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Identification of the Structure of Triethanolamine Oxygenation Products in Carbon Nitride Photocatalysis

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Triethanolamine (TEOA) is one of the most commonly used sacrificial agents in photocatalysis. Due to its more complex structure compared to, for example, ethanol, and its sacrificial role in photocatalysis, it gives a mixture of products. The structures of these molecules are not usually analyzed. Herein, we obtain and isolate the products of TEOA and *N-tert*-butyl diethanolamine oxygenation under photocatalytic conditions with ≈15% yield, and followingly characterized them by NMR and mass spectroscopy. The reaction is mediated by potassium poly(heptazine imide) (K-PHI) in the presence of O_2 and affords formyl esters of β-hydroxyethylene formamides from the corresponding ethanolamines.

Introduction

Photocatalysis facilitates chemical reactions through photo-induced electron transfer. Except for redox neutral reactions,[1–4] photocatalysis relies on sacrificial agents – organic and inorganic compounds as well as inorganic ions capable of accepting or donating electrons to the reaction mixture to enable a desired transformation. In net-oxidative reactions, O_2,[5] S_8,[6,7] $S_2O_8^{2-}$,[8] and Ag^+,[9] for example, have been used to extract photogenerated electrons from the excited photocatalyst and therefore promote oxidation of a substrate by the hole residing in the valence band (VB). In net-reductive processes, compounds with low oxidation potential, such as alcohols,[9] tertiary amines[10] and biomass,[11] quench the photogenerated hole and therefore promote reduction of a substrate by the electron temporarily stored in the conduction band (CB). However, sacrificial agents also possess plenty of other often undesirable roles.[12] For example, one-electron oxidation and deprotonation of an aliphatic alcohol gives a C-centred radical. It is a strong reductant, which upon injection of an electron into the conduction band of a semiconductor photocatalyst alters its photophysical properties. On the other hand, it is also a strong oxidant, which, for instance, in the hydrogen evolution reaction, competes with H^+ for photogenerated electrons.[13]

Carbon nitride materials are an emerging class of photocatalysts and have been applied in full water splitting,[15] as well as in proton reduction[16] and water oxidation half reactions,[17] and also in numerous organic reactions,[18] just to name a few. Among the sacrificial electron donors, triethanolamine (TEOA) is one of the most commonly used in carbon nitride photocatalysis. The scope of reactions where TEOA is employed ranges, from H_2 production,[19] CO_2 reduction to either HCOOH[20] or CO,[21] to the synthesis of cyclopentanoles[10] and γ,γ-dichloroketones from enones.[22] The last two reactions are mediated by potassium poly(heptazine imide) (K-PHI, Figure 1a), which is also used in this work.

Due to its low oxidation potential of +0.64 V vs. SCE in CH_3CN[10] and its more complex structure compared to simple aliphatic alcohols, such as ethanol and benzylalcohol (which, under anaerobic conditions, give aldehydes[23] and, in the presence of O_2, aldehydes and carboxylic acids[24]) oxidation of TEOA produces a greater variety of products. The pathway of TEOA oxidation depends on the conditions. Similar to aliphatic alcohols in non-aqueous anaerobic media, it was suggested that the product of TEOA oxidation is an aldehyde (Figure 1b, aldehyde path).[10],[14] In aqueous media, typically in the presence of O_2, TEOA forms an iminium cation which, upon hydrolysis, accompanied by the N–C bond cleavage gives diethanolamine and glycolaldehyde.[14] Nevertheless, the 'aldehyde pathway' could be complicated by formation of an iminium cation which, followed by intramolecular attack of a hydroxyl group, gives oxazolidine.[10]

Ghosh et al. synthesized *N,N*-dialkylformamides from trialkylamines – compounds structurally similar to TEOA, using Eosin Y as a homogeneous photocatalyst and O_2 from air.[25] Non-photocatalytic oxygenation of tertiary aliphatic amines with O_2 accompanied by C–C bond cleavage applied to the synthesis of *N,N*-dialkylformamides was reported by Li et al.[26]

The products of TEOA oxidation might react with substrates or target compounds and decrease the selectivity of a photocatalytic process. Therefore, knowing the structure of TEOA oxidation products is essential for designing photocatalytic reactions and identifying those in which using TEOA would be detrimental.

