Oxidative Decomposition of Rhodamine B Dye in the Presence of VO$_2^+$ and/or Pt(IV) under Visible Light Irradiation: N-Deethylation, Chromophore Cleavage, and Mineralization

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In order to make clear the roles of dissolved O$_2$ in the photocatalytic decomposition of organic pollutants and to discriminate different degradation pathways (N-deethylation, chromophore cleavage, and mineralization) during the degradation of dye, the photodegradation of rhodamine B (RhB) has been investigated using vanadate and/or platinum species as electron acceptors in the presence or absence of O$_2$ under visible light irradiation. It was found that with VO$_2^+$ as electron acceptor, RhB underwent efficient N-deethylation under visible light irradiation and O$_2$ was found to slow down this process significantly. Little mineralization has been observed in the presence and absence of O$_2$ in VO$_2^+$ systems. By contrast, Pt(IV) resulted in the cleavage of conjugated chromophore structure (bleaching) of RhB dye under the otherwise identical conditions. In this case, the presence of O$_2$ did not affect the bleaching rate of the dye, but enhanced greatly the mineralization. Both cleavage of conjugated chromophore structure and N-deethylation occurred simultaneously upon the coaction of VO$_2^+$ and Pt(IV) under visible light irradiation. The mineralization yield of the combined system was evidently higher than the expected summation of separate ones. TOC, XPS, and ESR results indicate that in the VO$_2^+$ and Pt(IV) combined system VO$_2^+$ not only oxidized RhB leading to deethylation but also oxidized the reduced Pt(II) to regenerate Pt(IV) leading to the further cleavage of chromophore structure of RhB, which behaved quite different from the separate ones. A mechanism was also proposed to interpret the different pathways for the oxidative photodecomposition of RhB under visible irradiation.

Introduction

It is known that dye can absorb visible light forming an electronically excited-state which exhibits much higher redox activity than its ground state. On the basis of this, visible-induced electron transfer of dyes have had extensive application in many fields such as the removal of pollutants, photochemistry, and photoelectrochemical devices. For example, various types of dyes can inject electron from the excited-state of the dye onto the conduction band of TiO$_2$, which would result in the degradation and mineralization of the dyes under visible irradiation.[1−5] The visible irradiation was also found to greatly accelerate the degradation of dyes by Fenton reagent (Fe^{III}/H$_2$O$_2$) via electron transfer from the excited dye to Fe^{III}.[6,7]

A foundational issue in the photocatalytic degradation of dye under visible irradiation is the relationship between the mineralization of the dye and dissolved O$_2$. It has been proposed that a series of reactive oxygen species, O$_2$•$^−$/HOO•, H$_2$O$_2$, and •OH that derived from dissolved O$_2$ in the TiO$_2$/dyes systems, play an important role on the degradation pathways of dyes under visible irradiation.[8,9] Owing to the complicacy of the heterogeneous system and differences between interfaces and aqueous solution, the role of O$_2$ during the degradation of dye under visible irradiation is still unclear.

During our earlier studies on TiO$_2$-mediated photodegradation of dyes under visible irradiation, we noted that some of *N*-alkylamine-containing dyes, such as rhodamine-B,[10] sulfo-

rhodamine-B,[11] and crystal violet,[12] appeared to photodegrade via two competitive pathways: an N-dealkylation process and a cleavage of the whole conjugated chromophore structure. To discriminate the two kinds of decomposition pathways is of high importance to better understanding visible-induced electron transfer and degradation of dyes. Depending on the photoreaction systems, we have proposed two reaction mechanisms for the different pathways. One is attributed to the different adsorption modes of the dye on the surface of the photocatalyst by the addition of anionic surfactant to change the adsorption modes.[11] Another proposed mechanism for the two pathways involves the formation of reactive oxygen species by photoelectrocatalytic study of a TiO$_2$-film electrode[13] and using SiW$_{12}$O$_{40}$$^{4−}$ as an analogue of the TiO$_2$.[14] However, the mechanistic details for the two pathways still remain unclear and need to be investigated further.

In acidic solution, vanadium(V) and Pt(IV) are moderately strong oxidizing agents. There have been numerous studies of oxidation of organic compounds stoichiometrically by aqueous solution of vanadium(V)[15−17] in the dark and Pt(IV)[18,19] under light irradiation. In these reactions, the high valent metals (V(V) and Pt(IV)) can be readily reduced to V(IV) and Pt(II), respectively, which are difficult to react with O$_2$ dissolved in the solution. If we employ vanadium(V) and Pt(IV) as oxidative species, the formation of reactive oxygen species, just as in the case of TiO$_2$ photocatalysis, can be purposely avoided, which makes it possible to investigate the reaction pathways of the dye radical cation following electron transfer. On the other hand, the different interaction modes of V(V) and Pt(IV) species with the dye also provide an excellent approach for our understanding

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of the interaction-dependent degradation pathways of dyes under visible irradiation.

