Visible Light Active Carbon Nitride Photocatalyst Enables Direct Upgrade of Raw Elemental Sulfur (S₈) to Value Added Chemicals

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Abstract: Potassium poly(heptazine imide), a carbon nitride based photocatalyst, combined with elemental sulfur S₈ (as a sacrificial electron scavenger and/or reagent) is a versatile photocatalytic system that enables challenging reactions and provides value added organic substances from cheap precursors: aldehydes from alcohols, dibenzyldisulfides from methylarenes, thioamides from amines and 1,3,4-oxadiazoles from N-acylhydrazones.

Keywords: Photocatalysis, Organic synthesis, Carbon nitride.

1. Introduction

The rising demands to the efficiency of chemical technology motivate chemists to develop more active, selective, cheaper, and stable catalysts to accomplish challenging chemical reactions. In this view, photocatalysis offers not only milder conditions, higher selectivity for the known processes, but also new reactions. Photocatalysis until now was successfully applied in many different C-C, C-N and C-O bond forming reactions. Despite organosulfur compounds are valuable reagents in chemical and pharma industry (surfactants, flavours and antibiotics), photocatalytic reactions aiming to prepare these compounds can be scarcely found in the literature. The reason is partially enclosed in sensitivity of the photocatalyst, especially metal-based, toward reactive organosulfur species. Both photocatalysis and “traditional” organic synthesis strongly rely on sulfur transfer reagents, for example, Lawesson reagent, P₄S₁₀, tetrathiomethalates, etc. Along with the target reaction of sulfur incorporation, they produce significant amounts of byproducts. Obviously, α-elemental sulfur S₈ as “S”-source would be an excellent choice as it is 100% atom efficient, i.e. there is no organic backbone or other elements that upon release would be converted into waste. This idea motivated us to develop a photocatalytic system that incorporates S₈ as a reagent. Potassium poly(heptazine imide) (K-PHI)¹ – a carbon nitride based photocatalyst, was found to be superior in this reaction among the different tested photocatalysts. This material took the best features from graphitic carbon nitride – absorption in the visible range, high thermal and chemical stability, but there are also features intrinsic only for this material: ability to exchange ions in the solid state² and highly positive position of the valence band, +2.54 V vs. RHE.³ Here, we present our recent achievements using K-PHI to enable new chemical reactions in which S₈ was employed as cheap and abundant reagent and/or sacrificial electron scavenger to produce different classes of organosulfur compounds.

2. Experimental

K-PHI was prepared according to the procedure reported in the literature.⁴ In the photocatalytic experiments, the mixtures of reagents with the suspended photocatalyst were degassed prior the reaction and then irradiated with blue LED (461 nm, 0.0517 W·cm⁻²) for a specific time. After reaction K-PHI was separated by centrifugation (13000 min⁻¹), washed with appropriate solvent and dried for subsequent reuse. The reaction mixtures were analyzed either using GC-MS or liquid NMR. Products were purified by chromatography and characterized by ¹H, ¹³C NMR, mass-spectra and in some cases FT-IR.

3. Results and discussion

We have started our investigation probing S₈ as an electron scavenger. We have found that under identical condition conversion and selectivity of benzyl alcohol to benzaldehyde photooxidation using S₈ as
the electron scavenger were 84.4% and 99.5% respectively versus 29% and 71%, when O₂ was used as an electron scavenger. Generated in situ aldehydes were then combined with multicomponent Hantzsch synthesis to produce 1,4-dihydropyridines. K-PHI combined with S₈ is also an excellent photocatalytic system for oxidative cyclization of N-acylhydrazones leading to substituted 1,3,4-oxadiazoles. The yields were significantly lower and products were contaminated with the products of N-acylhydrazones decomposition when O₂ was employed as an electron acceptor. These results clearly indicate high selectivity of S₈ as the electron acceptor.

Figure 1. Photocatalytic synthesis of 1,3,4-oxadiazoles via N-acylhydrazones oxidative cyclization. Selected examples are shown.

Furthermore, the valence band potential in K-PHI is high enough, +2.54 V, so the photogenerated holes easily oxidize C-H bond in methylarenes, while S₈ is reduced by the photogenerated electrons to polysulfide radical anion that in turn recombines with the product of methylarene oxidation. The net result of this reaction is formation of dibenzyldisulfides accompanied by hydrogensulfide evolution (Figure 2).

Figure 2. Photocatalytic synthesis of dibenzyldisulfides. Isolated yields are shown.

Finally, one-pot cascade reaction between both generated in situ H₂S and N-benzyl-1-phenylmethanimines furnishes in high yields and selectivity thioamides (Figure 3) – molecules that until now required special sulfuration reagents, e.g. P₄S₁₀, Lawesson reagent, harsh reaction conditions and laborious purification procedure.

Figure 3. Photocatalytic synthesis of thioamides.

4. Conclusions

K-PHI as a robust heterogeneous photocatalyst allows converting elemental sulfur (S₈) directly into disulfides and thioamides using methylarenes or amines respectively. Moreover, a combination of K-PHI with S₈ can be used to run very selectively oxidative cyclization of N-acylhydrazones to 1,3,4-oxadiazoles and oxidation of alcohols to aldehydes. The scope of the reactions, photocatalyzed by K-PHI is not limited to the reported above and more new photocatalytic reactions will be reported soon.

References