

Phosphonium nitrate ionic liquid catalysed electrophilic aromatic oxychlorination†

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Triocylmethylphosphonium nitrate ($P_{8,8,8,1}NO_3$), an ionic liquid made *via* a green synthesis, catalyses electrophilic aromatic chlorination of arenes with HCl and air at 80 °C. The aromatic oxychlorination is truly catalytic in nitrate, proceeds without added solvents, and uses atmospheric oxygen as oxidant. The extent of chlorination can be controlled to yield selectively mono or dichlorinated products, and the ionic liquid catalyst can be recycled. Dependence of the chlorination rate on HCl and nitrate concentrations as well as on the rate of re-oxidation of the nitrogen intermediates by air, allowed us to propose a reaction mechanism.

Introduction

Chlorinated aromatic hydrocarbons are of substantial economic significance, and are important starting materials and additives in the production of high-quality insecticides, fungicides, herbicides, dyes, pharmaceuticals, disinfectants, rubbers, plastics, textiles, and electrical goods.¹

Aromatic chlorination is usually achieved *via* electrophilic substitution. For example, the industrial syntheses of chlorobenzene and chlorotoluene are still largely based on the textbook liquid-phase chlorination process with gaseous chlorine in the presence of a Lewis acid catalyst² (*e.g.* $FeCl_3$). This system however has an intrinsically low atom economy³ since only one of the two chlorine atoms is incorporated in the product, the other being wasted as chloride (HCl or salt) which requires appropriate disposal. In addition the Lewis acid is often not catalytic, and the procedure requires chlorinated solvents. Since the methods involving chlorine gas are extremely well established from a process and economic standpoint, they are still widely preferred industrially despite the hazards and toxicity associated with their use. In this context therefore, any method which reduces the amount of chlorine upstream and downstream, and that improves on the environmental performance of the process is desirable.

Oxidative halogenation uses a more atom economical reagent for aromatic chlorination, *i.e.* the chloride (Cl^-) moiety. In this case all the chlorine ends up in the product, the downfall being that chloride needs to be oxidized to an electrophilic “ Cl^+ ” species, hence the need for an additional oxidant such as aqua regia,⁴ hypochlorous acid,⁵ or hydrogen peroxide.⁶ In these cases, atom efficiency can still be maintained provided the oxidant can be used in catalytic amounts (and successively reoxidized for

example with air). A process of this kind was developed by Gulf for the oxychlorination of benzene in the liquid phase with aqueous hydrochloric acid, catalytic quantities of nitric acid, and air or oxygen.⁷

Thionyl chloride and *N*-chloro amides⁸ as electrophilic chlorinating stoichiometric reagents are here mentioned for completeness, but are usually lab-scale setups and intrinsically inefficient from an atom economy standpoint.

The reaction here described is the electrophilic aromatic chlorination using hydrochloric acid as chlorine source and nitrate as oxidant. The peculiarity lies in the use of a phosphonium nitrate ionic liquid as oxidant, along the lines of the papers by the groups of Earle⁹ and Chiappe,¹⁰ the only other earlier studies on this kind of systems. The driving force for the research here described was our recent collaboration with an industrial partner who asked to improve their aromatic chlorination process for the production of polymer intermediates. The two main problem areas of the process were tackled: (i) the use of large quantities of dichloromethane (DCM) as solvent, and (ii) the use of Cl_2 as chlorinating agent. DCM is an effective but undesirable solvent, whose presence in consumer products is beginning to be regulated by the European Parliament¹¹ since it is a suspected human carcinogen. Cl_2 is dangerous and *anti*-atom economic—as stated earlier—because half of the Cl atoms end up as waste. In the present case, compared to the findings previously reported,^{9,10} a deeper understanding of the factors affecting selectivity, kinetics, and the reaction mechanism are reported. This knowledge was then used to improve the overall rate and conversion performance of the nitrate-promoted monochlorination step, and to achieve multiple stepwise chlorination of model substrates.

Results

Following the previous accounts on the use of nitrate ionic liquids as catalysts, the electrophilic chlorination of anisole as the model substrate was investigated using four different ionic liquids as nitrate sources. Along with the recently reported triocylmethylammonium ($N_{8,8,8,1}$) and -phosphonium

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† Electronic supplementary information (ESI) available: Pictures of a representative experimental set up, anisole chlorination GC/MS data, anisole dichlorination GS/MS data, *p*-xylene dichlorination GC/MS data and isolated dichlo-*p*-xylenes NMR spectrum. See DOI: 10.1039/c0gc00004c

($P_{8,8,8,1}$),¹² butylisoquinolinium (BuisoQ) and butylmethylimidazolium (bmim) nitrate salts were also used (Fig. 1).