In this paper, the visible-light-induced electron transfer and degradation of RhB were examined using VO_2^+, Pt(IV), and both of them as electron acceptors. The main aim of the present investigation was (a) to estimate the relative importance of O_2 in the degradation of organic compounds, (b) to gain insight into the relationship of the interaction modes between dye and electron acceptor with the degradation pathways of dye, (c) to uncover and assess the differences between VO_2^+ and Pt(IV), (d) to provide greater understanding of the reaction mechanism of the visible-light-induced degradation of dyes. It was found that RhB underwent an efficient N-deethylation process in the presence of VO_2^+ under visible light irradiation, while Pt(IV) resulted in the conjugated chromophore structure cleavage and even mineralization of RhB dye under otherwise identical conditions. Both conjugated chromophore structure cleavage and N-deethylation occurred simultaneously upon the coaction of VO_2^+ and Pt(IV) under visible light irradiation. Dissolved oxygen enhanced neither N-deethylation nor chromophore structure cleavage of RhB, but is essential to the mineralization of the dye.

Experimental Section

Materials. Rhodamine B, *N,N*-dimethylaniline (DMA), and benzoic acid were of analytical reagent grade and used without further purification. The H_2PtCl_6 was obtained from Shenyang Jinke Reagent Factory. K_2PtCl_4 was purchased from Beijing Chemicals Co. $Na_2(NH_4)_4V_{10}O_{28}$ and $VOSO_4$, which were purchased from Sigma-Aldrich Co., were used as the precursors of the V(V) and V(IV) species, respectively. It should be pointed out that there is a pH-dependent equilibrium among the oxovanadium species in aqueous solution. Under our experimental conditions (pH = 1.6), the V(V) species should be VO_2^+,[20] which will be used to denote the oxovanadium species except noted elsewhere. $NaVO_3$, purchased from Tianjin Yuanhang Chemicals Co., was used as another kind of V(V) species which showed similar experimental results to that of $Na_2(NH_4)_4V_{10}O_{28}$. Deionized and doubly distilled water was used throughout this study. The pH of the solutions was adjusted by dilute aqueous solutions of H_2SO_4.
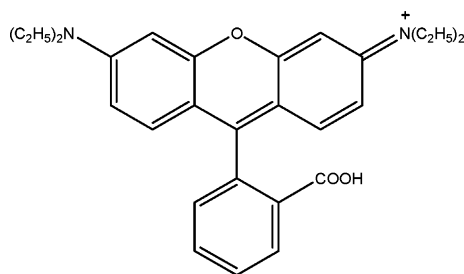
Rhodamine B (RhB)

Photoreactor and Light Source. A 500-W halogen lamp was positioned inside a cylindrical pyrex vessel surrounded by a circulating water jacket to cool the lamp. A cutoff filter was placed outside the jacket to completely remove any radiation below 450 nm and to ensure illumination by visible light only. The 100 W Hg lamp (Toshiba Lighting and Technology Corporation of Japan) was used as a UV light source.

Procedure and Analysis. All the irradiation experiments were carried out in a Pyrex vessel (50 mL). At given intervals, samples (3 mL) were taken out and then analyzed by a Lambda Bio 20 UV/visible spectrophotometer (Perkin-Elmer). Pt(IV) at
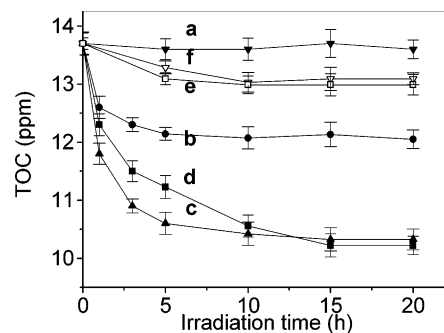

Figure 1. TOC changes of RhB under visible irradiation in the presence of VO_2^+ (1.6×10^{-3} M) (a), Pt(IV) (8×10^{-5} M) (b), Pt(IV) (3.2×10^{-3} M) (c), and VO_2^+ (1.6×10^{-3} M)/Pt(IV) (8×10^{-5} M) combined system (d) in the aerated solution; Pt(IV) (3.2×10^{-3} M) (e) and VO_2^+-(1.6×10^{-3} M)/Pt(IV) (8×10^{-5} M) combined system (f) under helium atmosphere. Initial concentration of RhB: 4×10^{-5} M.

higher concentration (1.6×10^{-4} M) completely destroyed the conjugated chromophore structure of RhB (2×10^{-5} M). Therefore, to understand and observe the role of VO_2^+, the concentration of Pt(IV) was optimized at 4×10^{-5} M, which practically degraded the RhB but allowed us to observe evidence for the role of VO_2^+ in the subsequent degradation of RhB. The concentration of VO_2^+ used was 8×10^{-4} M, which was sufficient enough to regenerate Pt(IV) involved in the degradation reaction. The experiments were carried out with air, He, or O_2 atmosphere bubbled through the reaction bottle separately. Electron paramagnetic resonance (EPR) experiments were performed with a Bruker (E500) spectrometer. The parameters for determination of vanadium signals were as follows: center field, 3525; sweep width, 1200.0G; microwave frequency, 9.78 GHz; power, 50 mW. The photodegradation of small molecules *N,N*-dimethylaniline (DMA) and benzoic acid was analyzed by high performance liquid chromatography (HPLC) on an Inertsil ODS-3 5 μm column (250 × 4.6 mm) at room temperature. Signals for *N,N*-dimethylaniline (DMA) were detected at 243 nm by using an eluent composed of methanol/water (65/35, v/v) and benzoic acid were detected at 229 nm by using methanol/water (50/50, v/v) at a flow rate of 1.0 mL min^{-1}. The determination of N-deethylation intermediates were performed according to our previous paper.[12] X-ray photoelectron spectroscopic (XPS) examination of the samples was carried out on the 2201-XL multifunctional spectrometer (VG Scientific England) using Al Kα radiation. Changes in total organic carbon (TOC) were determined using a total organic carbon analyzer (Model TOC-Aopllo 900). For TOC determination, the concentration of Pt(IV) was taken as 3.2×10^{-3} M that is theoretically sufficient for complete mineralization of RhB.

