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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.

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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 H₂O₂ can be accelerated and the hypohalous acids generated from hydrochloric or hydrobromic acid and H₂O₂ 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 H₂O₂ 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 H₂O₂ [2,5-8,12-21]. However, TiF₆²⁻-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, nontoxic, 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 H₂O₂ 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 SO₃H— 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°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 μ 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 (H₂TiF₆, 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): $366 \circ C$ (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 (D₂O, ppm): $\delta = 8.6$ (H, s, NC(H)N⁺), 7.3-7.4 (2H, NC(H)C(H)N⁺), 4.2 (2H, t, J = 7, N⁺C(H₂)C(H₂)C(H₂)SO₃H), 3.8 (3H, s, C(H₃)N), 2.8 (2H, t, J = 7, N⁺C(H₂)C(H₂)SO₃H), 2.2 (2H, m, N⁺C(H₂)C(H₂)C(H₂)SO₃H), 2.2 (2H, m, N⁺C(H₂)C(H₂)C(H₂)SO₃H). 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)

То the aqueous solution (100 mL) of 1-butyl-3methylimidazolium chloride ([Bmim]Cl, 0.1 mol), an aqueous solution of H₂TiF₆ (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 CH₂Cl₂. 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}): ν =3155 (m), 3100 (m), 1632 (m, C=N), 1460 (w, C=C), 747 (m), 568 (vs, TiF₆^{2–}). ¹H NMR (D₂O, ppm): δ =8.6 (H, s, NC(H)N⁺), 7.3–7.4 $(2H, NC(H)C(H)N^+), 4.1 (2H, t, J=7, N^+C(H_2)C(H_2)C(H_2)C(H_3)), 3.8$ $(3H, s, C(H_3)N), 1.7 (2H, m, J=7, N^+C(H_2)C(H_2)C(H_2)C(H_3)),$ 1.2 (2H, m, $N^+C(H_2)C(H_2)C(H_2)(H_3)$), 0.8 (3H, m. N⁺C(H₂)C(H₂)C(H₂)C(H₃). 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 H₂SO₄ aqueous solution was used in place of H₂TiF₆. FT-IR (KBr disc, cm⁻¹): ν =3155 (m), 3111 (m), 1579 (m, C=N), 1452 (w, C=C), 1108 (vs, broad, -SO₃H). ¹H NMR (D₂O, ppm): δ =8.5 (H, s, NC(H)N⁺), 7.2–7.3 (2H, NC(H)C(H)N⁺), 4.1 (2H, t, *J*=7.0, N⁺C(H₂)C(H₂)C(H₂)SO₃H), 3.7 (3H, s, C(H₃)N), 2.7 (2H, t, *J*=7, N⁺C(H₂)C(H₂)C(H₂)SO₃H), 2.2 (2H, m, N+C(H₂)C(H₂)C(H₂)SO₃H). 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 × 3 mL). The combined organic phase 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.

3. Results and discussion

3.1. Investigation on the catalytic performance of **1** for the oxidative halogenation

The bromination of anisole with H₂O₂ and NaBr was selected as the model reaction (Table 1). It was found that, without the presence of **1** as a catalyst, the reaction did not happen (Entry 1), while the conversion of anisole increased along with the amount of **1** at R.T. (25 °C) (Entries 2-4). In these cases, although excess NaBr was used as the bromination source, 4-bromoanisole was found to be the only mono-brominated product and no di-brominated product was formed at all. Once 4-bromoanisole was formed, the nucleophilicity of aryl ring got weakened due to the strong electronegativity of Br atom, leading to the unfavorable electrophilic attack by the second [BrO]⁻ and then the inhibited di-bromination. Under the similar conditions, when less NaBr (5 mmol) or H_2O_2 (5 mmol) was applied, the yield of 4-bromoanisole decreased dramatically (Entries 5 and 6). It was found that the self-decomposition of H₂O₂ under the applied conditions (no anisole, NaBr 10 mmol, H₂O₂ 10 mmol, H₂O 3 mL, R.T., time 3 h) was ca. 18% in the presence of 1 (2.0 mmol) or 15% in the presence of H_2SO_4 (2.5 mmol), which was measured by permanganimetric titration (standard KMnO₄ aqueous solution, 0.1 M), accounting for the requirement for the excess of H₂O₂ (2 mmol) for the complete oxidative bromination of anisole