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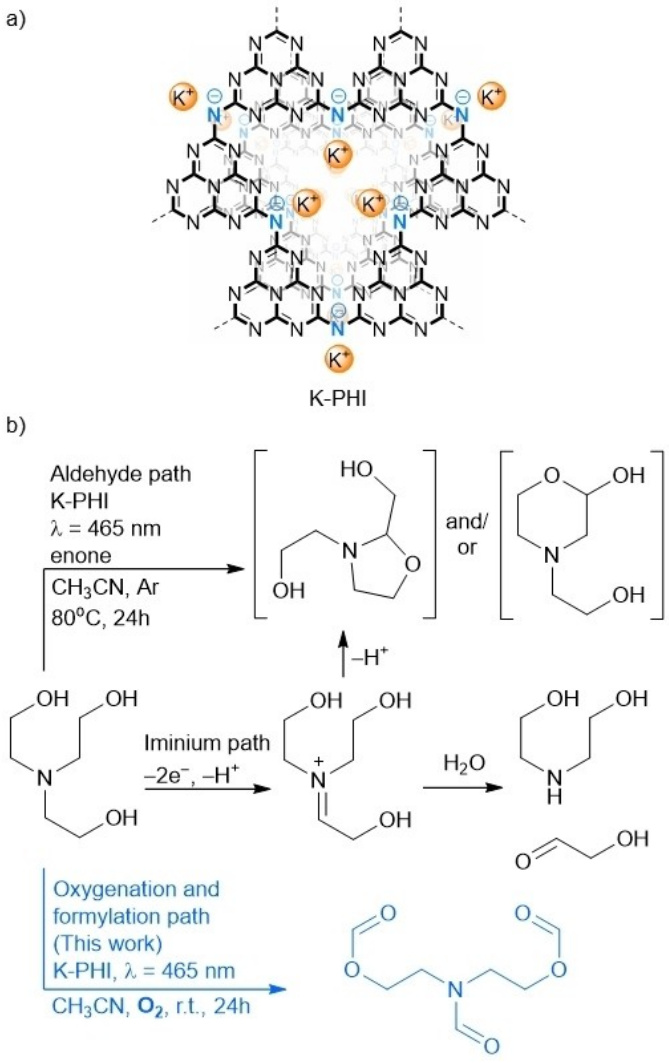
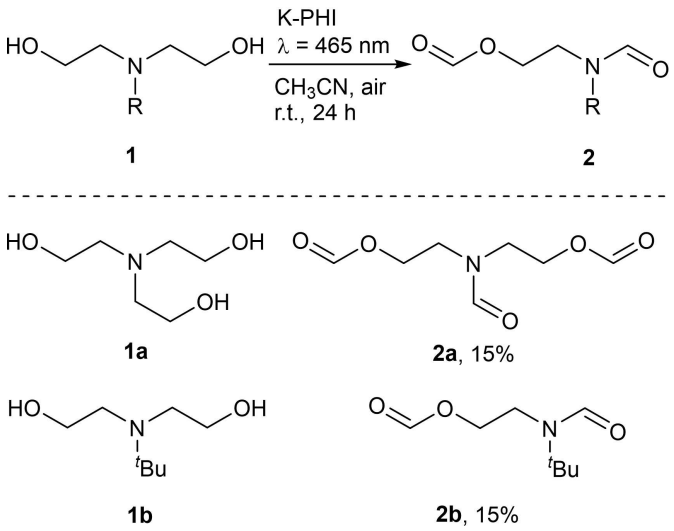


Figure 1. Concept of this work. a) Ideal structure of K-PHI. b) Reactivity of TEOA: aldehyde path implemented under anaerobic conditions;[10] iminium path typically implemented in aqueous medium and aerobic conditions;[14] Oxygenation and formylation path of TEOA by K-PHI studied in this work.

Herein, we study oxygenation of TEOA and *N-tert*-butyl diethanolamine by K-PHI in the presence of O_2 as the terminal oxidant. We isolate formyl esters of the corresponding *N,N*-di(β-hydroxyethylene) formamides (Figure 1b) and confirm their chemical structures by ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry.

Results and Discussion

A mixture of TEOA (0.05 mmol), K-PHI (5 mg) in CH_3CN (2 mL) was stirred under an air atmosphere (O_2 20 vol.%) and illumination with 465 nm photons for 24 h. After solvent concentration in vacuum, ^{1}H NMR spectroscopy of the reaction mixture in $CDCl_3$ revealed a complex composition, while compound **2a** was the major product (15%, Scheme 1). Upon reaction mixture work-up and purification, **2a** was isolated, and