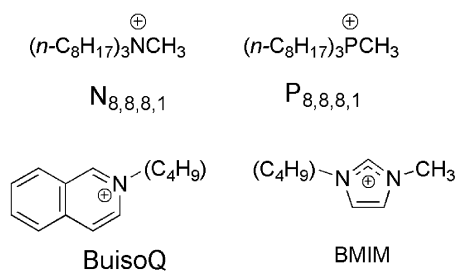
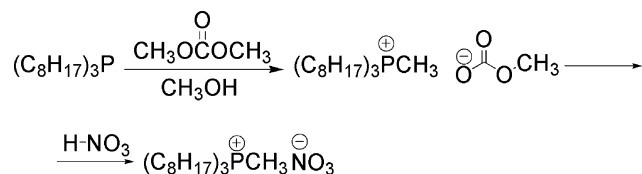


Fig. 1 Cations employed for the nitrate ionic liquids.

The $N_{8,8,8,1}NO_3$ and $P_{8,8,8,1}NO_3$ ionic liquids were prepared by a novel green synthetic procedure.¹² This methodology involved reacting trioctylphosphine ($n-C_8H_{17}$)₃P with dimethylcarbonate (DMC: $CH_3OCO_2CH_3$), and subsequently exchanging the methylcarbonate anion using nitric acid (Scheme 1 exemplifies the procedure for the phosphonium cation).



Scheme 1 Synthesis of $P_{8,8,8,1}NO_3$ from trioctylphosphine, dimethylcarbonate and nitric acid.¹²

All four nitrate ionic liquids promoted the chlorination of anisole with >80% conversion at 80 °C using a molar ratio 2.2:1:1 of HCl:anisole:IL respectively, in 23 h (Fig. 2). The reaction mixture was constituted by HCl_{aq} , anisole, and the IL, no other solvent being necessary.

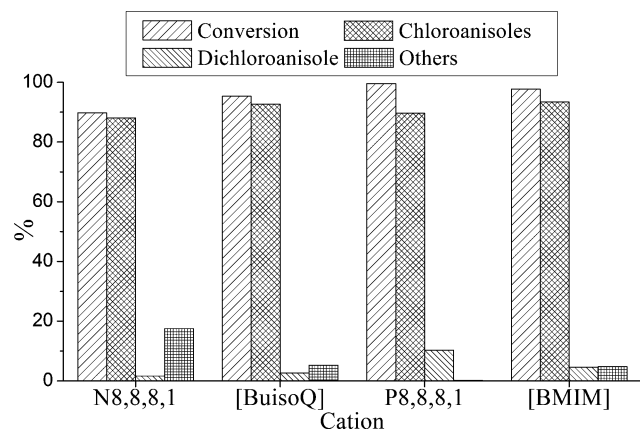


Fig. 2 Chlorinating efficiency of four nitrate ionic liquids.

Using $N_{8,8,8,1}NO_3$ as a nitrate source the conversion reached 90% with high selectivity (99%), but significant amounts of chlorooctane, deriving from IL breakdown, were formed (17%). BuisoQ and bmim nitrates behaved similarly to one another, and formed up to 5% of undesired products deriving from aromatic nitration. $P_{8,8,8,1}NO_3$ afforded the highest conversion (>99%) and chlorination selectivity (99% as sum of di- and

monochloroanisoles), with the lowest amount of side-products, and was used thereafter.

In order to determine the optimal amount of nitrate ionic liquid, the electrophilic chlorination of *p*-xylene (less reactive than anisole) was conducted with varying substrate/ $P_{8,8,8,1}NO_3$ molar ratios of 0.5–1.0–2.0–4.0, using 2.0 equivalents of HCl at 80 °C (Fig. 3).