Results and Discussion

Total Organic Carbon Changes. The decrease in the TOC of solution reflects the mineralization of dye. Temporal changes of TOC in the photodegradation of RhB in different systems are depicted in Figure 1. In the VO_2^+ system, the TOC value of the solution hardly changed during the photoreaction even under air atmosphere (curve a). In the Pt(IV) (3.2×10^{-3} M) case, mineralization of the dye molecules occurred only to a negligible extent under helium atmosphere (curve e). Under air atmosphere, however, the TOC decreased quickly from 13.7 to 10.6 ppm in the first 5 h reaction. After another 15 h of irradiation, the TOC almost did not change anymore (curve c), indicating that the dye cannot be mineralized completely even in the presence of excess Pt(IV), and that the degraded colorless fragments undergo no decomposition with further irradiation.
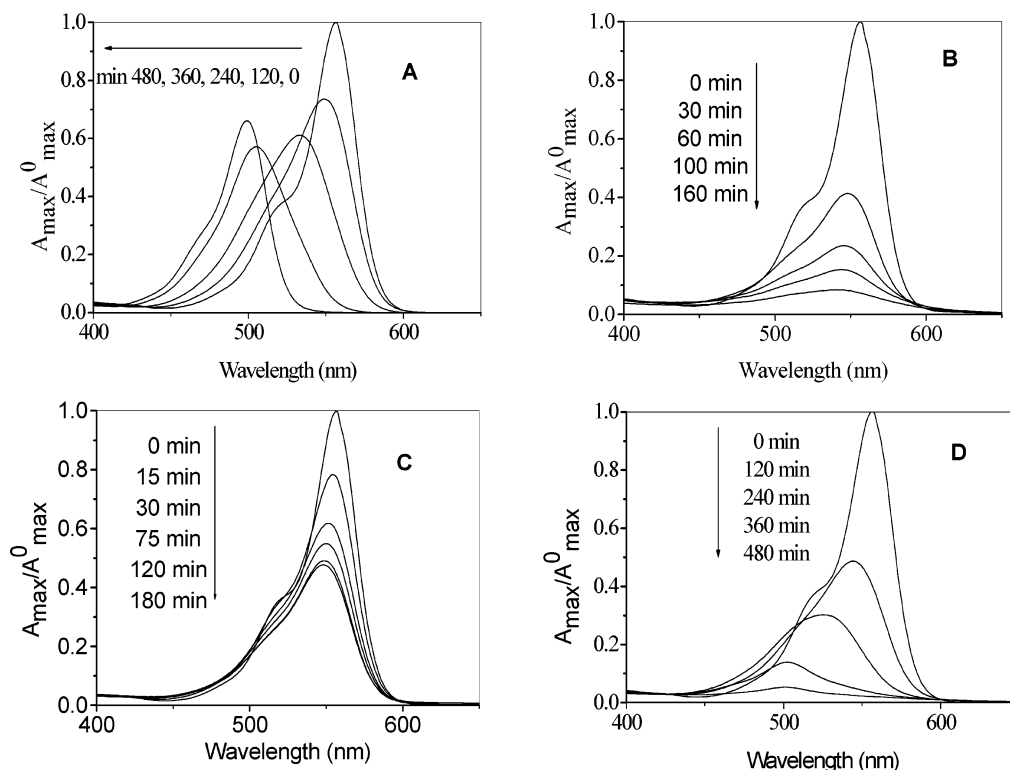
Figure 2. The temporal absorption spectrum changes of RhB taking place in the presence of VO_2^+ (A), Pt(IV) 1.6×10^{-4} M (B), Pt(IV) 4×10^{-5} M (C) and both Pt(IV) 4×10^{-5} M and VO_2^+ (D) under visible light irradiation in the aerated solution. The initial concentration: RhB 2×10^{-5} M, VO_2^+ 8×10^{-4} M, pH = 1.6.

When the initial concentration of Pt(IV) decreased to 2 times (8×10^{-5} M) that of RhB, the elimination of TOC in the RhB solution leveled off finally at a value of ca. 12.1 ppm under air atmosphere (curve b). In the combined VO_2^+ (16×10^{-4} M)/Pt(IV) (8×10^{-5} M) system, after 20 h of irradiation the TOC of the solution decreased to 10.2 ppm and about 25% of TOC was removed (curve d). The mineralization yield of the combined system is evidently higher than the expected summation of separate ones (curves a and b). The rate of mineralization of RhB was found to be highly dependent on the concentration of Pt(IV), e.g., the mineralization of RhB during the first hour of irradiation increased from 1.1 to 1.9 ppm as the initial concentration increased from 8×10^{-5} M (curve b) to 3.2×10^{-3} M (curve c). The mineralization rate of the aerated combined system, i.e., VO_2^+ (1.6×10^{-3} M)/Pt(IV) (8×10^{-5} M) (curve d), was slower than that of the Pt(IV) (3.2×10^{-3} M) only (curve c) system in the first 5 h because of its lower Pt(IV) concentration, and then the Pt(IV) was used up quickly in the Pt(IV) only system and mineralization stopped, while Pt(IV) was regenerated in the combined system to continue the mineralization process. Although the RhB solution was completely bleached in the presence or absence of O_2 (see below), no significant TOC removal of RhB was observed in all systems under helium atmosphere (curve f). It is apparent that O_2 is essential for the mineralization of dye.

