Mineralization of 4-Chlorophenol under Visible Light Irradiation in the Presence of Aluminum and Zinc Phthalocyaninesulfonates

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Photosensitized oxidation of 4-chlorophenol (4CP) by the title complexes (AlPcS and ZnPcS) in aerated aqueous solution upon visible light irradiation ($\lambda \geqslant 450$ nm) has been investigated using methanol as a disassociating reagent. It is confirmed that the monomeric species of the sensitizer is more active than the corresponding dimer in singlet oxygen generation for 4CP oxidation. However, the monomer is also the main component found in the sensitizer's photobleaching. In this regard, AlPcS is much more stable than ZnPcS, and the photobleaching is observed to proceed via singlet and triplet oxygen, respectively. The final products of 4CP oxidation in alkaline solution are carbon dioxide and chloride ions, while at pH = 7 and pH = 3 the *p*-benzoquinone is the product. The temperature is found to have influence on both the photosensitized degradation of methyl orange and ZnPcS photobleaching, with an activation energy of 15.8 and 24.2 kJ/mol, respectively.

Keywords   4-chlorophenol, aluminum phthalocyaninesulfonate, zinc phthalocyaninesulfonate, oxidation, aggregation, photosensitization, photobleaching

Introduction

Elimination of organic pollutants by molecular oxygen and solar light is one of attractive projects in recent years.[1-3] Many toxic and recalcitrant compounds such as substituted chlorophenols could be degraded completely into carbon dioxide, and/or transferred into more biodegradable molecules. The primary reaction is initiated by reactive oxygen species such as $OH^·$ and $O_2^{-·}$ radicals, generated *in situ* from H_2O_2 photolysis, Fe^{3+}/H_2O_2 Photo-Fenton reaction and TiO_2 photocatalysis under UV light irradiation ($\lambda < 400$ nm). Although these technologies are matured in some stages for commercialization, the development of a more efficient catalytic system that is able to utilize major fraction of solar light ($\lambda > 400$ nm) and activate subsequently the molecular oxygen, remains of great challenge.[3,4]

Metal phthalocyanines (MPc) are an important class of intensely colored macrocycle compounds. The long-lived triplet states, formed upon absorption of visible light ($\lambda > 400$ nm), allow for effective sensitization of triplet molecular oxygen to form more reactive species of singlet oxygen ($^1O_2$) with relatively high quantum yields. Because of that, they have been largely studied as photosensitizers for PDT (photodynamic therapy of cancer) and for fine chemical synthesis,[5,6] with AlPc and ZnPc derivatives being the most efficient and popular one. Recently, an increasing attention has been paid to environmental application.[7-11] Phenol and chlorophenols, a class of toxic and recalcitrant compounds existing in the wastewater of paper and dye manufacturing industries, could be oxidized in aerated aqueous solution or organic solvents under visible light irradiation in the presence of Al, Zn and Ga phthalocyaninesulfonates (MPcS) and other substituted phthalocyanines. The ring-cleavage product of CO_2 and fumaric/maleic acid were identified from phenol oxidation,[7] while only *p*-benzoquinone was detected as the final product of 4-chlorophenol (4CP) oxidation.[8] The monomeric species of MPcS was claimed to be more efficient than the corresponding dimer for the substrate oxidation, based on the system where surfactants (CTAC, SDS, TBAC *etc*.) were present,[7,11] or the photosensitzers with different number of sulfonate groups were used for comparison.[8] However, the photophysical and photochemical properties of the excited MPcS are influenced to some extend by detergent and sulfonation degree,[12] probably questioning the result obtained above.