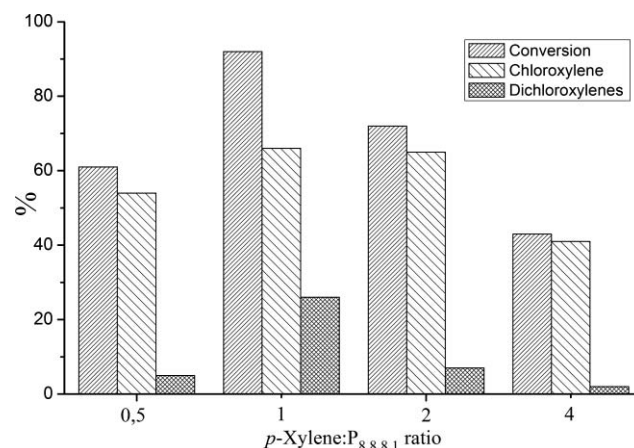


Fig. 3 Electrophilic chlorination of *p*-xylene with varying amounts of $P_{8,8,8,1}NO_3$.

After 24 h it was apparent that the optimal ratio was 1.0. Significantly, however, for xylene/ $P_{8,8,8,1}NO_3$ molar ratios of 2.0 and 4.0, the reaction proceeded to 72% and 43% conversions respectively, indicative of catalysis by $P_{8,8,8,1}NO_3$. In fact, the total moles of chloride that were converted per mole of $P_{8,8,8,1}NO_3$ were greater than unity (1.8 and 2.0 respectively). Furthermore, dichloroxylenes were observed in all cases, up to 25% for the xylene/ $P_{8,8,8,1}NO_3$ molar ratio of 1:1.

A number of aromatic model substrates was subjected to the electrophilic chlorination conditions using $P_{8,8,8,1}NO_3$: a mixture of aqueous HCl, the aryl reagent, and $P_{8,8,8,1}NO_3$ was heated at 80 °C for the required time, and the products analysed by GC-MS.¹³

Table 1 shows the results of the chlorination of different aromatics with HCl using $P_{8,8,8,1}NO_3$ as promoter. The molar ratio of aromatic substrate to ionic liquid was initially set to 1, based on the optimal amount of nitrate ionic liquid as determined above, as well as on the literature,^{9,10} although nitrate is in principle catalytic as seen before. The molar amount of substrate to HCl_{aq} was selected in the range between 1.0 and 2.4. One equivalent of HCl was sufficient for monochlorination of the activated substrates. In fact, anisole, xylene and toluene yielded the monochloro adducts respectively in 85%, 78%, and 90% yields after 3 to 4 days at 80 °C (entries 1, 5, 8 of Table 1). By doubling the molar amount of HCl the same activated substrates reached high conversions to the monochloro adduct significantly faster (3–24 h, entries 2, 6, 9 respectively). Under these conditions naphthalene was monochlorinated with good yields (75%) in 4 days as well (entry 4).

Deactivated aromatic substrates, such as chloro- and nitrobenzene yielded only traces of chlorinated products even in the presence of an excess of HCl (entries 11 and 12); while acetophenone and methoxyacetophenone underwent benzylic

Table 1 Chlorination of arenes using a molar ratio substrate/ $P_{8,8,8,1}NO_3 = 1^a$

#	Arene	Molar ratio Substrate/ $P_{8,8,8,1}NO_3$	HCl 37% (mol eq)	t/h	Cl ₁ ^b (%)	Cl ₂ ^c (%)
1	Anisole	1.0	1.0	60	85	—
2		1.0	2.2	3	97	—
3	Naphthalene	1.0	1.0	48	29	—
4		1.0	2.4	90	75	3
5	Xylene	1.0	1.2	96	78	1
6		1.0	2.4	24	62	26
7		2.0	1.2	96	75	1
8	Toluene	1.0	1.2	96	90	—
9		1.0	2.4	20	85	—
10		2.1	1.1	96	94	—
11	Chlorobenzene	1.0	4.3	24	7	—
12	Nitrobenzene	1.0	2.4	26	traces	—
13	Acetophenone	1.0	2.4	60	^d	^d
14	4-Methoxy acetophenone	1.0	2.4	60	^d	^d

^a Conditions: $T = 80\text{ }^\circ\text{C}$. ^b Monochlorinated products (by GC). ^c Dichlorinated products (by GC). ^d Benzylic oxidation products: Ar-COOH, Ar-CHO, ArCOCl.

Table 2 Catalyst recycling for anisole chlorination^a

Recycle	Conversion ^b (%)
1	95
2	92
3	93
4	94

^a Conditions: $T = 80\text{ }^\circ\text{C}$, molar ratio substrate/ $P_{8,8,8,1}NO_3 = 1$. ^b Conversion (by GC).

