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The oxidative halogenations of arenes in water using hydrogen peroxide and halide salts over an ionic catalyst containing sulfo group and hexafluorotitanate

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ABSTRACT

An ionic compound, bis[1-methyl-3-(3′-sulfopropyl)imidazolium] hexafluorotitanate (**1**), was proved to be the efficient and recyclable catalyst for the oxidative halogenations of arenes in water using H_2O_2 as the oxidant and halide salts as the halogenation sources. The mono-halogenated products were obtained selectively by this method. The synergetic catalytic effect coming from the two incorporated functionalities of $-SO_3H$ and $[TiF_6]^{2-}$ was manifested in **1**. The halogenation rate catalyzed by **1** was in the ranking of $NaBr \gg NaCl > KI$. The UV–vis and FT-IR analyses indicated that the successful formation and regeneration of the active peroxo-Ti species (**1A**) with the aid of proton acid guaranteed the recycling uses of **1**.

1. Introduction

Halogenation is an important electrophilic substitution reaction and halogenated organic compounds are essential in organic synthesis as useful synthetic intermediates for preparation of pharmaceuticals, pesticides, agricultural chemicals, and bioactive compounds [1,2]. They are also useful and important substrates for various cross-coupling reactions [3]. In the laboratory, however, halogen-based oxidants such as elemental halogens, organic and inorganic hypohalites, hypervalent iodine (III) and (V) reagents, dihalo-5,5′-dimethylhydantoins and N-halosuccinimides are often used for the selective halogenation of unsaturated hydrocarbons. Halogenations using such hazardous, toxic, and corrosive regents result in serious environmental problems with respect to the handling, transportation, storage, and stoichiometric amounts of waste [4,5].

In nature, electrophilic halogenation mainly occurs by oxidative halogenation through the catalyzed oxidation of the halide ion to form a halogenating reagent [1,4,6]. An exception is fluorination, since it is too difficult to oxidize fluoride [1]. The increased understanding of oxidative halogenation in biological systems has boosted research in the field of green oxidative halogenations. From green chemistry perspectives, halide salts are much safer and easier to be handled and can be oxidized to the corresponding positive halogens (Cl^+, Br^+, I^+) or hypohalous acids ($[XO]^-$, $X = Cl^+, Br^+, I^+$) by H_2O_2, which is an environmentally friendly oxidant [2,7,8]. Although the oxidation of these halides with H_2O_2 is thermodynamically favored, it is kinetically slow [9]; hence it is not a practical process. However, At lower pH, the oxidation of the halides with H_2O_2 can be accelerated and the hypohalous acids generated from hydrochloric or hydrobromic acid and H_2O_2 have been used for the successful halogenation of a variety of organic substrates although acid-sensitive functionality will not tolerate the reaction conditions [6,10]. In order to mimic the function of the haloperoxidases to catalyze the halide ion to form a halogenating reagent, chemists with growing ecological awareness have sought catalysts to activate H_2O_2 and to provide environmentally friendly means for the halogenation of organic substrates [2,5–8,11]. Many transition metal compounds (such as vanadium, molybdenum, cerium, tellurium, etc.) have been used as catalysts for oxidative halogenation of organic substrates with halide salts and H_2O_2 [2,5–8,12–21]. However, $TiF_6{}^{2-}$-based catalysts were rarely reported in these examples.

On the other hand, the use of polar organic solvents in most cases, such as CH_2Cl_2, THF, and CH_3CN largely defeats the environmental and economic advantages of oxidative halogenation with H_2O_2 and halide salts. The use of water as the reaction medium affords many benefits [8,22]. Water is a cheap and abundant, non-toxic, non-flammable and green solvent. In addition, in water, phase separation is easier because most organic compounds are

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not soluble in water and can be easily separated from the aqueous phase.

However, until now the inexpensive and environmentally friendly methods for the oxidative halogenations with halide salts and H_2O_2 in water, which are catalyzed by the recyclable catalysts, are scarce in the literature and are of interest from economical and environmental concerns.

