at each stage of the dehalogenation could be described by the inverse KSIE, as calculated from either the deca-BDE conversion or the nona-BDE yield. No significant difference was observed between the values of these two types of inverse KSIEs, thus indicating that the main reaction was consistent with that in Scheme 2. The result suggests that the dehalogenation reaction of deca-BDE did not proceed through the direct ET pathway or the typical solvent free-radical mechanism with a normal KSIE. Instead, the sp^2 hybridization of carbon for deca-BDE may have been affected by H^+/D^+-induced addition, which will be discussed below.

To investigate the effect of the alcohol solvent, we used [D_0]methanol/[D_1]methanol and [D_0]methanol/[D_3]methanol as the solvent to perform the same experiments, and the inverse KSIE also occurred in these two systems (see Table S2). In addition, we replaced the methanol solvent with ethanol and isopropanol to further confirm this inverse KSIE. Both solvents exhibited clear inverse KSIEs (Table S2). For the alcohols, oxidative dissociation of the C–H and O–H bond by the h^+_{vb} typically exhibits a normal H/D KIE,[11] and the C–O bond of the alcohols is converted into the C=O bond of an aldehyde or ketone, that is, conversion of the tetrahedral sp^3-configured carbon atom into an sp^2-configured carbon atom. The change does not result in an inverse KSIE. The inverse KSIE indicates that the dehalogenation reaction route involves a tetrahedral carbon-centered intermediate and may be highly dependent on deca-BDE combining with H^+/D^+, rather than the oxidation of the solvent itself.

We explored seven other organic halide substrates to determine whether the inverse KSIE behavior was universal. Substrates that did not possess polar functional groups, which could adsorb onto TiO_2 in methanol, all displayed inverse KSIEs ranging between 0.6 and 0.8 (Table 1, entries 1–5).

Table 1: Average rates of conversion and KSIEs for different halides at 298 ± 1 K.[a]

Entry	Substrates	Products	Conv. (H) [%][b]	Conv. (D) [%][b]	KSIE
1			19.0 44.6	28.5 65.0	0.67 0.69
2			22.0 52.0	33.1 73.0	0.67 0.71
3			21.6 39.5	31.2 53.3	0.69 0.74
4			37.2 46.9	50.7 62.7	0.73 0.75
5			13.5 21.8	19.0 32.1	0.71 0.68
6			26.7 51.5	9.5 21.2	2.81 2.43
7			39.5 53.6	38.5 48.0	1.02 1.12

[a] Other experimental conditions are listed in the Supporting Information. [b] Conv. (H) and Conv. (D) represent the percent conversion of deca-BDE in $[D_0]$methanol and $[D_4]$methanol, respectively.

Conversely, substrates with polar groups which typically bind to the TiO_2 surface sites exhibited normal KSIEs [approximately 2.6 and 1.1 for PBP and trichloroacetic acid (TCA), respectively; Table 1, entries 6 and 7]. The variation in the KSIEs for the different substrates clearly shows that the substrates' adsorption onto the TiO_2 surface played an important role in determining which reaction pathway to follow. Substrates such as PBP and TCA which contain polar groups can easily directly accept e^-_{cb} to generate a free-radical and a halide ion. In contrast, the reaction for the substrates without polar or coordinate groups may proceed by a less-direct route which will be discussed below.

We used in situ ATR-FTIR with a ZnSe crystal which was coated with a TiO_2 film (see Figure S3) to observe the possible protonation of the substrate. We compared the small adsorption of deca-BDE (Figure 2a, top) with the strong adsorption of PBP (see Figure 2a, bottom, and Figure S4a) on the TiO_2 film under otherwise identical reaction conditions before UV irradiation. Unlike the characteristic peaks of PBP,