Actually, it was noted that in 1, two catalytic sites were located. In order to elucidate the individual contribution of -SO₃H and $[TiF_6]^{2-}$ to the activation of the substrate, the oxidative bromination of anisole catalyzed by 2 and 3 was investigated in parallel. As shown in Entries 7 and 8, the absence of any function moiety led to much lower yields of 4-bromoanisole (2: 41%; 3: 39%) respectively, indicating that the cumulative contribution of 2 and 3 to the activation of anisole is less than that of 1 individually. These results revealed that the catalytic behaviors of -SO₃H and TiF₆²⁻ were reinforced each other when they were combined together in 1 as one unit, and that the observed cooperative effect in 1 was caused by a specific synergetic interaction between $-SO_3H$ and TiF_6^{2-} , but not attributable to pure statistic reasons. On the other hand, when the commercial inorganic acid of H₂TiF₆ (60% aqueous solution, 2 mmol) was used as the catalyst, the relatively lower yield of 80% was obtained in comparison with that over 1 (Entry 9). Reasonably, the catalytic nature for H₂TiF₆ and **1** are identical which are both featured with a combination of proton acid and TiF₆²⁻ counter-anion, but $H_2 TiF_6$ is absolutely hydrophilic, whereas **1** is amphipathic. Probably, the oxidation of NaBr by H₂O₂ catalyzed by 1 to yield [OBr]⁻ and the subsequent electrophilic bromination of the lipophilic anisole by hydrophilic [OBr]- are more favored over **1** than H_2TiF_6 . The amphipathicity of **1** might more adapt to the oxidative bromination of lipophilic anisole by hydrophilic NaBr and H₂O₂. On the other hand, **1** as a kind of organic acid is less corrosive than the inorganic strong acid of H₂TiF₆, which facilitates the experimental manipulation.

For the practical application, the request for easily separable and recyclable catalysts is driven by economic consideration and environmental concerns. Since catalyst **1**, H_2O_2 and NaBr were all very soluble in water, the separation of the lipophilic substrate of anisole and the brominated product from the aqueous phase could be conducted very easily through decantation. The left mixtures were reused for next run. The recycling uses of the recovered **1** for the bromination of anisole were given in Table 2. It was found that, upon completion of the 1st run, 100% yield of 4-bromoanisole was obtained along with the precipitation of the yellow solids from the aqueous phase (which were characterized in Figs. 1 inset and 2). When the left mixtures containing the aqueous phase and the yellow solids were treated with Na₂SO₃ to destroy the unreacted H₂O₂,



Fig. 1. The evolving processes of **1** in H_2O recorded by UV-vis spectra under different conditions: (a) **1**; (b) $1 + H_2O_2$; (c) $1 + H_2O_2 + NaBr + anisole; (d) <math>1 + H_2O_2 + NaBr + anisole + H_2SO_4$; (e) $1 + H_2O_2 + NaBr + anisole + H_2SO_4$; (e) $1 + H_2O_2 + NaBr + anisole + H_2SO_4$; (inset: the UV-vis spectra of the yellow solids (**1B**) precipitated from water upon completion of the 1st run reaction in Table 2).

and then reused in the 2nd run, only 19% yield of 4-bromoanisole was obtained, indicating the dramatic activity loss of **1**. Fortunately, if the left mixtures were further treated with the proton acid like H_2SO_4 , the yellow precipitates disappeared to afford a clear light-yellow aqueous solution, in which the oxidative bromination of anisole with H_2O_2 and NaBr could be carried out as well as the fresh **1**-catalyzed reaction. The cumulative Na_2SO_4 and H_2O showed negligible effect on the performance of **1**.