Herein, we introduced a new catalytic method using an ionic compound (**1**) containing two functional moieties of sulfo group ($-SO_3H$) and hexafluorotitanate (TiF_6^{2-}) as the efficient and recyclable catalyst for the oxidative halogenations of aromatic compounds. In this method, water was used as the solvent; the cheap and non-corrosive halide salts (NaBr, NaCl, and KI) were applied as the halogenation sources; the clean, non-toxic and inexpensive H_2O_2 was applied as the oxidant. The purpose of using halide salts as the halogenations sources instead of hydrohalic acids (HX, $X = Cl^+$, Br^+, I^+) was to elucidate the possible synergetic catalytic effects coming from SO_3H- and $[TiF_6]^{2-}$ in **1** and rule out the overlapping effect coming from the H^+ in HX against that in sulfo group. The characterization and identification of the peroxo-Ti species (**1A**) derived from **1** were studied by means of UV–vis and FT-IR spectroscopies.

2. Experimental

2.1. Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and used as received. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. UV–vis spectra were monitored on a SHIMADZU-UV 2550 spectrophotometer at ambient temperature. ^1H NMR spectra were recorded on a Bruker Avance 500 spectrometer. The Ti amount in the sample was quantified using an inductive coupled plasma atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). CHN-element analysis was performed on a Vario EL III Element Analyzer. TG/DTA was performed in air flow with a temperature ramp of $10\,^\circ C\,min^{-1}$ between 50 and 800 °C, using a Mettler TGA/SDTA 851e instrument and STARe thermal analysis data processing system. Gas chromatography (GC) was performed on a SHIMADZU-2014 equipped with a DM-1 capillary column ($30\,m \times 0.25\,mm \times 0.25\,\mu m$). GC–mass spectrometer (GC–MS) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector.

2.2. Synthesis

2.2.1. Bis[1-methyl-3-(3′-sulfopropyl)imidazolium] hexafluorotitanate (1)

Bis[1-methyl-3-(3′-sulfopropyl)imidazolium] hexafluorotitanate (**1**) was prepared according to our previously published method [23], with some modifications. The mixtures of 1,3-propanesultone (0.15 mol) in 100 mL acetone and N-methylimidazole (0.15 mol) in 100 mL acetone were stirred vigorously at ambient temperature. Gradually, the white solids were precipitated from the reaction solution. Upon completion of the reaction for 3 h, the precipitated white solids, through washing with acetone and drying under vacuum, were collected with the yield of 91%. The obtained white solids (0.10 mol) were added with 0.05 mol of aqueous hexafluorotitanic acid (H_2TiF_6, 60% aqueous solution, commercial). The resultant solution after stirring at ambient temperature for 24 h was stripped of solvent on a rotary evaporator. The obtained residues were treated with ethanol. After vigorous stirring, the mixtures were filtered to give the clear filtrate, which was concentrated under vacuum to yield the solids as the product of **1** (Yield 79%). TG/DTA (in air flow): 366 °C (thermal decomposition). FT-IR (KBr disc, cm^{-1}): $\nu = 3150$ (m), 3104 (m), 1562 (m, C=N), 1457 (w, C=C), 1267 (s, C—N), 1176 (vs, broad, $-SO_3H$), 1033 (s, $-SO_3H$), 752 (m), 624 (vs, TiF_6^{2-}). ^1H NMR (D_2O, ppm): $\delta = 8.6$ (H, s, $NC(\mathit{H})N^+$), 7.3–7.4 (2H, $NC(\mathit{H})C(\mathit{H})N^+$), 4.2 (2H, t, $J = 7$, $N^+C(\mathit{H_2})C(H_2)C(H_2)SO_3H$), 3.8 (3H, s, $C(\mathit{H_3})N$), 2.8 (2H, t, $J = 7$, $N^+C(H_2)C(H_2)C(\mathit{H_2})SO_3H$), 2.2 (2H, m, $N^+C(H_2)C(\mathit{H_2})C(H_2)SO_3H$). CHN-elemental analysis (wt%): C 29.02, H 4.88, N 9.23 (Calcd.: C 29.38, H 4.55, N 9.78).