In this work, methanol is employed as a disassociating reagent for the photosensitized oxidation of 4CP in the presence of AlPcS and ZnPcS in water. The relative concentration of monomer or dimer can be regulated simply by various portion of methanol in the mixed solvent. By each unique photosensitizer, therefore, the relative photosensitization activity and photostability can be evaluated without possible interference mentioned above. From this study, several new results are obtained: (1) although higher pho-

tosensitization activity of the monomeric species is confirmed, the monomers are found to be the main components responsible for the sensitizer photobleaching, the process occurred via attack to AlPcS and ZnPcS by singlet and triplet oxygen, respectively; (2) 4-CP can be decomposed finally into CO_2 and chloride ions; (3) both the photosensitization and the photobleaching are temperature-dependent.

Experimental

Materials

AlPcCl and ZnPc were synthesized in solid state by condensation of phthalonitrile (98%, Acros) in the presence of aluminum chloride or zinc sulfonate, followed by purification in sulfonic acid three times.[13] AlPcS and ZnPcS were then prepared from AlPcCl and ZnPc by sulfonation in chlorosulfonic acid containing small amount of thionyl chloride.[14] The unreacted MPc was removed by dissolving the dye in NaOH until pH = 10, and the filtrate was dried by evaporation to obtain the final products. The average numbers of sulfonate groups in AlPcS and ZnPcS, estimated by $BaCrO_4$ method after the sample was refluxed in nitric acid for several hours, were 3.98 and 1.40, respectively (note that the concentration expressed in the text was calculated based on tetrasulfonated phthalocyanine). Other chemicals of 4-chlorophenol, phenol, hydroquione, benozquinone, acetophenone, fumaric acid and alcohols were of the reagent grade from Shanghai Chemicals, Inc, and were used as received.

Photosensitized reactions and analysis

Continuous irradiation was carried out using a 500 W Halogen lamp. Before entrance into the reactor, the light beam passed through a chromate solution cell of 2-cm path length to ensure the irradiation by visible light at $\lambda > 450$ nm. Typically, the aerated solution containing 2.9×10^{-5} mol/L of the sensitizer and 2.2×10^{-4} mol/L of 4CP in a thermostatic open vessel was irradiated under steady stirring. At certain interval of reaction, the spectrum was recorded on a PE Bio 40 or Agilent 8453 UV-vis spectrometer, and the organic substrates were analysed on a HPLC (Varian 5000 or Agilent 1100, C18 reverse column, the eluent $CH_3OH : H_2O = 1 : 1$ at 1.0 mL/min). For all the experiments, the same solution was also set up in the dark for any catalytic reaction. All the prepared solutions were equilibrated in the dark overnight before initiation of light irradiation. For the experiment about the temperature effect the sample in a water bath at desired temperature (20.0—60.0 ℃) was further equilibrated in the dark for about 2 h.

The parameter of COD (chemical oxygen demand) was determined by a standard method of dichromate with silver sulfate as a catalyst. The products of 4CP (1.51×10^{-3} mol/L) photooxidation at pH = 13 using AlPcS (2.9

$\times 10^{-5}$ mol/L) as photosensitizer were determined as follow. The irradiated solution, after acidified by HCl to pH = 1, was extracted with CH_2Cl_2, and then the products dissolved in concentrated CH_2Cl_2 solution were identified on HP6890 GC/MS. The products of chloride and CO_2 were quantitatively measured on pHS-3C (Shanghai Kangning, PCI-1 selective electrode) and by $BaCO_3$ precipitation, respectively. The irradiated solution was acidified by H_2SO_4 to about pH = 1, and N_2 (99.9%) was immediately bubbled through and trapped in an aqueous $Ba(OH)_2$ solution. A blank experiment with an un-irradiated sample was carried out as a reference.