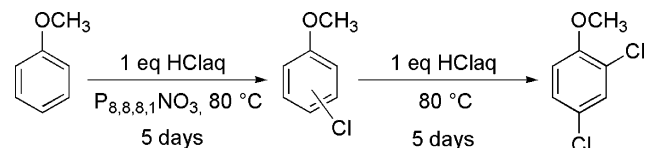
oxidation (entries 13 and 14) and yielded mixtures of the corresponding carboxylic acids, aldehydes and acyl chlorides. To verify consistency on a larger scale (~13 times), a reaction was run on 2.0 mL of anisole with the corresponding molar quantities of $P_{8,8,8,1}NO_3$ and HCl under the conditions of entry 2. Reaction was complete in three hours (90% chloroanisole by GC) and chloroanisole was obtained as a pure product by vacuum distillation in 76% yield.

$P_{8,8,8,1}NO_3$ recycling was demonstrated using anisole as substrate under the conditions of entry 1 of Table 1. Each recycle was conducted by extracting the organic products from the reaction mixture, removing residual water under vacuum, then adding fresh substrate and one equivalent of HCl and heating at $80\text{ }^\circ\text{C}$ for an additional 120 h (Table 2). No decrease in activity was observed after four cycles.

By using two equivalents of HCl, the dichlorination of the activated arenes (anisole, toluene and xylene) could also be accomplished. In this case, however, the presence of one additional equivalent of nitrate anion was required: this was added dropwise halfway through the reaction (*i.e.* after complete monochlorination) in the form of nitric acid (Table 3).

Dichloro-anisole, and mixtures of 2,5-dichloro-*p*-xylene and 2,3-dichloro-*p*-xylene were thus obtained after 60 and 72 h respectively (entries 1 and 2). Naphthalene yielded up to 50% dichloro-naphthalene after 90 h (entry 3); while toluene proved quite reluctant to dichlorination under these conditions (entry 4).

The dichlorination of anisole could also be carried out stepwise without the intermediate addition of nitric acid. The first step was performed in the presence of one equivalent of HCl: monochlorination of anisole occurred in 5 days, then the addition of a second equivalent of HCl yielded dichloroanisole (92%) after 5 more days (Scheme 2).

**Scheme 2** The two-step dichlorination of anisole catalysed by $P_{8,8,8,1}NO_3$.

The second step was partially inhibited when oxygen was excluded from the reaction.

Discussion

The synthesis of the $P_{8,8,8,1}NO_3$ ionic liquid is inherently green for a number of reasons.

1 It uses dimethylcarbonate, a non-toxic and safe reagent^{14,15} instead of toxic quaternarising reagents such as dimethylsulfate and methyl halides.¹⁶

2 The ionic liquids that are obtained are intrinsically halide free, generally an advantage since residual halides are an undesirable impurity.

3 Operatively, the synthesis is simple, and workup-free, as the only co-products methanol and CO_2 can be stripped simply by applying vacuum.

4 No waste is generated, thus eliminating the need for treatment, and the byproducts (methanol and carbon dioxide) can be easily removed and, in principle, recycled for the production of DMC.

5 No solvents, other than a small amount of methanol in the first step needed to homogenize the mixture, are used.

In addition, the liquids thus obtained are clear and colourless, as opposed to the ones made from dimethylsulfate and methyl halides that are often coloured.

Compared to other ILs, the $P_{8,8,8,1}NO_3$ ionic liquid proved to be the best in promoting the aromatic electrophilic chlorination reaction, in particular because the selectivity was higher than with all the other ionic liquids tested. In addition, with $P_{8,8,8,1}NO_3$ the reaction rate was significantly higher than that observed by Earle⁹ and Chiappe¹⁰ using respectively [bmim] NO_3 and [Hmim] NO_3 as can be seen in Table 4. For example anisole chlorination was achieved in only 3 h, using a 2.2 HCl molar ratio (also on a preparative scale of 2 g), with near quantitative conversion and selectivity in our case (entry 1), compared to 72 h (2.0 HCl molar ratio) or 48 h (1.0 HCl molar ratio, but only 70% of product obtained) (entries 2 and 3). Furthermore the $P_{8,8,8,1}NO_3$ ionic liquid promoted a particularly good selectivity: for example in the case of *p*-xylene no alkyl chlorination or oxidation was observed (entry 4). Chiappe¹⁰ instead observed large amounts of α -chloro-*p*-xylene (1-(chloromethyl)-4-methylbenzene) and the oxidation product 4-methyl-benzaldehyde (entry 5).