2.2.2. Bis-[1-butyl-3-methylimidazolium] hexafluorotitanate (2)

To the aqueous solution (100 mL) of 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, 0.1 mol), an aqueous solution of H_2TiF_6 (0.05 mol, 60%) was added. After vigorous stirring at ambient temperature for 24 h, the resultant solution was stripped of solvent on a rotary evaporator. The obtained residues were added with CH_2Cl_2. After vigorous stirring, the mixtures were filtered to give the clear filtrate, which was concentrated under vacuum to afford a sticky liquid as the product of **2** (Yield 82%). FT-IR (KBr disc, cm^{-1}): $\nu = 3155$ (m), 3100 (m), 1632 (m, C=N), 1460 (w, C=C), 747 (m), 568 (vs, TiF_6^{2-}). ^1H NMR (D_2O, ppm): $\delta = 8.6$ (H, s, $NC(H)N^+$), 7.3–7.4 (2H, $NC(\mathit{H})C(\mathit{H})N^+$), 4.1 (2H, t, $J = 7$, $N^+C(\mathit{H_2})C(H_2)C(H_2)C(H_3)$), 3.8 (3H, s, $C(\mathit{H_3})N$), 1.7 (2H, m, $J = 7$, $N^+C(H_2)C(\mathit{H_2})C(H_2)C(H_3)$), 1.2 (2H, m, $N^+C(H_2)C(H_2)C(\mathit{H_2})C(H_3)$), 0.8 (3H, m, $N^+C(H_2)C(H_2)C(H_2)C(\mathit{H_3})$. CHN-elemental analysis (wt %): C 44.24, H 7.27, N 12.33 (Calcd.: C 43.64, H 6.87, N 12.72).

2.2.3. Bis[1-methyl-3(3′-sulfopropyl)imidazolium] sulfate (3)

Bis[1-methyl-3(3′-sulfopropyl)imidazolium] sulfate (**3**) was prepared according to the similar procedures as described for **1**, but H_2SO_4 aqueous solution was used in place of H_2TiF_6. FT-IR (KBr disc, cm^{-1}): $\nu = 3155$ (m), 3111 (m), 1579 (m, C=N), 1452 (w, C=C), 1108 (vs, broad, $-SO_3H$). ^1H NMR (D_2O, ppm): $\delta = 8.5$ (H, s, $NC(\mathit{H})N^+$), 7.2–7.3 (2H, $NC(\mathit{H})C(\mathit{H})N^+$), 4.1 (2H, t, $J = 7.0$, $N^+C(\mathit{H_2})C(H_2)C(H_2)SO_3H$), 3.7 (3H, s, $C(\mathit{H_3})N$), 2.7 (2H, t, $J = 7$, $N^+C(H_2)C(H_2)C(\mathit{H_2})SO_3H$), 2.2 (2H, m, $N + C(H_2)C(\mathit{H_2})C(H_2)SO_3H$). CHN-elemental analysis (wt%): C 32.69, H 5.97, N 10.74 (Calcd.: C 33.19, H 5.17, N 11.06).

2.3. General procedures for bromination of arenes using NaBr and H_2O_2 catalyzed by 1

For the typical experiment, to 3 mL of water, anisole (or the other substrate, 5 mmol), NaBr (10 mmol), **1** (2.0 mmol), and 30% aqueous solution of H_2O_2 (10 mmol) were mixed sequentially in a single addition. The obtained mixture was stirred vigorously at room temperature. Upon completion of the reaction, the upper organic phase was separated by decantation and the left mixture was extracted by diethyl ether repeatedly ($2\,mL \times 3\,mL$). The combined organic phase was analyzed by GC and GC–MS. The conversion of anisole was based on GC analysis with *n*-dodecane as the internal standard. The selectivity of the product was based on GC analysis using the normalization method. The GC yield was obtained on the basis of conversion × selectivity. The products were further identified by GC–MS.

The left mixtures, containing the aqueous phase and the precipitated yellow solids, were added with the saturated Na_2SO_3 solution gradually to destroy the unreacted H_2O_2 until the KI-starch test paper changed to blue color. Afterwards, the obtained mixtures were recharged with anisole (5 mmol), NaBr (5 mmol), H_2O_2 (10 mmol), and H_2SO_4 (2.5 mmol) if required, for next run.