Results and discussion

Aggregation properties

AlPcS and ZnPcS prepared in this study are highly aggregated in the aqueous solutions. The aggregate has strong absorption at 618 and 628 nm, respectively (Fig. 1). In alcohols, the monomer $Q_{(0,0)}$ band becomes substantially narrowed and strong (the maximum located at 673 nm for AlPcS in methanol and at 668 nm for ZnPcS in ethanol, respectively). The spectra of ZnPcS agree well with those reported.[8,14,15] However, the Q_d band of AlPcS at 618 nm is blue-shifted by 15—31 nm in comparison with the dimer data of 636—649 nm.[12,14] Thus we attribute the absorption band at 618 nm to the higher-order aggregates of AlPcS.
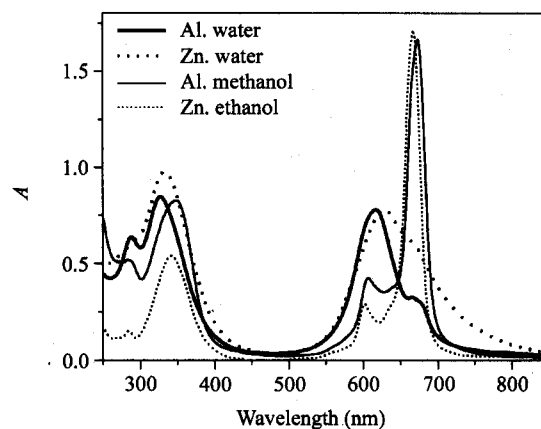

Fig. 1 UV-vis absorption spectra of AlPcS and ZnPcS in water (heavy line) and in alcohol (light line). Concentration in water is 2.9×10^{-5} mol/L, while AlPcS in methanol is 2.1×10^{-5} mol/L and ZnPcS in ethanol is 1.6×10^{-5} mol/L, respectively.

In addition, the AlPcS spectrum is influenced especially by pH. With pH increase from 3 to 12, the Q_d band is blue-shifted by several nanometers.[16] In alkaline solution, the monomer band is increased obviously, with equilibrium time. After AlPcS in 0.5 mol/L of NaOH was equilibrated overnight, the spectrum (not shown here) was almost similar to that in methanol (light line in Fig. 1). Under the same conditions, ZnPcS exhibited a similar

change, but the absorbance was increased only a little at pH = 12. The Lambert-Beer law was obeyed for all the cases in the range of 4×10^{-6}—2.54×10^{-5} mol/L, except that of AlPcS at pH = 12. The result suggests that there exists probably strong interaction between the Pc units,[8,17] and the disassociation is facilitated by alkaline anion, that can be coordinated axially to the central metal. Thus the monomer of AlPcS at pH = 12 is better described as Al(OH)PcS species, with maximum absorption located mainly at 673 nm. For the following photochemical studies, all the solutions after preparation were equilibrated in the dark overnight.

Photooxidation of 4CP

The photosensitized oxidation of 4CP under visible light irradiation, sensitized by present AlPcS and ZnPcS, was first carried out in the aqueous solution for comparison. Similar to the previous studies,[7,8] the reaction was efficient only in the alkaline solution (very slow at pH = 7 and pH = 3). The absorption peak of 4CP at 244 nm was decreased upon light irradiation, while the absorbance in the region of 260—400 nm was up first and then went down with irradiation time, indicating that the products were formed and reacted further *in situ*. By HPLC analysis, the apparent first-order rate constant was evaluated to be 1.9×10^{-3} and 4.8×10^{-4} s^{-1} for AlPcS and ZnPcS, respectively. The result shows that in aqueous solution AlPcS is more efficient than ZnPcS for 4CP photooxidation.

In the presence of methanol, the photooxidation of 4CP at pH = 12 was increased with methanol concentration in the mixed solvent (Table 1). It is noted from Fig. 1 that in the alcoholic solution both AlPcS and ZnPcS exists mainly in the monomeric form. The excited state of the monomer is lived much longer than the aggregates,[15] favoring the reactions with triplet O_2 to generate $^1O_2$ or O_2^- for 4CP oxidation, or the electron transfer directly with 4CP substrate.[18] It is noted that methanol present in solution decreases the value of K_D, dimerization constant, but the monomer concentration is indeed not linearly proportional to K_D.[20] This can be served as the reason why the reaction rate of 4CP oxidation does not response linearly to the change in methanol concentration (Table 1). However, the result obtained here demonstrates confidently that for each unique sensitizer the monomer is more efficient than the corresponding dimer for the photosensitized substrte oxidation.