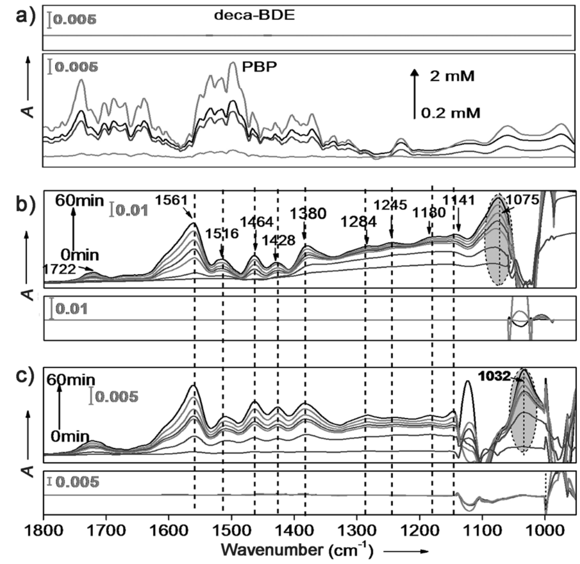


Figure 2. a) Top panel shows ATR-FTIR spectra of 0.1 mM deca-BDE in nonane on TiO_2 and ZnSe crystal. Bottom panel shows spectra for 0.2 mM, 0.7 mM, and 2 mM PBP in nonane on TiO_2 (the upper three), as well as 2 mM PBP on ZnSe crystal (the downmost). b,c) Time series spectra for 10^{-5} M deca-BDE on TiO_2 in $[D_0]$methanol and $[D_4]$methanol, respectively, with irradiation from 0 to 60 min. Bottom panels represent background spectra from methanol, thus showing interference peaks appearing in irradiation spectra in top panels.

which increased with the increasing concentration, almost no adsorption peak was observed in the spectra of deca-BDE (Figure 2a, top). The control experiment indicated that extremely hydrophobic polyhalogenated aromatics were indeed incapable of approaching the polar, hydrophilic TiO_2 surface for adsorption. Under UV irradiation (Figures 2b and c), several peaks in the 1030–1750 cm^{-1} region appeared and increased substantially with time. Among the peaks, the newly formed peak at 1722 cm^{-1} was identified as a C=O stretching vibration for formaldehyde, which was formed by the oxidation of methanol by h^+_{vb}, as was observed for $[D_4]$methanol. Most significantly, the four absorption bands between 1400–1600 cm^{-1} could not be attributed to the formaldehyde product (according to Figure S4b and S4c), but were instead assigned to the C=C stretching vibration of the benzene ring. The peaks at approximately 1380 cm^{-1} were attributed to the characteristic absorption of deca-BDE, according to its standard IR spectra. In addition, the peaks at approximately 1284 cm^{-1} corresponded to the C–O stretching vibration of deca-BDE, and the peaks between 1140 and 1240 cm^{-1} were identified as the various bending vibration modes with skeletal vibration of deca-BDE. Given that all the final products could not be adsorbed, and generated identical ATR-FTIR signals to that of deca-BDE, the peaks which were not significantly affected by either $[D_0]$methanol or $[D_4]$methanol demonstrated the formation of adsorbable intermediates which retained the typical skeletal vibrations of deca-BDE. Note that one peak was dramatically shifted in the $[D_0]$methanol system (1075 cm^{-1}; Figure 2b, in shadow) relative to its position in the $[D_4]$methanol system (1032 cm^{-1}; Figure 2c, shaded area). The shift of 43 cm^{-1} was in agreement with the H/D displacement of one bending vibration mode of the benzene ring and did not correspond to the primary isotope effect because the C–D and O–D stretching vibration wave numbers (2500–2000 cm^{-1}) were 0.7–0.8 times those of C–H and O–H (3500–3000 cm^{-1}). The result indicated that a) an aromatic cation intermediate, deca-BDE-H^+ or deca-BDE-D^+, was formed and could be adsorbed onto the photocatalyst surface and b) the ΔZPE of deca-BDE-D^+ was substantially smaller than that of deca-BDE-H^+.

We also observed that the amount of the intermediate continued to increase even after the irradiation was terminated (Figure S4 d and S4 e), thus demonstrating that the h^+_{vb} oxidation ended with the termination of the irradiation, whereas the combination of e^-_{cb} and H^+ was hysteretic. We calculated the intensity change of the peak at 1561 cm^{-1} after the light was shut off for both [D_0]methanol and [D_4]methanol. The plot of the intensity versus time (see Figure S5) shows linear relationships for both [D_0]methanol and [D_4]methanol. Considering the charged intermediate as the "initial reactant" in the dehalogenation, we obtained the actual KIE (not KSIE) between deca-BDE-H^+ and deca-BDE-D^+. The KIE behavior was caused by rehybridization of the sp^2-carbon atom of the aromatic ring to the sp^3-carbon atom (Figure 3), and was certainly inverse. Defining the