N-Deethylation and Conjugated Chromophore Structure Cleavage of RhB in the Presence of VO_2^+ or/and Pt(IV) under Visible Light Irradiation. RhB underwent pronounced photogradation in the presence of VO_2^+ or/and Pt(IV) under visible light irradiation. The temporal absorption spectra changes of RhB taking place in the presence of VO_2^+ or/and Pt(IV) under visible light irradiation are displayed in Figure 2. When VO_2^+ was used as an electron acceptor, the absorption maximum of the solution exhibited significant hypsochromic shifts during visible light irradiation. The maximum absorption band of the

solution shifted from 556 to 498 nm after irradiation for 480 min (Figure 2A), and the reacted solution had similar spectrum characteristics to those of the rhodamine 110 (the full N-deethylated products of RhB) solution. Our earlier studies[10,14] have proved that these hypsochromic shifts are attributed to the formation of a series of N-deethylated intermediates of RhB, and this time we also observed the stepwise N-deethylation intermediates of RhB using HPLC (Supporting Information Figure S1). From molar extinction coefficients (1.15×10^3 and 8.4×10^4 $M^{-1}cm^{-1}$ for RhB and rhodamine 110, respectivly[21]), about 91% of the xanthene-conjugated chromophore structure of RhB remained intact after 480 min of irradiation. This evidence clearly indicates that N-deethylation predominates over the cleavage of the aromatic ring of the RhB dye in the VO_2^+ system. After the *N*-ethyl groups were fully removed, the spectral changes of solution became rather slow and nearly stopped with further irradiation. Since the amount of VO_2^+ (8×10^{-4} M) is much greater than that of the RhB (2×10^{-5} M), the stop of the photoreaction implies that the full N-deethylated product of RhB has little photoreactivity with VO_2^+. The controlled experiment by using rhodamine 110 as the initial dye also supported this argument. When $VOSO_4$ was used as the oxidant, however, no photoreaction of RhB was observed, suggesting that V(IV) has no activity when reduced from V(V) in the VO_2^+/RhB photoreaction system.

In the presence of Pt(IV) (1.6×10^{-4} M), however, the characteristic absorption of RhB around 556 nm decreased to about zero within 160 min. In contrast to the VO_2^+ system, the hypsochromic shift of the absorption maximum was relatively insignificant (Figure 2B). It indicates that, instead of the N-deethylation as in the VO_2^+ case, the visible irradiation leads to a dominant cleavage of the whole conjugated chromophore structure of RhB in the presence of Pt(IV). When the initial concentration of Pt(IV) decreased to 4×10^{-5} M, however, the maximum absorption decreased rapidly at the initial 2 h and

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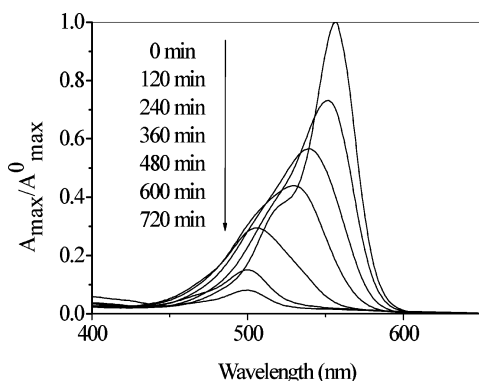*J. Phys. Chem. B, Vol. 110, No. 51, 2006* **26015**

Figure 3. The temporal absorption spectrum changes of RhB taking place in the presence of Pt(II) and VO_2^+ under visible light irradiation in the aerated solution. The initial concentration: RhB 2×10^{-5} M, Pt(II) 4×10^{-5} M, VO_2^+ 8×10^{-4} M, pH = 1.6.

then remained at that level under the continued irradiation (Figure 2C). Moreover, when, instead of Pt(IV), Pt(II) was used as the oxidant of RhB, no reaction was observed under visible light irradiation. All these facts suggest that the stop of the photoreaction is due to the Pt(IV) being reduced to Pt(II).