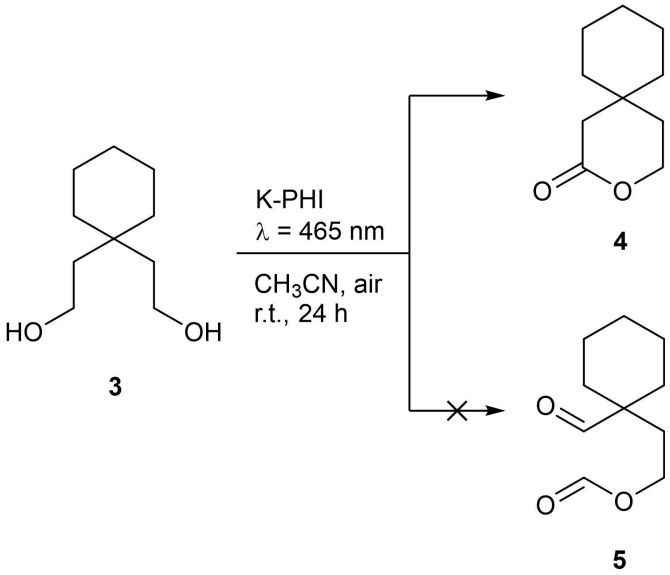


Scheme 1. Oxygenation and formylation of TEOA and *N-tert*-butyl diethanolamine with O_2 by K-PHI under visible light.

the identity of its chemical structure was unambiguously confirmed by counter synthesis, namely by reacting diethylamine with formic acid (see Experimental Section for details). Similar to *N,N*-dimethylformamide, due to the high rotational barrier around the R_2N–C(O)H bond, the ^{1}H NMR spectrum of **2a** shows four methylene groups appearing as four triplets. Under the same conditions, commercial *N-tert*-butyl diethanolamine gave formamide **2b** with a comparable 15% yield. As reported earlier, (^{n}C$_6$H$_{13}$)$_3$N and (^{n}C$_8$H$_{17}$)$_3$N gave *N,N*-dialkylformamides with relatively low 35–38% yields,[25] which points at the high reactivity of aliphatic amines and their "sacrificial" role in photocatalysis. Therefore, using ethanolamines as substrates in photocatalysis remains a challenge to selectively access products of their oxygenation and formylation.

Substituted pentane-1,5-diol **3** that lacks a tertiary amine moiety gave lactone **4**, while aldehyde **5** was not formed (Scheme 2). These results clearly indicate that, when the substrate lacks a NR_3 moiety, as expected, the hydroxyl group is oxidized at first instance, followed by nucleophilic attack of the adjacent hydroxyl group and dehydrogenation of hemiacetal to lactone, which is likely to be a photocatalytic process as well.[5]

A tentative mechanism of TEOA oxygenation-formylation is shown in Figure 2. Overall, our results and those reported earlier by König et al. confirm that oxidation of TEOA and *N-tert*-butyl diethanolamine proceeds at the nitrogen lone pair rather than at the primary alcohol.[25] Given that the oxidation potential of aliphatic tertiary amines is in general lower (E_{ox}(TEOA) = +0.64 V vs. SCE in CH_3CN[10]) than that of aliphatic alcohols (E_{ox}(PhCH$_2$OH) > +2.2 V vs. SCE in CH_3CN[27]), single electron transfer (SET) from the nitrogen lone pair with the formation of intermediate I is thermodynamically more feasible. Earlier reports indicate that the rate of hole quenching in K-PHI and related semiconductors by 4-methylbenzyl alcohol is 1.43×10^7 M^{-1} s^{-1}.[23] The relatively low CB potential in K-PHI (−0.75 V vs. SCE[28]) is at least partially, responsible for the thermodynamic stability of K-PHI radical anion.[29–31] Therefore, *reductive*



Scheme 2. Synthesis of lactone **4** by dehydrogenation of diol **3**.

quenching of the K-PHI excited state, similar to earlier reports,[32] rather than *oxidative quenching* might be operative in the present case as well. Similar to the cross-dehydrogenative coupling of tetrahydroisoquinolines with various nucleophiles employing O_2 as the electron acceptor,[33] intermediate I is first converted into the iminium cation II via hydrogen atom transfer (HAT) to $O_2^{\bullet-}$. Formation of intermediate III is suggested based on oxygenation of the benzylic position in tetrahydroisoquinolines with O_2.[34] Therein, however, lactams are obtained with high selectivity upon elimination of H_2O from organic hydroperoxide III, which is likely due to the stabilizing effect of the aromatic ring. Ethanolamines **1** are missing any conjugation, which could stabilize the intermediate IV. As such, cleavage of the C–C bond in a β-position of the peroxide IV moiety leads to the intermediate V. Due to the low O–O bond dissociation free energy (BDFE) in organic peroxides (≈44 kcal mol^{-1}[35]) such as in tentative intermediate III, its cleavage produces a highly reactive hydroxyl radical that likely to enable side reactions and therefore reduces selectivity towards **2**. Intermediate V reacts with one, in case of **1b**, or two equivalents of formic acid, in case of **1a**, and produces **2**. The mismatch between the number of HCOOH molecules produced upon C–C bond cleavage in a substrate (one molecule) and a number of HCOOH molecules required to convert V derived from TEOA into ester **2a** (two molecules) might be an additional reason for the low selectivity toward **2a**. In the ^{1}H NMR spectrum of the crude reaction mixture, we observed several peaks at ≈8.03 ppm, which could be assigned to formic acid.

