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Imidazolium Ionic Liquids as Solvents for Cerium(IV)-Mediated Oxidation Reactions

Hasan Mehdi,[†] Andrea Bodor,[†] Diána Lantos,[†] István T. Horváth,[†] Dirk E. De Vos,[‡] and Koen Binnemans*,[§]

Department of Chemical Technology and Environmental Chemistry, Eötvös University, Pázmány Péter Sétány 1/A, 1117 Budapest, Hungary, Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, B-3001 Leuven, Belgium, and Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

Koen.Binnemans@chem.kuleuven.be

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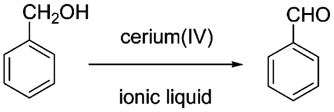

Use of imidazolium ionic liquids as solvents for organic transformations with tetravalent cerium salts as oxidizing agents was evaluated. Good solubility was found for ammonium hexanitratocerate(IV) (ceric ammonium nitrate, CAN) and cerium(IV) triflate in 1-alkyl-3-methylimidazolium triflate ionic liquids. Oxidation of benzyl alcohol to benzaldehyde in 1-ethyl-3-methylimidazolium triflate was studied by in-situ FTIR spectroscopy and ^{13}C NMR spectroscopy on carbon-13-labeled benzyl alcohol. Careful control of the reaction conditions is necessary because ammonium hexanitratocerate(IV) dissolved in an ionic liquid can transform benzyl alcohol not only into benzaldehyde but also into benzyl nitrate or benzoic acid. The selectivity of the reaction of cerium(IV) triflate with benzyl alcohol in dry ionic liquids depends on the degree of hydration of cerium(IV) triflate: anhydrous cerium(IV) triflate transforms benzyl alcohol into dibenzyl ether, whereas hydrated cerium(IV) triflate affords benzaldehyde as the main reaction product. Reactions of ammonium hexanitratocerate(IV) with organic substrates other than benzyl alcohol have been explored. 1,4-Hydroquinone is quantitatively transformed into 1,4-quinone. Anisole and naphthalene are nitrated. For the cerium-mediated oxidation reactions in ionic liquids, high reaction temperatures are an advantage because under these conditions smaller amounts of byproducts are formed.

Introduction

Tetravalent cerium salts are strong one-electron oxidizing agents that can be used as reagents for a wide variety of organic transformations.[1−7] Typical examples are oxidation of benzyl alcohols to benzaldehydes,[8,9] toluene to benzaldehyde,[10] and 1,4-hydroquinones to the corresponding 1,4-quinones.[11,12] The reactivity and selectivity of cerium(IV) salts strongly depend on the choice of anion and other reaction conditions including the nature of the solvent. The most popular salt for cerium(IV)-mediated organic reactions is ammonium hexanitratocerate(IV), $(NH_4)_2[Ce(NO_3)_6]$, which is also known as cerium ammonium nitrate, ceric ammonium nitrate, or as CAN.[3,5,6] Other useful cerium(IV) reagents are cerium(IV) triflate[13−16] and cerium(IV) methanesulfonate.[13]

[†] Eötvös University.

[‡] Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven.

[§] Department of Chemistry, Katholieke Universiteit Leuven.

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Although most cerium(IV)-mediated organic reactions require use of at least stoichiometric amounts of cerium(IV) salts, few examples of catalytic reactions based on cerium(IV) have been described. Cerium(IV) can be a redox mediator in electrosynthesis[17] or catalytic amounts of cerium(IV) salts can be used in combination with co-oxidants like sodium bromate[18,19] or potassium persulfate.[20] A special type of catalytic reaction is the cerium-mediated oxidation reaction by molecular oxygen in which cerium(IV) very likely acts as an intermediate.[21−23] The relatively high molecular mass of cerium(IV) salts is a disadvantage for stoichiometric reactions, especially because cerium(IV) salts are only one-electron donors. However, these salts can be regenerated by either chemical oxidation (for instance, with $K_2S_2O_8$ or O_3) in acidic media[7] or electrochemical oxidation.[14] Another problem that hampers the applicability of cerium(IV) salts in organic transformations is their poor solubility in organic solvents. In contrast, many cerium(IV) salts are very soluble in water, but the presence of an acid is required to avoid hydrolysis of the cerium(IV) ions.[24,25] Moreover, organic substrates are often poorly soluble in water. Micellar systems can be used to overcome the solubility problems of the organic reactants, but separation of the products can be cumbersome.[26,27] Another possibility is to use hydrophobic cerium(IV) reagents[28] or work under phase-transfer conditions.[29] Many different solvents have been used for cerium(IV)-mediated reactions, but the most popular solvents besides water are acetonitrile, dichloromethane, THF, and methanol.[7] It is common practice to choose a solvent in which the organic substrate is soluble but the cerium(IV) salt is not, so that the reactions are carried out under heterogeneous conditions. Of course, the insolubility of the cerium(IV) salts in the reaction medium has a negative effect on the reactivity.