The proton acid such as **3** possessing sulfo group has been found to be able to catalyze the bromination of anisole to afford 4-bromoanisole (%) with the yield of 39% (Entry 8 of Table 1). Similarly, when 2.5 mmol of H_2SO_4 was used in place of **1**, anisole could be brominated to 4-bromoanisole with the yield of 44% under the same conditions. Hence, when H_2SO_4 (2.5 mmol) was added additionally in each run in Table 2 (Runs: 3rd–6th), it not only played the role in regenerating the deactivated **1**, but also acted as the acid-catalyst to further spur the oxidative bromination, leading to the successful reuses of **1** along with the excellent yields of 4-bromoanisole.



Fig. 2. The FT-IR spectra of H₂TiF₆, 1, and the yellow solids (1B).

Table 1

The oxidative bromination of anisole using H_2O_2 and NaBr catalyzed by $\mathbf{1}^a$



Entry	Catalyst (mmol)	NaBr (mmol)	H_2O_2 (mmol)	Conv. (%) ^b	Sel. (%) ^{b,c}	Yield (%) ^{b,c}
1	None	10	10	-	-	-
2	1 (1.0)	10	10	30	100	30
3	1 (1.5)	10	10	78	100	78
4	1 (2.0)	10	10	100	100	100
5	1 (2.0)	5	10	56	100	56
6	1 (2.0)	10	5	62	100	62
7	2 (2.0)	10	10	41	100	41
8	3 (2.0)	10	10	39	100	39
9	$H_2 TiF_6$ (2.0)	10	10	84	100	84
8 9	3 (2.0) H ₂ TiF ₆ (2.0)	10 10	10 10	39 84	100 100	39 84

^a Anisole 5 mmol, H₂O 3 mL, room temperature (R.T., 25 °C), time 3 h.

^b Determined by GC.

^c To 4-bromoanisole.

Table 2

The recycling of $\mathbf{1}$ as the catalyst for the oxidative bromination of anisole using H_2O_2 and NaBr^a

Run	Catalyst	H ₂ SO ₄ (mmol)	NaBr (mmol)	Conv. (%) ^b	Sel. (%) ^{b,c}	Yield (%) ^{b,c}
1st (fresh)	1	_	10	100	100	100
2nd	_	-	5 ^e	19	100	19
3rd	-	2.5 ^d	5 ^e	97	100	97
4th	-	2.5 ^d	5 ^e	95	100	95
5th	-	2.5 ^d	5 ^e	99	100	99
6th	-	2.5 ^d	5 ^e	99	100	99
7th	-	2.5 ^d	5 ^e	98	100	98
8th	-	2.5 ^d	5 ^e	99	100	99

^a 1 2.0 mmol, anisole 5 mmol, H₂O₂ 10 mmol, 3 mL H₂O, room temperature (R.T. 25 °C), time 3 h.

^b Determined by GC and GC-MS.

^c To 4-bromoanisole.

 d 2.5 mmol H₂SO₄ was added additionally in each run.

^e 5 mmol of NaBr was added in consideration of the cumulative NaBr in the previous run.

The total loss of **1** in term of Ti amount after eight-runs in the combined organic phase was below the detection limit (<0.1 μ g/g on the basis of the ICP analysis), indicating that the leaching of **1** in the organic phase is negligible in the courses of reaction and separation.

Next, the oxidative halogenations using NaCl and KI were examined in Table 3 in parallel. In comparison with chlorination and bromination, iodination is more concerned by organic chemists due to the availability of the abundant iodinated aromatic compounds for accomplishing coupling reactions. Since NaI was very hygroscopic, KI was used in the case of iodination. However, when KI was used as the iodination source, no iodinated product was formed at all even if the reaction temperature increased to $60 \,^\circ$ C (Entries 2 and 3). It was noted that, in the course of the oxidation of KI by H₂O₂ over **1**, the formed non-polar iodine (I₂) was precipitated completely from the aqueous solution due to its poor

able 3
he oxidative bromination of anisole with H_2O_2 and other halide salts catalyzed by ${f 1}$