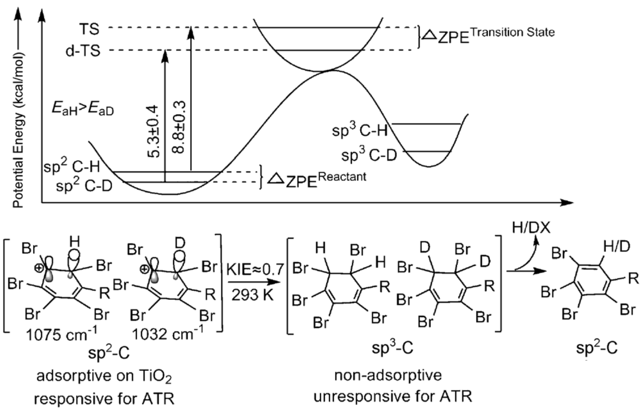


Figure 3. Potential diagram of the deca-BDE dehalogenation by TiO_2 photocatalysis.

reciprocal of the slope as the consumption rate of the protonated intermediate, resulted in a KIE of approximately 0.72 for the "reaction" at approximately 293 K. The value shows that the KSIE for the complete reaction between deca-BDE and an alcohol included the KIE for the consumption of deca-BDE-H^+/D^+. By separately determining the temperature-dependent rates (Arrhenius plots) for both [D_0]methanol and [D_4]methanol (see Figure S6), we calculated the difference in the activation energies ($\Delta E_{H/D} \approx 3.5$ kcal mol^{-1}; case D had a lower activation energy) which was associated with the formation of the tetrahedral intermediate, thus illustrating the activation energy for the vibration of the C–D bond is smaller than that of the C–H bond (Figure 3).

Both theory and experiment show that the aromatic ring can be protonated by a superacid, such as a magic acid or HF-SbF_5, to form a carbocation.[12] In the present system, the methanol was oxidized by h^+_{vb} to release two protons which may have quite strong acidity because there is no free formed conjugate base except for the electrons in the conduction band of the TiO_2. Thus, the conjugate base may have been the weakest base because the bulky nanoparticle could significantly delocalize the negative charges.[13] Therefore, any addition of common acids into the reaction system, as a result of the synchronous introduction of the conjugated base, would weaken the strong acidity of protons and thus inhibit the reaction.[9a] Thus, we concluded that, after the diffusion equilibrium, the redundant protons diffused into the solution and reacted with deca-BDE to form an adsorbable, protonated intermediate, and then adsorbed to the TiO_2 surface where they were stable enough to be observed by ATR-FTIR, and underwent an ET reaction with e^-_{cb} to form dehalogenated products.

In conclusion, we discovered a clear inverse KSIE in the TiO_2 photocatalysis of intermolecular dehalogenation reactions between alcohols and aromatic halides which were intrinsically incapable of being adsorbed onto the TiO_2. Protonation of these substrates was required for the next ET on TiO_2 surface.

Received: September 23, 2014
Published online: [redacted]

Keywords: electron transfer · isotope effects · photocatalysis · surface chemistry · titanium