One can wonder whether ionic liquids are useful solvents for cerium(IV)-mediated organic transformations, taking into account the popularity of ionic liquids as alternative solvents for organic reactions.[30−38] To the best of our knowledge, ionic liquids have not been explored for reactions with cerium(IV) salts yet, although several examples of rare-earth-mediated organic reactions in ionic liquids have been described.[39−44] It should be noted that ionic liquids combined with an excess of DMSO have been investigated as a solvent for cerium(IV)-mediated reactions.[45]

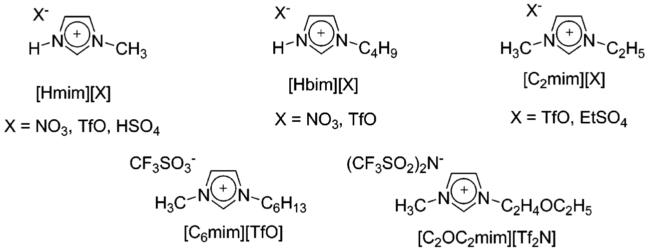

FIGURE 1. Overview of the ionic liquids studied as solvents for cerium(IV)-mediated oxidation reactions.

In this paper we evaluate various ionic liquids as solvents for cerium(IV)-mediated organic reactions (Figure 1). First, the solubility of different cerium(IV) salts in ionic liquids has been tested. Second, we studied the oxidation of benzyl alcohol to benzaldehyde by in-situ spectroscopic techniques (NMR, FTIR) to obtain some insight in the mechanisms involved. Finally, the reaction was extended to other substrates as well.

Results and Discussion

Solubility Tests. In order to find the best combination of a cerium(IV) salt and an ionic liquid that could provide a homogeneous reaction system, the solubility of cerium(IV) salts in different ionic liquids was tested. The following cerium(IV) salts were selected: ammonium hexanitratocerate(IV), cerium(IV) sulfate dihydrate, cerium(IV) ammonium sulfate, cerium(IV) ammonium sulfate dihydrate, cerium(IV) hydroxide, cerium(IV) triflate, and hydrated cerium(IV) triflate. The ionic liquids include several 1-alkylimidazolium and 1-alkyl-3-methylimidazolium salts combined with trifluoromethanesulfonate (triflate, TfO), bis(trifluoromethylsulfonyl)imide (Tf_2N), hydrogen sulfate, ethylsulfate, and nitrate anions (Figure 1). Hexafluoro-

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TABLE 1. Solubility of Cerium(IV) Salts in Imidazolium Ionic Liquids[a]

	$(NH_4)_2[Ce(NO_3)_6]$	$Ce(TfO)_4 \cdot xH_2O$
[Hmim][NO_3]	2	2
[Hmim][TfO]	2	2
[Hmim][HSO_4]	3	3
[Hbim][NO_3]	2	2
[Hbim][TfO]	2	2
[C_6mim][TfO]	1	1
[C_2mim][TfO]	1	1
[C_2mim][$EtSO_4$]	3	3
[C_2OC_2mim][Tf_2N]	3	3

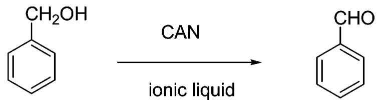
[a] Solubility codes: 1 = soluble in ionic liquid (at least 1 mmol of cerium salt dissolves in 10 mmol of ionic liquid); 2 = soluble in ionic liquid having a high melting point (at least 1 mmol of cerium salt dissolves in 10 mmol of ionic liquid). The solubility was measured at 50 °C. 3 = insoluble or the solubility is less than 1 mmol of cerium salt in 10 mmol of ionic liquid. $Ce(SO_4)_2 \cdot 2H_2O$, $(NH_4)_2Ce(SO_4)_3$, $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$, and $Ce(OH)_4$ are not soluble in any of these ionic liquids up to 100 °C.