When VO_2^+ and Pt(IV) (4×10^{-5} M) coexisted in the RhB aqueous solution, after 480 min of irradiation by visible light, the maximum absorption band shifted from 556 to 498 nm and concomitantly the absorbance of the solution decreased rapidly to about zero (Figure 2D), indicating that both the N-deethylation and the cleavage of the conjugated chromophore structure occurred simultaneously in the presence of both VO_2^+ and Pt(IV) solution. As mentioned above, no photoreaction occurred in the Pt(II) or VO^{2+} case. However, after addition of VO_2^+ into the Pt(II)/RhB solution, both the N-deethylation and the conjugated chromophore cleavage of RhB were observed under visible light irradiation (Figure 3), which was similar to the results observed in the RhB/VO_2^+/Pt(IV) system. More interestingly, after Pt(IV) was reduced completely to Pt(II) by the visible light-excited RhB (as in Figure 2C), the addition of VO_2^+ into this system not only led to the hypsochromic shift of the maximum absorption of the reacted solution, as observed in the VO_2^+ alone system, but also a rapid decrease in the absorption maximum occurred concomitantly (Supporting Information Figure S2), which was also similar to the result in the combination system of Pt(IV) and VO_2^+. From the viewpoint of thermodynamics, the redox potentials of $E^0(PtCl_6^{2-}/PtCl_4^{2-})$ = +0.68 V vs NHE[22] is lower than that of $E^0(VO_2^+/VO^{2+})$ = +1.00V vs NHE.[23] Therefore, it is evident that the Pt(II) species can be oxidized to Pt(IV) by the VO_2^+ (see below for further support) and the formed Pt(IV) species are responsible for the conjugated structure cleavage of RhB. This suggests that, in the coexistence system of Pt(IV) and VO_2^+, the role of VO_2^+ is 2-fold: the first role is to propel the N-deethylation process of RhB by accepting electrons from the excited dye, just as in the VO_2^+ only system. The second role is to regenerate the reduced Pt(II) to its original Pt(IV) form; the regenetated Pt(IV) species can then degrade the dye again.

In control experiments, we heated up the reaction solution to 60 °C in the dark and found that Pt(IV) did not cause the degradation of RhB, but VO_2^+ led RhB to N-deethylate slowly, which was insignificant compared with that under visible light irradiation. In the absence of VO_2^+ and Pt(IV), negligible degradation of RhB was observed under visible light irradiation. Neither benzoic acid nor DMA, which are analogues of the carboxyl and N-ethyl moieties of the RhB molecule, respectively, showed significant decomposition under visible light

irradiation in the presence of Pt(IV) or/and VO_2^+. These observations indicate that photoreaction is initiated from the excited-state of RhB by visible light in both systems, which is similar to that in the TiO$_2$/RhB/visible light[6] and Fe(III)/H$_2$O$_2$/RhB/visible light[7] systems.

Effect of Dissolved Oxygen on the Photoreaction of RhB. The changes in the absorption maxima of the solutions during the photodegradation of RhB in VO_2^+, Pt(IV) and combined Pt(IV)/VO_2^+ systems in the presence (aerated or purged by O$_2$) and absence (deaerated by He) of O$_2$ are illustrated in Figure 4. In the presence of VO_2^+ (Figure 4A), the absorption maxima decreased in the early stage of the photoreaction, which is attributed to the decrease in molar extinction coefficients of the N-deethylated intermediates relative to the parent RhB (ϵ_{max} = 11.5, 5.5, 7.2, 6.1, and 8.4×10^4 M^{-1} cm^{-1} for RhB, one-, two-, three-, and four-deethylated intermediates, respectivly[21]). At the late stage, the full N-deethylated intermediate has a higher molar extinction coefficient than other intermediates, and then the absorption maxima began to increase and finally remained unchanged after irradiation for 5 and 8 h under He and air atmospheres, respectively. Correspondingly, the maximum absorption band of the solution shifted from 556 to 498 nm in 5 and 8 h in the deaerated and aerated systems (inset in Figure 4A), respectively. It is evident that the absorption band shift in the deaerated system was faster than that in the aerated solution. It should also be pointed out that about 97% of the xanthene-conjugated chromophore structure of RhB remained in the deaerated system after complete N-deethylation, which is higher than that in the air (91%). This suggests that the presence of O$_2$ can lead to the cleavage of the conjugated structure of RhB in the VO_2^+ system to some extent. It seems that O$_2$ in the system participates in the deeper oxidation (conjugated chromophore structure cleavage) and slows down the deethylation process. In the Pt(IV) case, O$_2$ has no obvious effect on the decrease rate of the absorption maxima of RhB (Supporting Information Figure S3). This may be due to the cleavage of the conjugated chromophore structure of RhB in the presence or absence of O$_2$ and the rapid reaction between RhB and Pt(IV). In the combined VO_2^+/Pt(IV) system, the decrease rate of the absorption maxima and the maximum absorption band shift under O$_2$ atmosphere were slower than that under the air atmosphere (Figure 4B, curves c and b, respectively), whereas the rates became higher under the helium atmosphere (Figure 4B, curve a). However, the mineralization yield of RhB under the air atmosphere outclassed that under the helium atmosphere. The slower changes in the absorption maxima and the lambda shift when oxygen was present in the combined system may also be due to the competing reaction of O$_2$, which leads to the deeper oxidation (mineralization) of RhB. The detailed mechanism of the effect of O$_2$ needs further study.