Conclusion

Despite the presence of few electron-rich sites in triethanolamine, that is, the NR_3 moiety and three primary alcohols, the initial SET from triethanolamine to the photoexcited K-PHI takes place at the nitrogen atom with subsequent formation of the iminium cation. The generality of this pathway was illustrated for two substrates, triethanolamine and *N-tert*-butyl diethanolamine. The products of their oxygenation are formyl esters of the corresponding β-hydroxyethylene formamides.

Experimental Section

Chemicals. Diethanolamine (≥99%) was purchased from Fluka. Triethanolamine (≥99%), 5-aminotetrazole monohydrate (97%), and formic acid (≥95%) were purchased from Sigma-Aldrich. CH_3CN (hypergrade for LC-MS) was purchased from Merck. LiCl (≥99%) and KCl (≥99.5%) were purchased from Carl Roth. *N-tert*-

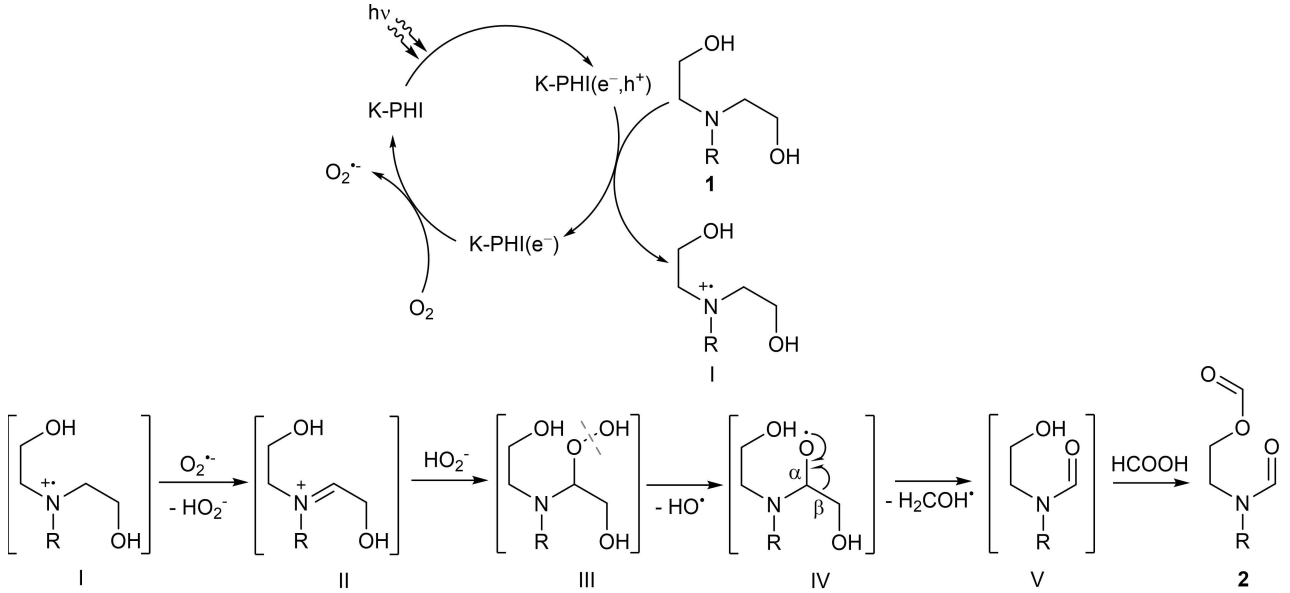


Figure 2. Tentative mechanism of TEOA oxygenation-formylation by K-PHI using O_2.

butyl diethanolamine (>97%) was purchased from TCI. All chemicals were used as received.