Table 1   Effect of methanol addition on 4CP photooxidation in aerated methanol-water solutions at pH = 12[a]

Methanol (%)	0	25%	50%
AlPcS	65	69	94
ZnPcS	29	68	96

[a] The data are the percentage of 4CP disappearance after 10 min of irradiation with visible light. Methanol concentration is expressed in percentage by volume.

The reactions performed at pH = 3 and 7 in the aqueous methanol solutions were again very slow, even though the concentration of monomeric species for each sensitizer was obviously increased. The result indicates that for efficient oxidation of organic substrates not only the monomer is important, but also the redox potential of the target molecules (it is reported[8] that 4CP in the molecular form much less oxidizable than the deprotonated 4CP). This has been further proved by the reactions with several recalcitrant textile dyes such as X3B and Rhodamine B, which are hardly degraded, while methyl orange can be easily oxidized even in water at pH = 7 (see below).

To clarify any difference in the reactive species for 4CP oxidation, sodium azide (0.01 mol/L) was used as $^1O_2$ quencher for the reactions in 50% methanol solutions. The reaction for complete loss of 4CP took more than 2 h, whereas in the absence of the quencher it needed only about 10 min (Table 1). This indicates that the solvent does not change obviously the reaction pathway, and the 4CP oxidation in the alcoholic solution proceeds via singlet oxygen, that is generated by energy transfer from excited AlPcS or ZnPcS to the ground state of triplet molecular oxygen. Therefore the increased rate of 4CP oxidation in the alcoholic solution can be then attributed to the increased rate of $^1O_2$ generation. No obvious salt effect of sodium azide on the aggregation properties of the phthalocyanines was observed at the used concentration. On the other hand, the quantum yield of $^1O_2$ generated by ZnPcS in DMF was reported to be higher than that for AlPcS.[7] The photoactivity of ZnPcS similar to AlPcS in 50% methanol solution (Table 1) might be due to the incomplete disaggregation of ZnPcS dimer (Figs. 1 and 2 below). Thus, it is suggested that a better solvent capable of making complete dissociation of the aggregates is needed for more accurate evaluation of the relative photosensitizing activities among different sensitizers.

Photostablities of the sensitizers

The stability of the dye during the reaction is important for its reuse in practical application. However, no much study has been made on this issue. It is noted from several reports that both the AlPcS and ZnPcS are not absolutely stable toward light irradiation.[7-12] Compared in 50% methanol solution, ZnPcS is much less stable than AlPcS during 4CP photooxidation at pH = 12 (Fig. 2). After 2 h of irradiation, almost all of ZnPcS is bleached while only about 1%—7% for AlPcS. By using difference spectra, we find that the monomeric species are the main components in the photobleaching (Fig. 3). This process was observed independent of the 4CP substrate present or absent in the solutions (10^{-4} to 10^{-3} mol/L), but the bleaching rate was affected by pH and methanol concentration in the solvent. Before irradiation, AlPcS at pH = 12 shows the spectrum characteristic of a large amount of the aggregates (Fig. 2a). After irradiation, however, the difference spectrum (Fig. 3, top) resembles the one of