Table 3 Dichlorination of arenes^a

#	Arene	HCl 37% (mol eq)	Cl ₁ ^b (%)	t ₁ ^c /h	HNO ₃ ^d (mol eq)	Cl ₂ ^e (%)	t ₂ ^f /h
1	Anisole	2.2	97	3	1.0	92	60
2	Xylene	2.4	62	24	2.0	85 ^g	72
3	Naphthalene	2.4	78	90	1.0	53	90
4	Toluene	2.4	85	20	2.0	10	72

^a Conditions: $T = 80\text{ }^{\circ}\text{C}$, molar ratio substrate/ $\text{P}_{8,8,8,1}\text{NO}_3 = 1$. ^b Monochlorinated products (by GC). ^c Time for complete monochlorination. ^d HNO_3 added once monochlorination was complete. ^e Dichlorinated derivatives (by GC). ^f Time for dichlorination. ^g Isolated yield = 68%.

Table 4 Chlorination of arenes: comparison between $\text{P}_{8,8,8,1}\text{NO}_3$, [bmim] NO_3 ,⁹ and [Hmim] NO_3 ¹⁰

Run	Arene	Ionic liquid	Molar ratio substrate/IL	HCl (mol eq)	$T/^{\circ}\text{C}$	Cl ₁ ^a (%)	Other (%)	Time ^b /h
1	Anisole	$\text{P}_{8,8,8,1}\text{NO}_3$	1.0	2.2	80	97	—	3
2		[bmim] NO_3	1.25	2.0	100	99	—	72
3		[Hmim] NO_3	2.0	1.0	80	70	—	48
4	Xylene	$\text{P}_{8,8,8,1}\text{NO}_3$	1.0	1.2	80	78	—	96
5		[Hmim] NO_3	2.0	1.0	80	33	17	48
6	Naphthalene	$\text{P}_{8,8,8,1}\text{NO}_3$	1.0	2.4	80	75	—	90
7		[Hmim] NO_3	2.0	1.0	80	24	—	48

^a Monochlorinated (by GC). ^b Time for monochlorination.

The comparison summarised in Table 4 indicated that the outcome of the chlorination reaction was strongly influenced by the structure of the cation of the ionic liquid.

A clear understanding of whether the electrophilic chlorination with $\text{P}_{8,8,8,1}\text{NO}_3$ and HCl was catalytic in nitrate was needed, in view of our aim to make this synthetic procedure useful on a preparative scale, and thus to address the issues on the chlorination process outlined in the beginning.

In previous accounts of similar reactions, slightly greater than equimolar amounts (1.25 eq⁹ at best), or up to 2 equivalents¹⁰ of nitrate ionic liquid as “catalyst” for the reaction were employed. Chiappe’s work¹⁰ provided a first answer by demonstrating that by using 1.00 eq of HCl as chlorinating agent with respect to the aromatic, the ionic liquid was recovered unchanged and that it could be recycled repeatedly. It failed however to explain why two equivalents of [Hmim] NO_3 were needed, or to give evidence for the purported formation of chlorine gas as the chlorinating agent, and for nitrosyl chloride (NOCl) as the first intermediate towards nitrate regeneration. In fact, the nitrate ionic liquid was defined by them as a “stoichiometric catalyst”, or “promoter”.