Entry	Halogenation source	Solvent	Temp. (°C)	Conv. (%) ^b	Sel. (%) ^{b, c}	Yield (%) ^{b,c}
1	NaBr	H ₂ O	R.T.	100	100	100
2	KI	H ₂ O	R.T.	-	-	-
3	KI	H ₂ O	60	-	-	-
4	KI	$[Bmim]PF_6-H_2O(v/v=2:1)$	R.T.	39	100	39
5	KI	$[Bmim]PF_6-H_2O(v/v=2:1)$	60	68	100	68
6 ^d	NaCl	H ₂ O	R.T.	44	77/23	34/10
7 ^e	NaCl	H ₂ O	60	76	78/22	59/17

^a 1 40 mol%, anisole 5 mmol, halide salt 10 mmol, H₂O₂ 10 mmol, solvent 3 mL, time 3 h.

^b Determined by GC.

^c To 4-halogenated anisole.

^d 77% selectivity to 4-chloroanisole with the yield of 34%, and 23% selectivity to 2-chloroanisole with the yield of 10%.

e 78% selectivity to 4-chloroanisole with the yield of 59%, and 22% selectivity to 2-chloroanisole with the yield of 17%.

Table 4

The generality of $\mathbf{1}$ as a catalyst for the oxidative halogenation of different substrates with H_2O_2 ^a

Entry	Substrate	Product	X-source	Temp. (°C)	Time (h)	Conv. (%) ^b	Sel. (%) ^b	Yield (%) ^b
1	ОСН3	Br-CH3	NaBr	R.T.	3	100	100	100
2	Н ₃ С-СН3	H ₃ C-CH ₃ Br	NaBr	R.T.	3	95	100	95
3	CH ₃	Br CH ₃	NaBr	60	3	92	100	92
4		Br-CH ₃	NaBr	60	3	65	100	65
5	CI-CI	Br	NaBr	60	5	68	100	68
6			NaCl	60	3	76	78	59
		CI CH3					22	17
7	OCH3		NaCl	60	3	71	78	55
							22	16
8	CH3	CI CH ₃	NaCl	60	3	62	100	62
9	H ₃ C-C-OCH ₃		NaCl	60	3	87	100	87
10 ^c			KI	60	3	46	100	46
11 ^{c,d}			KI	60	3	63	100	63
12 ^{c,d}	СН3		KI	70	4	62	100	62
13 ^{c,d}	CH3	CH3	KI	70	5	10	100	10

^a **1** 35 mol%, substrate 5 mmol, halide salt 10 mmol, 3 mL H₂O, H₂O₂ 10 mmol.

^b Determined by GC and GC–MS respectively.

^c [Bmim]PF₆ 2 mL + 1 mL H₂O.

^d H₂O₂ 15 mmol.

solubility in water. Consequently, the further oxidation of I₂ to [IO]⁻ by H₂O₂ was depressed, leading to unaccomplished electrophilic iodination of anisole by [IO]⁻. Therefore, when the hydrophobic IL of [Bmim]PF₆ was used as the co-solvent, 39% of anisole was converted to the corresponding 4-iodoanisole with 100% selectivity at R.T. (Entry 4); while the temperature increased to 60 °C, 68% yield

of 4-iodoanisole was obtained (Entry 5). As for NaCl as the chlorination source, the mono-chlorinated products were obtained with the yield of 76% at $60 \,^{\circ}$ C, including 59% of 4-chloroanisole and 17% of 2-chloroanisole (Entry 7).

It has been proposed that the overall oxidative halogenation including two steps: the first one is catalytic oxidation of halide (X^-) to hypohalous ion ($[XO]^-$); the second one is electrophilic halogenation with $[XO]^-$ as the active electrophile (non-catalytic reaction) [5,7]. Although the oxidation of X⁻ happens with increasing ease from Cl⁻ to I⁻, the electrophilic activity of the resultant $[XO]^-$ is in the ranking of $[CIO]^- > [BrO]^- > [IO]^-$. Consequently, the oxidative bromination using NaBr with moderate reactivity both in catalytic oxidation and electrophilic halogenation exhibits the fastest reaction rate. It means that the reaction rate of oxidative halogenation catalyzed by **1** is in the ranking of NaBr \gg NaCl > KI.