Methods. ^{1}H and ^{13}C NMR spectra were recorded on an Agilent 400 MHz (at 400 MHz for Protons and 101 MHz for Carbon-13) NMR spectrometer. Chemical shifts are reported in ppm downfield from the $CHCl_3$ residual peak: 7.26 ppm in ^{1}H NMR and 77.2 ppm in ^{13}C NMR. An Agilent 6890 Network GC System coupled with Agilent 5975 Inert Mass Selective detector (electron ionization) was used for reaction mixture composition analysis and to obtain mass spectra of the products.

Potassium poly (heptazine imide) (K-PHI) was synthesized according to the previously described procedure with some adaptation.[10] A mixture of lithium chloride (3.71 g), potassium chloride (4.54 g) and 5-aminotetrazole monohydrate (1.65 g) was ground in a ball mill for 5 min at a shaking rate of 25 s^{-1}. The reaction mixture was transferred into a porcelain crucible and covered with a lid. The crucible was placed in the oven and heated under constant nitrogen flow (15 L min^{-1}) and atmospheric pressure at the following temperature regime: heating from room temperature to 550 °C within 4 h, annealing at 550 °C for 4 h. After completion of the heating program, the crucible was allowed to cool slowly to room temperature under nitrogen flow. The crude product was removed from the crucible, washed with deionized water (100 mL) for 3 h in order to remove salts, and separated by centrifugation (4000 rpm, 10 min). The solid was redispersed in deionized water (1.5 mL) and separated by centrifugation (13000 rpm, 5 min). Redispersion-centrifugation was repeated 3 times in total. The solid was dried in a vacuum oven (20 mbar) at 65 °C overnight.

Photocatalytic oxidation of ethanolamines

A mixture of ethanolamine (0.05 mmol) and K-PHI (5 mg) in CH_3CN (2 mL) was loaded into 4 mL vial and sealed with a rubber septum. A balloon filled with air (O_2 20 vol.%) was connected, via a needle, to the reaction mixture head space through the septum. The reaction mixture was stirred under illumination with a 465 nm LED (electrical power 50 W) for 24 h. K-PHI was separated by centrifugation. The solution was concentrated in vacuum (50 °C, 150 mbar), the residue was dissolved in $CDCl_3$ and analyzed by NMR spectroscopy. For product separation, $CDCl_3$ was concentrated in vacuum (50 °C, 150 mbar), followed by purification by HPLC (JASCO LC-4000 series equipped with CAPCELL PAK MG II C18 20 mm I. D.x250 mm column, CH_3CN 10 mL min^{-1}).

(Formylazanediyl)bis(ethane-2,1-diyl) diformate 2 a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.05 (s, 1H), 8.04 (s, 1H), 4.32 (t, J = 5.4 Hz, 2H), 4.28 (t, J = 5.3 Hz, 2H), 3.64 (t, J = 5.5 Hz, 2H), 3.60 (t, J = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 160.7, 160.5, 61.3, 60.7, 47.0, 41.9. MS (70 eV): *m/z* (%): 160.0 (2) $[M–C(O)H]^+$, 143.1 (100) $[M–C(O)OH]^+$. Molecular ion not observed.

2-(*N-tert*-butylformamido)ethyl formate 2 b

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 1H), 8.06 (s, 1H), 4.30 (t, J = 6.6 Hz, 2H), 3.58 (t, J = 6.6 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 161.0, 61.5, 55.7, 39.8, 29.8. MS (70 eV): *m/z* (%): 173.1 (69) $[M]^+$, 158.1 (100) $[M–CH_3]^+$.

Synthesis of (formylazanediyl)bis(ethane-2,1-diyl) diformate 2 a from diethanolamine

A solution of diethanolamine (0.35 g, 3 mmol) in formic acid (3 mL) was stirred at reflux for 2 h. Formic acid was distilled off in vacuum (50 °C, 50 mbar). The residue was dissolved in CH_2Cl_2 (5 mL), washed with $NaHCO_3$ solution. Organic phase was separated, dried over anhydrous Na_2SO_4, concentrated in vacuum. Yield: 0.51 g, 90%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.05 (s, 1H), 8.04 (s, 1H), 4.32 (t, J = 5.4 Hz, 2H), 4.28 (t, J = 5.3 Hz, 2H), 3.64 (t, J = 5.4 Hz, 2H), 3.60 (t, J = 5.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 160.9, 160.7, 61.1, 60.5, 47.4, 42.3.

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Conflict of Interest

A patent WO/2019/081036 has been filed by Max Planck Gesellschaft zur Förderung der Wissenschaften E.V. in which O.S. is listed as a co-author.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: carbon nitride · formamide · oxygenation · photocatalysis · triethanolamine

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