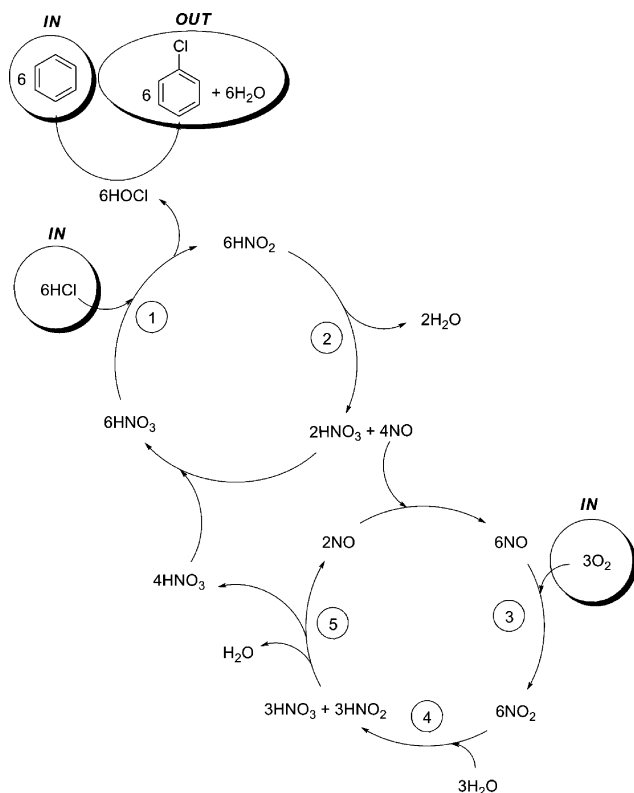
Our experiments confirmed that the phosphonium ionic liquid could be recycled, in fact anisole could be monochlorinated at least four times with the same $\text{P}_{8,8,8,1}\text{NO}_3$. It was however significant that recycling the system was possible only by using a stoichiometric amount of HCl and very long reaction times (120 h). As noted before, with no excess of acid the reaction became longer even with a very active aromatic substrate like anisole (Scheme 2). Attempts to accelerate the reaction by operating with a large excess of HCl killed the catalyst. The spent $\text{P}_{8,8,8,1}\text{Cl}$ catalyst was characterised by chloride titration. At the end of each cycle the catalyst could be regenerated by adding concentrated aqueous nitric acid, thus exchanging the chloride anion with nitrate. Similarly, Earle’s work⁹ reported electrophilic chlorination using bmim chloride together with

nitric acid, indicating that a metathetic anion exchange took place *in situ*.

In summary, when an excess of hydrochloric acid was used the nitrate ionic liquid worked as a stoichiometric reagent and fast reactions occurred. At the other extreme, when HCl was used in equimolar amounts, the reaction was very slow, and the rate determining re-oxidation of the reduced nitrogen species by air permitted high conversion and catalyst reutilization. This was demonstrated by recycling experiments and by chlorinating both *p*-xylene and toluene using a 2:1 substrate:IL ratio. Under these conditions close to quantitative conversion was observed with very high selectivity (Table 1, entries 7 and 10), implying that the nitrate ionic liquid is in fact a catalyst.

The above evidence prompted us to reconsider the mechanism previously reported, and to propose a new hypothesis to account for the nitrate catalysed electrophilic aromatic chlorination (Scheme 3), that does not require formation of Cl_2 or NOCl. It involves oxidation of chloride by nitrate to yield nitrous acid (HNO_2) and hypochlorous acid (HOCl), the active chlorinating species (step 1), based on literature reports.¹⁷ Regeneration of nitric acid can then occur by disproportionation of nitrous acid (HNO_2) to nitric acid (HNO_3) and nitric oxide (NO) (step 2). Nitric oxide is then oxidised instantaneously by air to observable brown nitrogen dioxide (NO_2) (step 3), which in turn reacts with water to give nitric (HNO_3) and nitrous (HNO_2) acids (step 4). The latter disproportionates again to nitric acid and nitric oxide (step 5). The molar sum of all these redox and disproportionation reactions involving nitrogen-oxygen species shows that only one mole of nitrate is consumed and continuously regenerated for each mole of reactant and of chloride. No benefits were observed by carrying out the reaction under pure oxygen.

The global reaction (eqn (1)) is therefore catalytic in nitrate, and uses oxygen as oxidant.



Scheme 3 Proposed mechanism for nitrate catalysed electrophilic chlorination with HCl.



Dichlorination was more difficult, in fact addition of an excess of hydrochloric acid from the beginning did not yield quantitative amounts of dichlorinated products and further addition of HCl did not drive the reaction to completion but rather caused the catalyst to become inactive. The trick to achieve dichlorination was to add one equivalent of nitric acid half-way through the reaction (Table 3) to regenerate the $\text{P}_{8,8,8,1}\text{NO}_3$ catalyst.

Further evidence for the proposed catalytic mechanism, where the rate determining step is reoxidation to nitrate, was obtained by running the dichlorination in two steps (Scheme 2). In this case, only one equivalent of $\text{P}_{8,8,8,1}\text{NO}_3$ was used and no further addition of nitric acid was necessary, on condition that a long period was allowed for spontaneous regeneration of NO_3^- . In addition, exclusion of air from the reaction of Scheme 2 inhibited the second step, indicating that regeneration of the catalyst requires oxygen. In this example the atom economy was optimal as 100% of chlorine was incorporated in the product and the nitrate ionic liquid was effectively catalytic.

