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2,2,6,6-Tetramethyl-1-oxopiperidinetribromide and two forms of 1-hydroxy-2,2,6,6-tetramethylpiperidinium bromide salt: Syntheses, crystal structures and theoretical calculations

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ABSTRACT

The reaction of the nitroxy radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) with Br_2 has been investigated with CCl_4 and hexane to obtain TEMPO-Br salts: 2,2,6,6-tetramethylpiperidine-1-oxopiperidine tribromide [TEMPO][Br_3^-] (**I**), and the 1-hydroxy-2,2,6,6-tetramethylpiperidinium bromide salts [$TEMPH^+OHBr^-$] (**II** and **III**). The salt **I** was isolated in crystalline form directly from the synthesis and **II** and **III** by only changing the solvent. The crystals of **I** belong to the orthorhombic crystal systems with space group $Cmc2_1$, a = 10.5596(4) Å, b = 14.0464(4) Å, c = 9.4202(5), and with asymmetric unit of Z = 4. Crystals **II** belong to *Pnna* a = 11.9860(3) Å, b = 23.6720(9) Å, c = 7.7051(3) Å while **III** belongs to $Cmc2_1$ with a = 10.2686(3) Å, b = 10.7661(3) Å, c = 10.0274(2) Å; the asymmetric unit of **II** and **III** was Z = 8 and Z = 4, respectively. The crystal structure of **I** shows the Br_3^- ion as [Br—Br—Br]$^-$ for each molecule of TEMPO. The crystal structure of **II** shows a weak intermolecular hydrogen bond between —N-H···Br(1) and O(1)H···Br(2) due to the presence of the $-N^+HOH-$ moiety. In contrast, crystal **III** shows intermolecular hydrogen bonding between O(1)H···Br(1)···HN(1) due to the $-N^+HOH-$ moiety. The resulting compounds were characterized by FT-IR and UV—vis spectroscopy. The structural parameters have been compared with the related hydroxylaminotrichlorosilane known from the literature and with results of DFT calculations.

1. Introduction

2,2,6,6-Tetramethylpiperidine-*N*-oxyl (TEMPO), a stable organic nitroxyl radical [1] and its derivatives have been used for numerous purposes over the past decades [2–8]. In recent years, the unpaired electron situated at the oxygen atom has been used to perform spin labeling of biomolecules such as peptides or proteins to gain structural information, for example, in the surface topology of a protein, which can be obtained by the determination of pseudo-contact shifts (PCS) [9]. On the other hand, the oxoammonium salts (OS) reported by Golubev [10] have become widely used and represent an environmentally benign method for the conversion of primary and secondary alcohols to aldehydes and ketones, respectively [11–16]. The oxidation of an alcohol by using a stoichiometric quantity of a preformed OS is readily accomplished [17–20]. More commonly, oxidations are conducted via a catalytic process that involves *in situ* generation of the oxoammonium cation by one-electron oxidation of a small quantity of a nitroxide species, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), either electrochemically [21–26] or with a stoichiometric quantity of a primary oxidant [11–16] such as sodium hypochlorite [23–26]. The rate of oxidation of both primary and secondary alcohols by oxoammonium cations is increased with increasing pH of the reaction medium and therefore, most catalytic processes are carried out under basic conditions. The oxoammonium cation was the active oxidant described in the work of Bobbitt and colleagues

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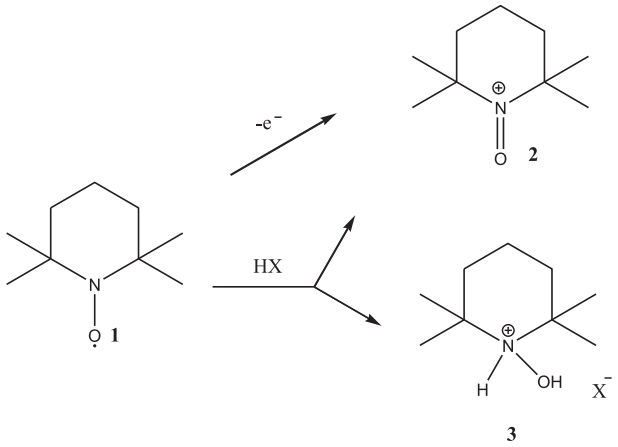
[17,20,27] (Scheme 1a). The mechanism involving the oxoammonium cations showed that no hydrogens on the carbons were attached to nitrogen (α-hydrogens), because no double bond was formed between nitrogen and one of the adjacent carbons [11,28,29].