AlPcS monomer (Figs. 1 and 2c). For the case at pH = 7, the disappearing AlPcS is mainly the monomer (Fig. 3, top), while before irradiation the AlPcS consists mainly of the aggregates (Fig. 1, heavy line). At pH = 3, the photobleached species (Fig. 3, top) are mainly aggregates with a little amount of the monomers. It has been demonstrated above that the aggregate disassociation is facilitated by the presence of hydroxide anions in the solution. The similar changes were also observed in the irradiated aqueous solutions of ZnPcS (Fig. 3, bottom), where the absorption of Q band relative to Q_d increases with pH. Less clear change in the spectra of irradiated ZnPcS than AlPcS is due to the minor effect of alkaline anion on the disaggregation of ZnPcS in aqueous solution as discussed in the section above. The result here suggests that the monomer is more bleachable than the aggregate in the photobleaching process. In fact, the monomeric absorption in the difference spectra increases with the increasing of methanol present in solution. For example, the difference spectrum of photobleached AlPcS in 50% methanol solution at pH = 7 was almost the same as that of AlPcS monomer (Fig. 3, top at pH = 12).
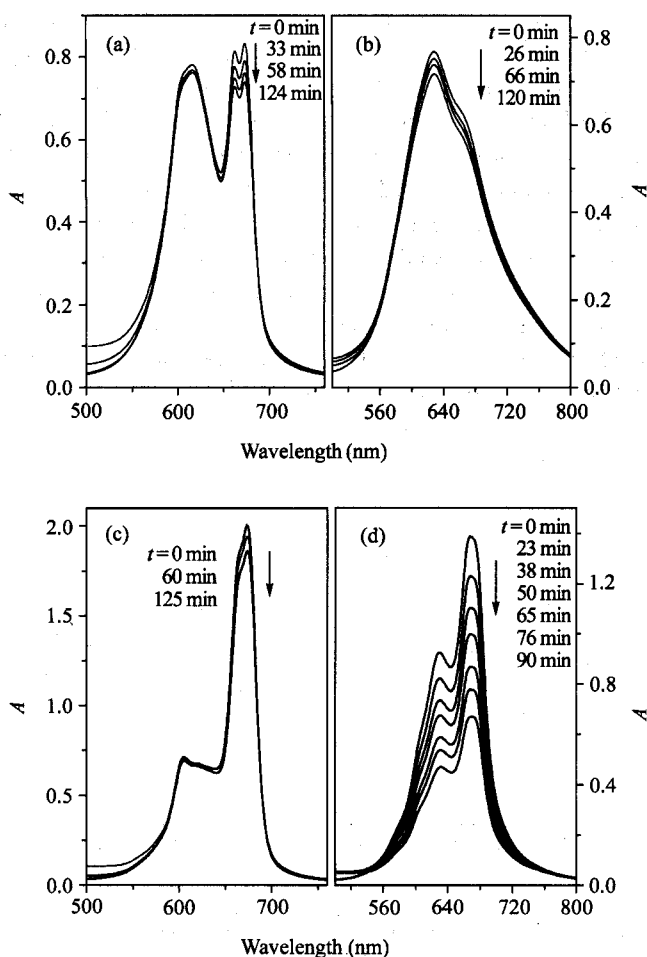

Fig. 3 Difference spectra of the irradiated AlPcS (top) and ZnPcS (bottom) in the aqueous solution of 4CP at different pH. The spectrum before irradiation was used as the reference.

The intermediates formed from the dye photobleaching were not clear. In the difference spectra the absorptions in the regions of 400—550 and 700—900 nm were increased a little in the beginning and then decreased with irradiation time. But the products are probably small in size, since the intermediates from photobleaching of sensitizer alone exhibited an absorption peak at 220 nm which was decreased gradually upon further irradiation.

The photobleaching mechanism for both the dyes is different. In the presence of sodium azide (0.01 mol/L), no photobleaching of AlPcS was observed either in water or in alcoholic solution at pH = 12. Together with the evidence that the bleaching rate was decreased by about a half in the presence of 4CP, the AlPcS photobleaching is initiated clearly by singlet oxygen generated *in situ*. For ZnPcS, however, the photobleaching rate was unaffected by either sodium azide or 4CP present in solution. ZnPcS was photostable in a degassed solution by N_2. Based on the redox potential,[19] ZnPcS in the triplet excited state is more oxidized than AlPcS. Clearly, ZnPcS photobleaching occurs via electron transfer from excited ZnPcS to triplet oxygen forming O_2^{-} radicals and Pc^{+} cation with subsequent decomposition.