Reduced Pt and V Species during Photoreaction of RhB. H$_2$PtCl$_6$ is one of the simplest coordination compounds of platinum and can be reduced to Pt(0) or Pt(II) via four-electron or two-electron reduction, respectively. In this study, XPS technique was employed to examine the final valence state of the reduced Pt species after the degradation of RhB in the combined system under visible light irradiation as shown in Figure 5. With either Pt(IV) or Pt(II) as the precursors of Pt species in the presence of VO_2^+, the XPS spectra showed similar features for Pt(II) (with banding energy of 72.5 eV) and Pt(IV) (with banding energy of 74.3 eV), and the ratios between Pt(IV) and Pt(II) were ca. 1:5 in both cases, suggesting that the platinum exists as the same valence states after the reaction regardless of its initial form. The presence of Pt(II) in the VO_2^+/
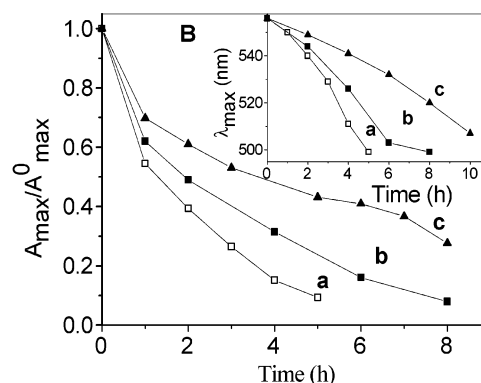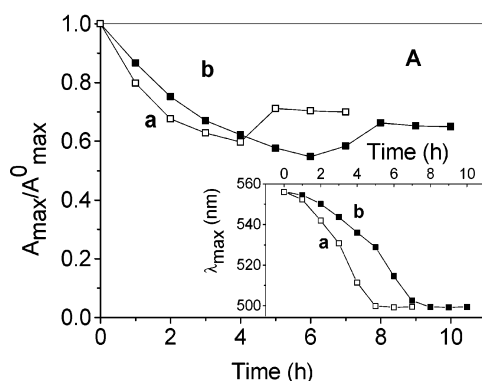
Figure 4. The changes in the absorption maxima of the solutions during the photodecomposition of RhB in VO_2^+ (A) and combined $Pt(IV)/VO_2^+$ (B) systems in the absence (a is He atmosphere) and presence (b is air atmosphere, and c is O_2 atmosphere) of O_2. The insets in A and B: the corresponding maximum absorption band shift of the solutions during irradiation. The initial concentration: RhB 2×10^{-5} M, VO_2^+ 8×10^{-4} M, Pt(IV) 4×10^{-5} M pH = 1.6.

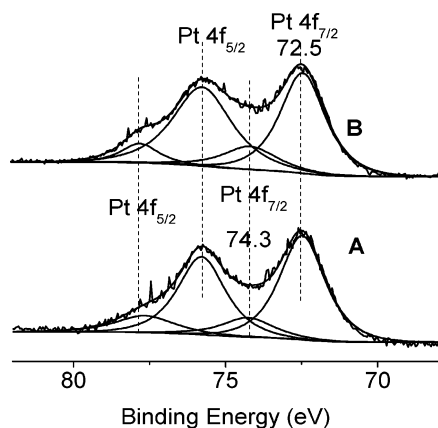**Figure 5.** X-ray photoelectron spectra of Pt species at the end of the visible light-induced bleaching of RhB. A: $VO_2^+/Pt(II)/RhB$. B: $VO_2^+/Pt(IV)/RhB$.

Figure 6. EPR spectra. a: VO_2^+ aqueous solution in the dark. b: after N-deethylation of RhB (2×10^{-5} M) in the presence of VO_2^+ (8×10^{-4} M) under visible irradiation (8 h). c: RhB degradation in the presence of both VO_2^+ (8×10^{-4} M) and Pt(IV) (4×10^{-5} M) under visible irradiation for 8 h.

Pt(IV)/RhB system indicates the Pt(IV) was reduced to its lower valence Pt(II) by the excited dye (Figure 5B). When Pt(II) was used as the precursor of Pt species, the Pt(IV) was formed during the reaction, which is derived from the oxidation of Pt(II) by the VO_2^+ (Figure 5A). No elemental Pt(0) (of which the binding energy is 70.9 eV) was found in both systems, indicating that Pt(IV) is difficult to reduce to Pt(0) under the present experimental conditions.

It has been reported that VO_2^+(V) aqueous solution is EPR-silent, but VO^{2+}(IV) has a single unpaired electron in its lowest nondegenerated d_{xy} orbital. In a magnetic field, this electron interacts with the ^{51}V nucleus which has a nuclear spin $I = 7/2$, producing a sharp isotropic eight-line ESR spectrum at room temperature.[24,25] In this study, the EPR was employed to examine the valence state of reduced V(IV). The EPR spectra under different conditions are illustrated in Figure 6. For the VO_2^+(V) solution, as expected, no EPR signal was detected (curve a). After the N-deethylation photoreaction in the RhB/VO_2^+ system, the solution presented strong eight-line EPR signals of VO^{2+} (curve b), which indicates that VO_2^+(V) is reduced to VO^{2+}(IV) via visible-light-induced electron transfer from the excited dye to VO_2^+(V). The addition of Pt(IV) into the RhB/VO_2^+ system led to a great enhancement in signal intensity of VO^{2+}(IV) signals (curve c), which is attributed to reduction of VO_2^+ by the formed Pt(II) during the photoreaction.