[1] a) A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37; b) Z. Zou, J. Ye, K. Sayama, H. Arakawa, *Nature* **2001**, *414*, 625–627; c) A. Kudo, Y. Miseki, *Chem. Soc. Rev.* **2009**, *38*, 253.
[2] a) F. Parrino, A. Ramakrishnan, H. Kisch, *Angew. Chem. Int. Ed.* **2008**, *47*, 7107–7109; *Angew. Chem.* **2008**, *120*, 7215–7217; b) H. Kisch, *Angew. Chem. Int. Ed.* **2013**, *52*, 812–847; *Angew. Chem.* **2013**, *125*, 842–879; c) M. R. Hoffmann, S. T. Martin, W. Y. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96.
[3] a) H. Park, W. Choi, *J. Phys. Chem. B* **2004**, *108*, 4086–4093; b) X. J. Lang, W. H. Ma, C. C. Chen, H. W. Ji, J. C. Zhao, *Acc. Chem. Res.* **2014**, *47*, 355–363; c) X. J. Lang, X. D. Chen, J. C. Zhao, *Chem. Soc. Rev.* **2014**, *43*, 473–486.
[4] a) D. Mitoraj, H. Kisch, *Angew. Chem. Int. Ed.* **2008**, *47*, 9975–9978; *Angew. Chem.* **2008**, *120*, 10123–10126; b) J. W. Tang, J. R. Durrant, D. R. Klug, *J. Am. Chem. Soc.* **2008**, *130*, 13885–13891.
[5] a) C. D. Jaeger, A. J. Bard, *J. Phys. Chem.* **1979**, *83*, 3146–3152; b) C. Maillard-Dupuy, C. Guillard, H. Courbon, P. Pichat, *Environ. Sci. Technol.* **1994**, *28*, 2176–2183; c) N. M. Dimitrijevic, E. Rozhkova, T. Rajh, *J. Am. Chem. Soc.* **2009**, *131*, 2893–2899; d) P. Pichat, *Appl. Catal. B* **2010**, *99*, 428–434.
[6] a) R. Nakamura, A. Imanishi, K. Murakoshi, Y. Nakato, *J. Am. Chem. Soc.* **2003**, *125*, 7443–7450; b) R. Nakamura, Y. Nakato, *J. Am. Chem. Soc.* **2004**, *126*, 1290–1298; c) R. Nakamura, T. Okamura, N. Ohashi, A. Imanishi, Y. Nakato, *J. Am. Chem. Soc.* **2005**, *127*, 12975–12983.
[7] a) W. Y. Choi, M. R. Hoffmann, *Environ. Sci. Technol.* **1995**, *29*, 1646–1654; b) S. Higashimoto, K. Okada, M. Azuma, H. Ohue, T. Terai, Y. Sakata, *RSC Adv.* **2012**, *2*, 669–676; c) P. K. J. Robertson, D. W. Bahnemann, L. A. Lawton, E. Bellu, *Appl. Catal. B* **2011**, *108*, 1–5.
[8] L. N. Li, W. Chang, Y. Wang, H. W. Ji, C. C. Chen, W. H. Ma, J. C. Zhao, *Chem. Eur. J.* **2014**, *20*, 11163–11170.

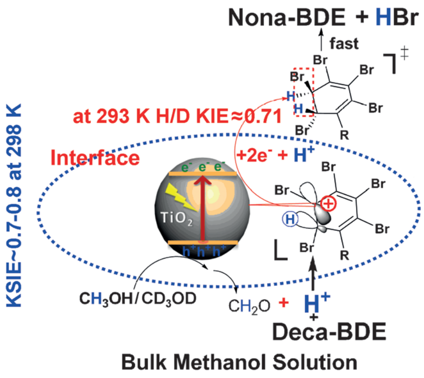
[9] a) C. Y. Sun, D. Zhao, C. C. Chen, W. H. Ma, J. C. Zhao, *Environ. Sci. Technol.* **2009**, *43*, 157; b) C. Y. Sun, C. C. Chen, W. H. Ma, J. C. Zhao, *Sci. China Chem.* **2012**, *55*, 2532 – 2536.
[10] E. V. Anslyn, D. A. Dougherty, *Morden Physical Organic Chemistry*, University Science Books, Herndon, VA, **2005**, pp. 401 – 420.
[11] D. S. Muggli, J. T. McCue, J. L. Falconer, *J. Catal.* **1998**, *173*, 470 – 483.
[12] a) J. Sommer, M. Hashoumy, J. C. Culmann, J. Bukala, *New J. Chem.* **1997**, *21*, 939 – 944; b) J. Jašík, D. Gerlich, J. Roithová, *J. Am. Chem. Soc.* **2014**, *136*, 2960.
[13] J. N. Schrauben, R. Hayoun, C. N. Valdez, M. Braten, L. Fridley, J. M. Mayer, *Science* **2012**, *336*, 1298.

Communications

Surface Chemistry

W. Chang, C. Sun, X. Pang, H. Sheng, Y. Li, H. Ji, W. Song, C. Chen, W. Ma,* J. Zhao* ——— ■■■■–■■■■

Inverse Kinetic Solvent Isotope Effect in TiO_2 Photocatalytic Dehalogenation of Non-adsorbable Aromatic Halides: A Proton-Induced Pathway



A change up: Reported herein is an inverse kinetic solvent isotope effect (KSIE) for the reductive dehalogenation of decabromodiphenyl ethers (deca-BDEs). The transformation under TiO_2 photocatalysis involves a proton adduct intermediate which accompanies a hybridization change from sp^2 to sp^3 for an aromatic carbon atom. The protonation event leads to adsorption of the aromatic halides onto TiO_2 with a subsequent electron-transfer reaction to form dehalogenated products.