Intermediates of 4CP *oxidation*

Benzonquinone (BQ) has been reported to be only

Fig. 2 Visible spectral changes observed during the photosensitized oxidation of 4CP at pH = 12 in the aqueous solutions (top), and in 50% methanol (bottom) using AlPcS (a, c) and ZnPcS (b, d) as the photosensitizers.
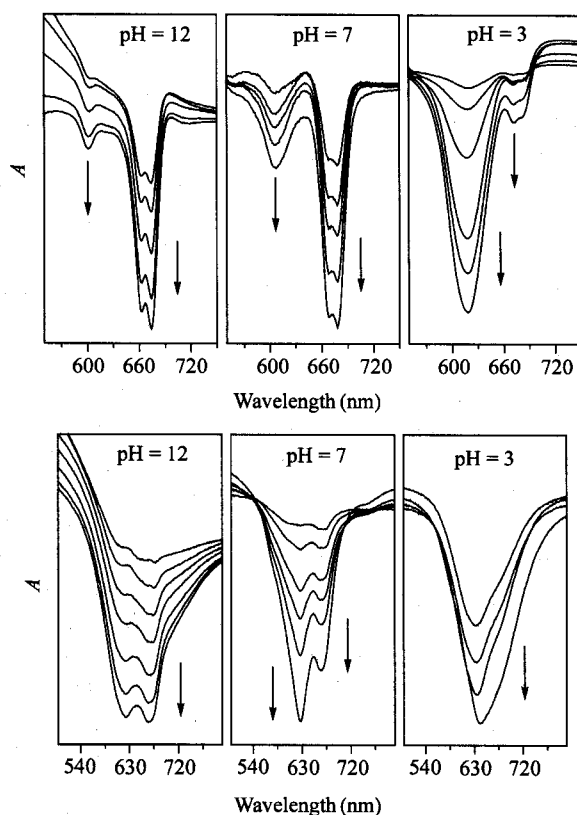
the product of 4CP oxidation, sensitized by AlPcS.[8] This was confirmed in the present study using relatively photostable AlPcS as sensitizer at pH = 3 and pH = 7, where the characteristic peak of BQ at 245 nm was increased exponentially with irradiation time. In the basic solution (pH = 12), however, different intermediates were formed. In the difference absorption spectra, the intermediates exhibited an absorption peak at 269 nm and broad band in 290—400 nm centered at 320 nm, all of which, after reaching a maximum, were decreased with further irradiation. Furthermore, the ratio of absorbance 269 to 320 nm in 50% methanol solution was much higher than that in water, suggesting that two different intermediates formed at least. By HPLC analysis, there appeared four un-resolvable peaks in the range of retention time from 1.2 to 2.5 min (4CP at 7.8 min). Both the retention time and the spectral characters of the intermediates were not in agreement with those of BQ, hydroquinone, phenol or fumaric acid under the conditions studied. GC-MS analysis was also failed to identify any reasonable products, except some impurities, probably because of the GC-MS difficulty in detection of small molecules with either high or low boiling point (the sample in CH_2Cl_2 was concentrated by bubbling with N_2).

The unspecified intermediates are degradable in the system. This is evidenced not only by the spectral changes mentioned above, but also by COD (chemical oxygen demand) and CO_2 measurements. The COD removal yield was 41% and 58% for the reactions of 2 h and 5 h, respectively. In order to determine quantitatively the expected final products of CO_2 and chloride ions, high concentration of 4CP (1.51×10^{-3} mol/L) was employed (see the experimental section). After 10 h of irradiation, 1.504×10^{-3} mol/L of Cl^- and 0.0148 g of $BaCO_3$ were obtained. This corresponds to 99.7% of Cl^- and 16.6% of CO_2, respectively, from expected complete decomposition of 4CP. If the solution was irradiated for 30 h, the formation yield of CO_2 reached up to 38.8% (99.8% has been obtained in our laboratory using another photostable MPcS as the sensitizer). The result demonstrates that the MPcS photosensitization is effective for complete mineralization of 4CP.