phosphate ionic liquids were excluded from this study due to their well-known instability in the presence of water.[46]

The results of the solubility tests are summarized in Table 1. A general observation is that cerium(IV) salts can only with difficulty be dissolved in imidazolium ionic liquids. Our criterion for good solubility was that 1 mmol of the cerium(IV) salt dissolves in 10 mmol of the ionic liquid, resulting in a clear solution at room temperature or higher temperatures. In the case of low solubility, use of an ultrasonic bath did not have a significant impact on the dissolution process. The data show that the solubility strongly depends both on the type of cerium salt and ionic liquid. Among the cerium(IV) salts that were investigated, only ammonium hexanitratocerate(IV) (CAN) and cerium(IV) triflate (anhydrous and hydrated) were very soluble. The triflate ionic liquids were the best choice to solubilize cerium(IV) salts. 1-Alkylimidazolium nitrate ionic liquids are one of the simplest types of ionic liquids that can be used as they can easily be prepared by reaction of 1-alkylimidazole and nitric acid. Unfortunately, they exhibit low stability in the presence of cerium(IV) salts, resulting in formation of brown nitrogen dioxide gas upon heating. The 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides are some of the more popular ionic liquids due to the resistance of the $[Tf_2N]^-$ ion to hydrolysis,[47] but these ionic liquids are not very useful for cerium(IV)-mediated oxidation reactions because of the poor solubility of the cerium(IV) salts. On the basis of the results of the solubility tests, triflate ionic liquids were selected for further exploration of the oxidation of benzyl alcohol by cerium(IV) salts (Scheme 1). Benzyl alcohol and other organic substrates that were investigated are very soluble in the triflate ionic liquids.

Oxidation of Benzyl Alcohol: Test Reactions. Oxidation of benzyl alcohol to benzaldehyde was selected as a model reaction for cerium(IV)-mediated oxidation reactions in ionic liquids. Test reactions were run by mixing cerium(IV) salts with ionic liquids in a 1:10 molar ratio (Ce^{4+}:ionic liquid) followed by addition of benzyl alcohol under nitrogen atmosphere. Benzyl alcohol was readily converted to benzaldehyde by CAN in 1-alkylimidazolium nitrate, [Hmim][NO_3], and [Hbim][NO_3] at 50 °C, but the high melting point of these ionic liquids resulted in solidification of the reaction mixture at room temperature. Formation of benzaldehyde was established by TLC and NMR experiments, but part of the benzyl alcohol was over-oxidized to benzoic acid. In addition, evolution of a brown gas was observed. Similar results were obtained when $Ce(TfO)_4$ was used instead of CAN. Because partially over-oxidation of benzyl alcohol to benzoic acid was observed in nitrate ionic liquids whatever cerium(IV) salt was used, it is evident that nitrate ionic liquids are not suitable solvents for conversion of benzyl alcohol to benzaldehyde. It should be noted that this over-oxidation of benzyl alcohol to benzoic acid is not caused by tetravalent cerium but by the oxidizing power of nitrogen oxides, like NO_2 (which is known to be a strong oxidizing agent).[48−50]

SCHEME 1. Oxidation of Benzyl Alcohol to Benzaldehyde by $(NH_4)_2[Ce(NO_3)_6]$ (CAN) in Ionic Liquids



In a second series of experiments the nitrate ionic liquids were replaced by 1-butylimidazolium trifluoromethanesulfonate, [Hbim][TfO]. TLC and NMR experiments confirmed oxidation of benzyl alcohol to benzaldehyde, but formation of a brown gas was still observed. When CAN was replaced by anhydrous $Ce(TfO)_4$, no brown gas was formed. However, although benzyl alcohol was quantitatively converted, benzaldehyde or benzoic acid could be detected only as side products (see description of NMR spectra later in the text). The same side reactions occurred when reactions were carried out with $Ce(TfO)_4$ in 1-hexyl-3-methylimidazolium trifluoromethanesulfonate, [C_6mim][TfO]. It is noteworthy that formation of brown gases only occurs at longer reaction times when CAN was used in [C_6mim][TfO]. Monitoring the reaction by gas chromatography revealed that oxidation of benzyl alcohol to benzaldehyde was almost complete after 4 h at 100 °C. [C_2mim][TfO] was tested since it has similar chemical properties to [C_6mim][TfO] but has lower viscosity and molecular weight. The yield of benzaldehyde was 97% after 6 h at 100 °C.