The generality of **1** as a catalyst for the oxidative halogenation by H_2O_2 was examined on a series of aromatic compounds with different electronic and steric effects. As shown in Table 4, the mono-bromination of the activated aromatic compounds such as anisole and 1-methoxy-4-methylbenzene were all performed well at room temperature (Entries 1 and 2). 92% of 2-methylnaphthalene with bulky steric hindrance was brominated to 1-bromo-2-methylnaphthalene in 3 h at 60 °C (Entry 3). The bromination of toluene required the higher temperature and prolonged reaction time (Entry 4). As for the bromination of 4chlorobenzene with the strong electron-withdrawing effect, the moderate conversions of 68% were obtained with the excellent selectivity to the *para*-mono-brominated product (Entry 5).

The oxidative chlorination of the aromatic compounds with NaCl was listed in Entries 6–9. The activated substrates such as anisole, 1-methoxy-4-methylbenzene, and 2-methylnaphthalene were converted to the corresponding mono-chlorinated products at 60 °C in good to moderate yields (Entries 6–9). However, two types of mono-chlorinated products were found in each case, due to the most active electrophilic activity of [ClO]⁻. 2-Chloroanisole and 2-chlorotoluene were found as the minor products in Entries 6 and 7. 62% of 2-methylnaphthalene was chlorinated to 1-chloro-2-methylnaphthalene with 100% selectivity (Entry 8); while 1-methoxy-4-methylbenzene possessing two kinds of electron-donating substituents ($-OCH_3$ and $-CH_3$) was converted to 2-chloro-1-methoxy-4-methylbenzene in the yield of 87%, without formation of other by-products (Entry 9).

The oxidative iodination of the aromatic compounds with KI in [Bmim]PF₆-H₂O was listed in Entries 10–13. The corresponding mono-iodinated product of 4-iodoanisole was obtained with the yield of 46% (Entry 10). Under the similar conditions, the yield of 4-iodoanisole was improved up to 63% by using 3 equivalent of H₂O₂ (15 mmol, Entry 11). As for toluene, it was iodinated to 4-iodotoluene with the yield of 62% in 4 h at 70 °C (Entry 12). However, the conversion of 2-methylnaphthalene to 1-iodo-2-methylnaphthalene was quite sluggish even at the increased temperature and prolonged reaction time, due to the bulky steric hindrance and the relatively weak electrophilicity of [IO]⁻ (Entry 13).

3.2. Characterization of peroxo-Ti species

The peroxo-Ti complexes are believed to be the active species in the catalytic oxidations of organic compounds [24–27]. But the formation and characterization of the peroxo-Ti species in the oxidative halogenation are rarely reported. In this part, the characterization of the active peroxo-Ti species derived from the oxidation of **1** by H_2O_2 was investigated by means of UV–vis spectra.

The UV–vis spectra were recorded on a SHIMADZU-UV 2550 spectrophotometer at ambient temperature (ca. 25 °C). The concentration of 1 in H₂O was ca. 4.0×10^{-5} M.

As shown in Fig. 1, there was no any absorbance observed for 1 in H_2O (Fig. 1a). When H_2O_2 was added to $1-H_2O$, a strong absorbance band appeared at ca. 363 nm immediately (Fig. 1b), which was ascribed to the ligand-to-metal (O-to-Ti) charge transfer (CT) transition of the formed peroxo-Ti species (1A), in accordance to Zecchina's observations [27]. When the formed 1A was mixed



Scheme 1. The catalytic mechanism for the oxidative halogenations using H_2O_2 and halide salts catalyzed by 1.

with small amount of NaBr and anisole, the absorbance of 363 nm shifted to 354 nm rapidly, indicating the transformation of **1A** to the other species (defined as **1B**) accompanied by the concurrent oxidative bromination of anisole to 4-bromoanisole (Fig. 1c). The subsequent addition of H_2SO_4 (98%) led to the red-shift of 354 (**1B**) to 368 nm instantaneously (Fig. 1d). The band of 368 nm blue-shifted back to 363 nm (**1A**) again after the addition of H_2O_2 , indicating the complete regeneration of **1A** (Fig. 1e). It has been found that in the aforementioned results, upon completion of the 1st run reaction over **1** (Entry 1 of Table 2), the precipitated yellow solid from water also showed a typical UV–vis absorbance band at 354 nm (Fig. 1inset), which was believed to be the same compound as **1B** in Fig. 1c.