Conclusions

The work here described improves the understanding of the electrophilic aromatic chlorination process with HCl, of its mechanism and of the factors that control rates, yields and selectivity. Catalysis by nitrate ionic liquids is established, as well as the fact that the kinetic bottleneck is represented by regeneration of the nitrate oxidant with atmospheric oxygen. Methods to overcome this drawback are indicated. By using $\text{P}_{8,8,8,1}\text{NO}_3$, chloroanisoles were obtained more than twenty times

faster compared to the previously reported procedure involving the use of $[\text{bmim}]\text{NO}_3$,⁹ and at a lower reaction temperature (80 °C instead of 100 °C). Furthermore, quantitative (*i.e.* 100% selectivity) ring chlorination could be obtained for *p*-xylene with $\text{P}_{8,8,8,1}\text{NO}_3$, in contrast with 66% selectivity (due to concurrent benzylic chlorination and oxidation) in the case of $[\text{Hmim}]\text{NO}_3$.¹⁰ The knowledge collected here provides deeper comprehension of points that have emerged previously in the literature, and poses the basis for implementation of this synthetic methodology. In addition, the reported electrophilic aromatic chlorination reaction uses HCl as chlorine source and is catalysed by $\text{P}_{8,8,8,1}\text{NO}_3$ in the absence of organic solvents, making it a greener alternative to processes which involve Cl_2 and organic (usually chlorinated) solvents: the products can be isolated by distillation, no solvent is required for purification, and 100% of chlorine is utilised. The reactive electrophilic species is an oxidized form of chlorine “Cl⁺”—presumably HOCl—that is generated by the oxidation of chloride by nitrate, which in turn is regenerated by oxidation with air. With respect to traditional procedures, the present methodology improves on at least 6 of the 12 principles of green chemistry: better atom economy, use of catalysis, use of an alternative solvent¹⁸/catalyst (made by a green synthesis), reduced waste, use of safer reagents, safer synthetic procedures, lower potential for accidents. It represents an improvement from implementing one or two of the principles (greenish chemistry), to abiding by as many of the principles as possible (greener chemistry).

Experimental section

General

Reagents were ACS grade and used as received.

GC-MS analyses were performed with a HP-5890 gas-chromatograph equipped with a HP-5MS capillary column (30 m × 0.25 mm; coating thickness 0.25 μm) and a HP-5970 quadrupole mass detector (EI, 70 eV).

Analytical conditions: injector and transfer line temperatures 260 and 280 °C respectively; oven temperature programmed from 50 °C (isothermal condition for three minutes) to 250 °C at 10 °C min⁻¹; carrier gas helium at 1 ml min⁻¹; split ratio 1 : 20. The ¹H NMR spectra were obtained in CDCl₃ with a 400 MHz instrument using TMS as the internal reference.

Ionic liquids

Phosphonium and ammonium ionic liquids were prepared according to a new method recently reported by us.¹² As reported in Scheme 1, trioctylamine and trioctylphosphine were set to react with dimethylcarbonate to obtain methyltrioctylammonium and methyltrioctylphosphonium methylcarbonate salts respectively. These compounds were anion-exchanged by reaction with nitric acid (Scheme 1) to yield the corresponding nitrate salts $\text{N}_{8,8,8,1}\text{NO}_3$ and $\text{P}_{8,8,8,1}\text{NO}_3$.

N-Butyl isoquinolinium bromide was prepared by *N*-alkylation of isoquinoline with butyl bromide. *N*-Alkylisoquinolinium nitrate (BuisoQNO₃) was prepared by metathesis in methanol solution from the respective bromide salts with an equimolar amount of AgNO₃.

1-*n*-Butyl-3-methylimidazolium chloride (bmimCl) was prepared by *N*-alkylation of methylimidazole with butyl chloride. 1-*n*-Butyl-3-methylimidazolium nitrate (bmimNO₃) was prepared by metathesis in methanol solution from the respective chloride salts with an equimolar amount of AgNO₃.