There are many examples of these kinds of OSs [11], but the most common ones are based on a piperidine nucleus. In Scheme 1(b), the redox properties of nitroxyl radicals **1**, OS **2**, and hydroxylamines or their salts **3**, have been reported as well as their general methods of preparation and decomposition. The best-known compound is 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), **1**. TEMPO is a stable oxygen free radical discovered in 1962 [19,20]. The removal of one electron from TEMPO in the presence of a suitable anion yields OS **2** (2,2,6,6-tetramethylpiperidine-1-oxonium or 2,2,6,6-tetramethyl-1-oxopiperidinium salt). The addition of one electron with a suitable anion and acid to TEMPO gives the hydroxylamine salt **3** (1-hydroxy-2,2,6,6-tetramethylpiperidinium salt). In a remarkable disproportionation reaction in strong acid, TEMPO is converted to one molecule of **2** and one molecule of **3** (Scheme 2). According to Scheme 1(b), an alcohol oxidation involves a two-electron reaction in which the OS **2** is converted to a hydroxyammonium salt **3**.

Recent studies by Stefan et al. [30], reported different products other than the silicon-containing product (TEMPO-$SiCl_3$) from the reaction of nitroxyl radical (TEMPO) with $SiCl_4$. These authors reported the formation of an OS of $TEMPO^+Cl^-$. The TEMPO-$SiCl_3$ decomposed due to hydrolysis yielding several TEMPO-containing species, which were characterized by crystallographic methods. Also these authors compared the structural parameters of the related hydroxylaminotrichlorosilane known from the literature and the DFT calculations. In principle, the replacement of a chlorine radical from $SiCl_4$ may occur in the presence of TEMPO, accompanied by the liberation of elemental chlorine. In Ref. [30], the products $TEMPO^+$ Cl^-, TEMPOH·HCl and TEMPO·HCl obtained from TEMPO-$SiCl_3$ are reported. The authors proposed that $TEMPO^+$ Cl^-, TEMPOH·HCl and TEMPO·HCl are presumably formed by hydrolysis of TEMPO-$SiCl_3$ concomitantly with the formation of HCl.

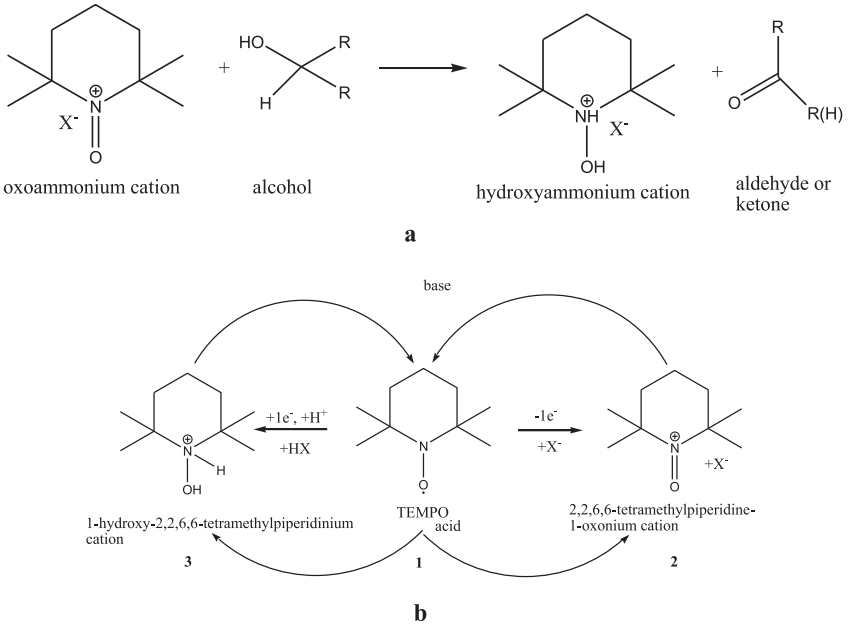
The oxoammonium salts may be obtained by suitable chemical oxidants, for instance, halogens or hypohalites, where the counter ion of the OS is generally derived from the oxidant. An alternative way to prepare OS is by an acid-catalyzed disproportion of nitroxide **1**, as shown in Scheme 2.



Scheme 2. Alternative pathway synthesis of OS in presence of acid [17].

The use of tetrafluoroboric acid or perchloric acid led to a mixture of the OS and the corresponding hydroxylammonium salts **3** [31]. Either the two salts were isolated or the hydroxylamine was oxidized separately to the oxoammonium salt, or the hydroxylammonium derivative could be oxidized *in situ* by hypohalites to produce OS in good yields. Depending on the oxidation procedure, this method may give rise to some ambiguity of the composition of the OS. For instance, using bromide as the oxidant may give rise to a bromide, a tribromide, or a mixture of them [31].

Recently in our laboratory, we endeavored to obtain compounds containing TEMPO. Herein, we report the products from the reaction of TEMPO with Br_2 in order to clarify the type of salt formed. The reaction was carried out at 1:1 and 1:0.5 M ratios in two solvents at room temperature. The products were characterized by IR spectroscopy and X-Ray crystallography. Although the 2,2,6,6-tetramethylpiperidine-1-oxopiperidine tribromide compound had



Scheme 1. (a) oxidation of alcohols using OS (a) and TEMPO redox reactions (b) [11,17].