Reaction Pathway. There are many investigations for oxidative N-dealkylation of alkylamine in electrochemical, enzymatic, and photochemical systems.[26−28] The proposed mechanism for the P-450-mediated dealkylation by overall two-electron oxida-
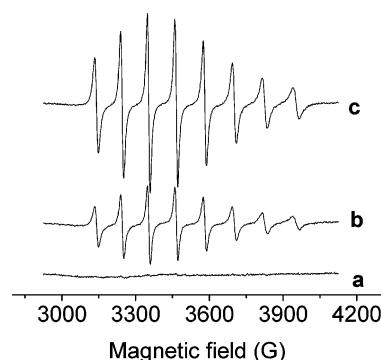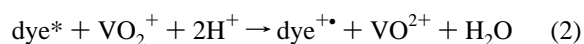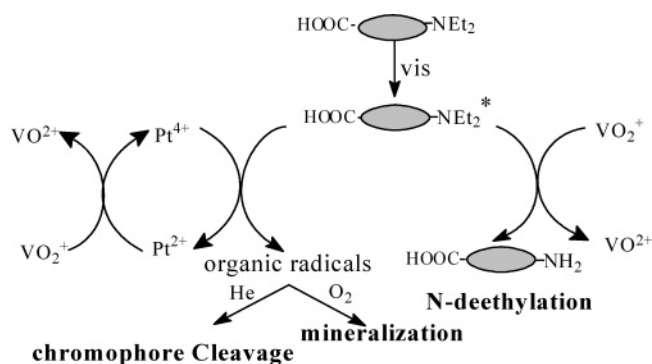
tion focused on either the single electron transfer (SET) from the nitrogen lone pair of the substrate to the catalyst or an initial hydrogen atom transfer (HAT) from the α-carbon atom of the substrate to catalyst.[27] In the photochemical systems, both the SET and HAT pathways were proposed. For example, the N-dealkylation of atrazine has been attributed to HAT in the polyoxometalate-mediated photodegradation under UV irradiation.[28] In the study on visible-induced photoreaction in the RhB/CdS system, Honda et al. inferred a primary step for N-deethylation of RhB in which the electron from the singlet excited RhB* to CdS particles came from the nitrogen atoms.[21,26] They also investigated the cyclic voltammogram of RhB and indicated that this dye can undergo one-electron oxidation. In our experiments, the redox potential of VO_2^+ (+1.00 V versus NHE) is more positive than that of the excited state of the dye (RhB*, −1.09 V versus NHE), which favors electron transfer from the excited dye to VO_2^+. Additionally, there seems few species for the abstraction of hydrogen atom in our system. All these factors tend to support a single electron transfer (SET) mechanism for N-deethylation; that is, the N-deethylation of dyes is initiated by the excitation of the dye followed by an electron transfer to VO_2^+, and subsequently, the resulting dye radical cations are hydrolyzed to lose one alkyl group. Concomitantly, the VO_2^+ was reduced to VO^{2+} (as eqs 1−3).

$$\text{dye} \xrightarrow{\text{vis}} \text{dye*} \tag{1}$$

$$\text{dye*} + VO_2^+ + 2H^+ \rightarrow \text{dye}^{+\bullet} + VO^{2+} + H_2O \tag{2}$$

$$\text{dye}^{+\bullet} \rightarrow \text{N-deethylation} \tag{3}$$

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SCHEME 1: Oxidation Pathways of RhB in the Presence of VO$_2^+$ or/and Pt(IV)

It has been reported that Pt(IV) can be used as photocatalyst for the photochemical oxidation of some organic compounds under visible light irradiation. For example, primary and secondary alcohols can be selectively converted to the corresponding aldehyde or ketone in the presence of Pt(IV) under visible irriadiation.[29] Inoue et al.[30] reported that dye ([Sb^{V}TPP(OCH$_3$)$_2$]-Br) can efficiently sensitize the photooxygenation of cyclohexene by using K$_2$PtCl$_6$ as an electron acceptor, in which PtCl$_6^{2-}$ can be reduced to PtCl$_4^{2-}$ by excited sensitizer under visible light irradiation. In our study, no photoreaction for colorless small organic molecules such as *N,N*-dimethylaniline (DMA) and benzoic acid was observed in the presence of Pt(IV) under visible irradiation. Therefore, the photobleaching of RhB in the presence of Pt(IV) is also proposed to be initiated by the electron transfer from the excited dye to the Pt(IV) species.