Chlorination reactions

Note. All the reactions were carried in a flask equipped with a reflux condenser open to the air. At the end of reactions the mixtures, after cooling at room temperature, were extracted with hexane (4 × 2 mL). The % composition of the combined extracts was determined by GC-MS. For a representative product (dichloroxylenes, entry 2, Table 3), the yield was confirmed by isolating and purifying the product *via* FCC. All structures were assigned by comparison to authentic samples *via* GC-MS and ¹H NMR.

Chloroanisoles. Aqueous HCl (37%, 3.14 mmol, 0.26 mL) was added to anisole (1.4 mmol, 0.15 mL) and P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C for 3 h (97%: 75% *para* and 22% *ortho* isomers).

Dichloroanisole (Method A). To the previously described reaction mixture, after 3 h at 80 °C was added aqueous HNO₃ (69%, 1.4 mmol, 0.09 mL) and the reaction mixture was maintained at the same temperature for 60 h (92%: 90% *ortho-para*, 2% *ortho-ortho* isomers and 3% trichloro anisole).

Dichloroanisole (Method B). Aqueous HCl (37%, 1.4 mmol, 0.12 mL) was added to anisole (1.4 mmol, 0.15 mL) and of P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C for 5 days. Then additional aqueous HCl (37%, 1.4 mmol, 0.12 mL) was added. The mixture was allowed to react at the same temperature for 5 more days (92%: 91% *ortho-para* and 1% *ortho-ortho* isomers).

Chloroanisoles (larger scale). Aqueous HCl (37%, 40.5 mmol, 3.35 mL) was added to anisole (18.39 mmol, 2.00 mL) and P_{8,8,8,1}NO₃ (18.39 mmol, 8.24 g). The resulting mixture was heated at 80 °C for 3 h. (90%: 2:1 *para* - *ortho* ratio). The products were recovered and vacuum distilled to yield 2.003 g of chloroanisoles (76%).

Chloro-*p*-xylene. Aqueous HCl (37%, 1.7 mmol, 0.15 mL) was added to 1,4-dimethylbenzene (1.4 mmol, 0.17 mL) and P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C for 96 h (78%).

Dichloro-*p*-xylenes. Aqueous HCl (37%, 3.4 mmol, 0.28 mL) was added to 1,4-dimethylbenzene (1.4 mmol, 0.17 mL) and P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C. After 24 h aqueous HNO₃ (69%, 1.4 mmol, 0.09 mL) was added and the resulting mixture stirred for 48 h. Then one additional equivalent of nitric acid was introduced and the reaction was carried out for an additional 48 h (85%: 60% 2,5 and 40% 2,3 isomers).

Chlorotoluene. Aqueous HCl (37%, 1.7 mmol, 0.15 mL) was added to toluene (1.4 mmol, 0.15 mL) and P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C for 96 h (90%: 47% *para* and 43% *ortho* isomers).

Dichlorotoluene. Aqueous HCl (37%, 3.4 mmol, 0.28 mL) was added to toluene (1.4 mmol, 0.15 mL) and P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C. After 24 h HNO₃ (69%, 1.4 mmol, 0.09 mL) was added and the mixture was stirred for an additional 72 h (10%).

1-Chloronaphthalene. Aqueous HCl (37%, 3.4 mmol, 0.28 mL) was added to naphthalene (1.5 mmol, 192 mg) and P_{8,8,8,1}NO₃ (1.5 mmol, 670 mg). The resulting mixture was heated at 80 °C for 90 h (78%).

Dichloronaphthalene. To the previously described reaction mixture, after 90 h at 80 °C, aqueous HNO₃ (69%, 1.5 mmol, 0.10 mL) was added, and the reaction mixture was maintained at the same temperature for an additional 90 h (53%).

Recycling procedure. In the first cycle, aqueous HCl (37%, 1.4 mmol, 0.12 mL) was added to anisole (1.4 mmol, 0.15 mL) and P_{8,8,8,1}NO₃ (1.4 mmol, 630 mg). The resulting mixture was heated at 80 °C for 120 h. After product extraction, traces of organic solvents and water were eliminated under reduced pressure. A fresh amount of substrate and HCl (1.4 mmol, 0.12 mL and 1.4 mmol, 0.15 mL, respectively) were then added to the residual mixture which was then heated again for the next cycle.

Chloride assay. A 50 μM aqueous solution of AgNO₃ was used to titrate a sample of spent ionic liquid (around 200 mg) dissolved in methanol (100 mL). 1 mL of a solution of K₂Cr₂O₇ (10% w/v) was used for each sample as indicator.

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