The FT-IR spectra of such yellow solid (**1B**) were shown in Fig. 2. In comparison to **1**, the disappearance of the vibration bands at 3152 and 3101 (ν C–H), 1569 and 1458 (ν C=N, C=C), and 1267, 1173 and 1037 (ν SO₃⁻) revealed that **1B** was a kind of inorganic compounds not holding the SO₃H-grafted imidazolium tag. The appeared peaks for **1B** at 1126 and 905 might be ascribed to the vibrations of Ti–O–Ti bond [28]. The characteristic vibration of TiF₆²⁻ at 620 cm⁻¹ for **1** red-shifted to 539 cm⁻¹ for **1B**, indicating the bond energy of Ti-F in **1B** was weakened due to the increased polarity. According to the FT-IR spectra, **1B** was attributed to be the polymerized derivative of [O–TiF₄–O]_n with poor aqueous solubility.

Based on the results in UV–vis (Fig. 1) and FT-IR analyses (Fig. 2), a catalytic mechanism for the oxidative halogenations over **1** is proposed tentatively in Scheme 1. The strong hydrogen-bond interaction between F. . .H in **1** facilitates the oxidative insertion of H_2O_2 into the weak Ti–F bonds in the axial position due to their relatively longer bond length than those in the equatorial plane [29], leading to the successful formation of 1A (363 nm), and the consequent release of HF and the Zwitterionic salt. Subsequently, the formed 1A undergoes two pathways derivatively, including the catalytic cycle and the deactivation. In the catalytic cycle, 1A as an active peroxo-Ti species oxidizes X⁻ into [OX]⁻, which rapidly reacts with the substrate to afford the halogenated product (ArX) and OH⁻, along with the regeneration to 1A by H_2O_2 insertion. Simultaneously, the formed OH⁻ neutralizes HF released at the initial stage, leading to the complete consumption of H⁺ without risk of the presence of HF in the reaction system. Unfortunately, the deactivation of 1A (363 nm) into **1B** (354 nm) occurs simultaneously, accompanied by the formation of H₂O and O₂. The resultant **1B** as a kind of polymerized inorganic compound, in which four F-atoms are located in the equatorial plane and two O-atoms in the axial positions, can be depolymerized to 1C (368 nm) by the aid of the proton acid, which is oxidized by H_2O_2 back to **1A** again. Obviously, the formed 1B is the deactivated catalyst. Its regeneration to 1A can be accomplished through the hydrolysis under acidic condition and the subsequent oxidation by H₂O₂. However, the formed alkaline OH⁻, besides of the halogenated product, during the electrophilic halogenation of arenes with [XO]⁻, destroys H⁺ in **1** completely and then inhibits the hydrolysis of 1B, that is the reason why H₂SO₄ is required additionally in the next run for the catalyst regeneration.

4. Conclusions

In summary, the ionic compound of **1**, containing two functionalities of $-SO_3H$ and TiF_6^{2-} , was proved to be an efficient and recyclable bifunctional catalyst for the oxidative halogenations in water using halide salts (NaCl, NaBr, and Kl) as the halogenations sources and H_2O_2 (30%) as the terminal oxidant. The catalytic behaviors of $-SO_3H$ and TiF_6^{2-} were reinforced each other when they were combined together in **1** as one unit. The reaction rates of the oxidative halogenations over **1** were in the ranking of NaBr \gg NaCl > KI. A wide range of arenes with different electronic and steric effects, were successfully converted to the corresponding mono-halogenated products by this method. With the supportive evidences from the UV–vis and FT-IR spectra, it is proposed that the active peroxo-Ti species (**1A**) derived from **1** can be transformed into the inactive polymerized derivative (**1B**), which is able to be regenerated to **1A** with the aid of proton acid and H_2O_2 .

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