Effect of temperature

While solar light is used to initiate photochemical reaction, the illumination often causes the system be heated gradually. Examination of the temperature effect is thus necessary on the photosensitized organic oxidation and on the sensitizer photostability as well. The investigation was made using methyl orange (MO) as a model organic substrate, since MO concentration can be determined conveniently by its characteristic peak at 463 nm, where the sensitizer has minor absorption. Although MO could be degraded efficiently at pH = 7 in water, the experiment was

carried out at pH = 12 in methanol : water (1 : 1) solution using AlPcS as the photosensitizer, so as to mimic the conditions used above for 4CP oxidation and to minimize the temperature effect on AlPcS disassociation. As temperature increased from 30 to 60 °C, the initial rate of MO degradation, detected at 437 nm, was observed to increase from 4.94×10^{-3} to 9.96×10^{-3} unit of the decreased absorbance per minute. The change of the initial rate with temperature fits well the Arrhenius plot (Fig. 4), from which the activation energy (E_a) was obtained to be 19.4 kJ/mol. It was noted that the initial absorbance due to AlPcS monomer was also increased a little with temperature, from 1.8447 to 2.1103 at 673 nm, which would contribute partially into the increased rate. Since the initial rate was observed to change linearly with the monomer concentration, the E_a was then calibrated to be 15.8 kJ/mol. On the other hand, the photobleaching of AlPcS was observed not to increase obviously with temperature, probably due to its relatively high photostability. But the enhanced photobleaching was clearly observed for ZnPcS sensitizer. By performance in methanol : water (1 : 1) at pH = 12, the initial rate of ZnPcS bleaching, determined at 667 nm, was increased from 1.04×10^{-2} to 4.04×10^{-2} unit of absorbance per minute, when the temperature increased from 20 to 60 °C. The linear Arrhenius plot (Fig. 4) gave the measured E_a of 27.8 kJ/mol, and a calibrated E_a of 24.2 kJ/mol, respectively. In the organic oxidation by TiO_2 photocatalysis, the activation energy is generally quite small, around several kJ per mole,[21] which is attributed to the diffusion of $OH^\cdot$ and $O_2^{-\cdot}$ radicals to the target molecule on the catalyst surface. Although considerable value of E_a obtained here has been not well understood at this moment, the result does draw an attention to the temperature factor for both the $^1O_2$ initiated organic reaction and the sensitizer photostability.
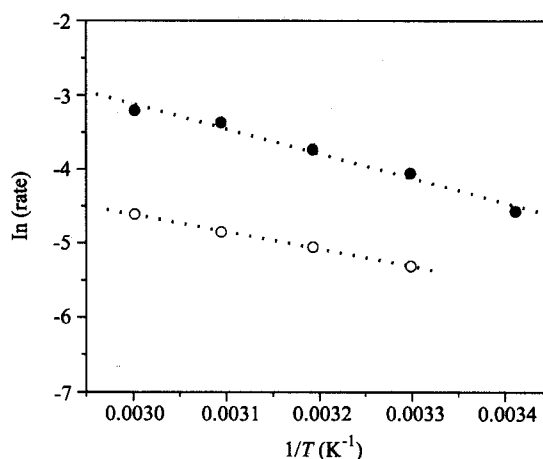

Fig. 4 Arrhenius plot for methyl orange degradation sensitized by AlPcS (open circle) and for ZnPcS bleaching (solid circle) in 50% methanol aqueous solution at pH = 12. The initial rate for methyl orange degradation was measured by the decreased absorbance per min at 437 nm, and ZnPcS bleaching at 667 nm, respectively.

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