The oxidation pathways of RhB in the presence of VO$_2^+$ or/and Pt(IV) are illustrated in Scheme 1. Since the photoreactions of dye in the both VO$_2^+$ and Pt(IV) systems should be initiated by the electron transfer from the excited RhB dye to the corresponding electron acceptor, the difference in their degradation pathways is unexpected and interesting. During our earlier study, we have proposed two reaction mechanisms for the different pathways. One is attributed to the different adsorption modes of dye on the surface of the photocatalyst.[11] It was found that when sulforhodamine-B (SRB) is adsorbed on the positively charged TiO$_2$ via its negative sulfonate group, its degradation under visible light irradiation predominately leads to cleavage of the dye chromophore structure. In the presence of anionic surfactant, dodecyl benzenesulfonate (DBS), however, SRB is adsorbed on the negatively charged DBS/TiO$_2$ interface via positive diethylamine groups, in which the initial steps in the dye degradation occurs preferentially via the stepwise N-deethylation. Another proposed mechanism for the two pathways involves the formation of reactive oxygen species. By photoelectrocatalytic study of TiO$_2$-film electrode[13] and using SiW$_{12}$O$_{40}^{4-}$ as an analogue of the TiO$_2$,[14] we have shown that the whole conjugated chromophore structure cleavage of RhB is attributed to both the formation of the dye cationic radical (via photoinduced electron transfer) and the active oxygen species (O$_{2\bullet}^-$), while the N-deethylation of RhB arises from the hydrolysis of the dye cationic radical in the absence of active oxygen species. In the present study, since the reductive states (VO^{2+} and Pt (II)) of the both electron acceptors cannot be reoxidized by O$_2$, the formation of the O$_{2\bullet}^-$ in this way is avoided in both systems at initial steps of the photoreaction. Accordingly, the formation of active oxygen species does not seem to be responsible for the differences in degradation pathways. Since the VO$_2^+$ could oxidize Pt (II) to Pt (IV), VO$_2^+$ should have stronger oxidative ability than Pt (IV). Also, the

oxidation ability cannot account for the differences in degradation pathways.

To better understand the different interactions of the *N*-ethyl and carboxyl moieties of the RhB molecule with VO$_2^+$ and Pt(IV) and their reaction pathways in the photoreaction, *N,N*-dimethylaniline (DMA) and benzoic acid were selected to be analogues of the two moieties of RhB. In the presence of VO$_2^+$, N-demethylation of DMA was rather rapid under UV light irridiation, but no degradation was observed for benzoic acid even under UV light irradiation. In addition, as observed in the RhB system, negligible cleavage of aromatic ring was observed in the DMA/VO$_2^+$ solution under UV irradiation. In the Pt(IV) case, the degradation of benzoic acid rapidly occurred under UV light irradiation until the Pt(IV) was reduced completely. In contrast to benzoic acid, DMA has only minor degradation under otherwise identical conditions. The RhB dye contains both diethylamine groups and a carboxyl group located at different positions in the dye molecule. It is reported that the platinum species has strong coordination with the carboxyl moiety of RhB.[31] By contrast, VO$_2^+$ can coordinate with both the carboxyl group and the amine group of *N*-(phosphonomethyl)iminodiacetic acid,[32] so in the RhB case, it should also coordinate in this way. The experimental results suggest that Pt(IV) tends to establish an electron-transfer channel via the carboxyl moiety of RhB, by which Pt(IV) gets electrons from the excited RhB preferentially. However, VO$_2^+$ gets electrons from excited RhB via the nitrogen atom. Therefore, the difference in the reaction pathways is proposed to be attributed to the different interaction modes of RhB/VO$_2^+$ and RhB/Pt(IV) and the different effective electron-transfer channels.

In the Pt(IV) or VO$_2^+$/Pt(IV) combined systems, only bleaching of the dye molecules was observed in the absence of oxygen, while mineralization of the dye could occur in the presence of O$_2$, which indicates that O$_2$ plays an essential role in the mineralization of RhB. In the earlier reports on the photocatalytic degradation of dye by TiO$_2$, the mineralization of dyes were attributed to formation of a series of active oxygen species such as O$_{2\bullet}^-$/HOO$\bullet$, which are derived from the reduction of O$_2$ by the conduction band electron. Since the Pt-(II) is very difficult to reoxidize by O$_2$ to Pt(IV) in the present study, it is impossible to ascribe initial steps for the mineralization to formation of active oxygen radicals. Another notable fact that the chromophore cleavage of RhB occurred in the Pt(IV) system independent of the presence of O$_2$ suggests that the mineralization might be initiated from the reaction between O$_2$ and organic radical intermediates. It is well-known that organic radical species can faciley react with O$_2$ to produce peroxy radical,[33,34] which can initiate a series of radical chain reactions to lead to the mineralization of the organic compounds.

Conclusion

RhB dye undergoes effective photoreaction using VO$_2^+$, Pt(IV), and combined VO$_2^+$/Pt(IV) as electron acceptors in the presence or absence of O$_2$ under visible light irradiation. In the VO$_2^+$ system, the photoreaction leads mainly to N-dealkylation of RhB. By contrast, in the Pt(IV) case, cleavage of the whole conjugated chromophore structure predominates. In the combined VO$_2^+$/Pt(IV) system, both cleavage of conjugated chromophore structure and N-deethylation occur simultaneously. The differences are derived from the interaction of the dye with the electron acceptors. O$_2$ is essential for the mineralization of dye in the Pt(IV) or VO$_2^+$/Pt(IV) combined system, and the mineralization might be initiated from the reaction between O$_2$ and organic radical intermediates. Mineralization yield in the

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combined system in the presence of O_2 is much higher than the expected summation of separate ones, this cooperative effect results from the recycle of the Pt(IV) species through the reoxidation of Pt(II) to Pt(IV) by VO_2^+.

Supporting Information Available: The results of the HPLC analysis of the N-ethylation products during the photo-degradation of RhB, the absorption spectrum changes of RhB after VO_2^+ introduced when the photoreaction nearly stopped in the Pt(IV)/RhB system in the aerated solution, and the absorption spectrum changes of RhB in the RhB/Pt(IV) pho-todecomposition system in the absence and presence of O_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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