The workup of these reaction mixtures turned out to be cumbersome because of the difficulties to separate the organic compounds from the ionic liquid. Separation by extraction was attempted. Of the different solvents that have been tested (among them diethyl ether, hexane, and toluene), the best results were obtained with toluene. However, even with toluene quantitative extraction was not possible: no more than 91−92% of the benzaldehyde could be extracted from [C_2mim][TfO] or [C_6mim][TfO] by repeated extraction with aliquots of toluene.

Formation of Nitrogen Dioxide. During the oxidation experiments formation of a brown gas was often observed. This brown gas was formed during all the experiments with nitrate ionic liquids (whatever tetravalent cerium salt was used). Generation of this brown gas was also noted during oxidation of benzyl alcohol by CAN in triflate ionic liquids, although CAN caused no formation of the brown gas when it was heated in 1-alkyl-3-methylimidazolium triflate ionic liquids (in the absence of benzyl alcohol). We confirmed that this brown gas was

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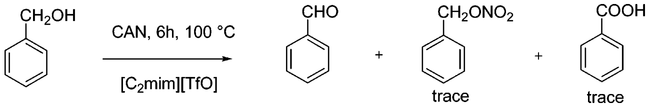
SCHEME 2. Reaction Products Observed upon Oxidation of Benzyl Alcohol by Ceric Ammonium Nitrate (CAN) in the Ionic Liquid 1-Ethyl-3-methylimidazolium Triflate



nitrogen dioxide by its reaction with Saltzman's reagent [sulfanilic acid and *N*-(1-naphthyl)-1,2-ethylenediamine] in acidic media.[51−53] For this test the reaction was carried out in a Schlenk flask attached to a gas bubbler containing Saltzman's reagent. When the brown gas was slowly purged to the gas bubbler with nitrogen, a dramatic color change from colorless to purple occurred, as expected. To the best of our knowledge, formation of nitrogen oxides during CAN-mediated oxidation reactions of alcohols has not been reported yet. Morey and Saá carried out oxidation of hydroquinones by CAN in the solid state by grinding the substrate and CAN together with a pestle and mortar followed by keeping the mixture for several days in a closed vial.[54] They observed formation of red-brown nitrogen dioxide, which acted as an efficient oxidant. The reaction was much slower in open vials, from which the nitrogen dioxide could escape. Whereas the presence of nitrogen dioxide is advantageous for oxidation of hydroquinones to quinones, its presence should be avoided during oxidation of benzyl alcohol to benzaldehyde because nitrogen dioxide further oxidizes benzaldehyde to benzoic acid.

Taking into account the conditions in which we observe formation of nitrogen dioxide, it is very likely that water-free nitric acid is the source of this brown gas. Upon heating (and in the presence of light even at room temperature), anhydrous nitric acid is partially decomposed to nitrogen dioxide[55]

$$2HNO_3 \rightarrow H_2O + 2NO_2 + {}^1/_2O_2$$

From the balanced equation for the oxidation of benzyl alcohol by CAN, it is understandable why we observed formation of nitrogen dioxide for solutions of CAN in triflate ionic liquids only after addition of benzyl alcohol

$$PhCH_2OH + 2(NH_4)_2[Ce(NO_3)_6] \rightarrow PhCHO + 2(NH_4)_2[Ce(NO_3)_5] + 2HNO_3$$

By oxidation of benzyl alcohol, nitric acid is released. When the reaction is carried out in aqueous medium, formation of nitric acid will result in acidification of the aqueous phase. However, when a dry ionic liquid is the solvent, anhydrous nitric acid can be decomposed at the elevated reaction temperatures (100 °C) to nitrogen dioxide.

Oxidation of Benzyl Alcohol by CAN in [C$_2$mim][TfO]. To obtain insight into the reaction mechanism of the oxidation of benzyl alcohol by CAN in the triflate ionic liquid [C$_2$mim]-[TfO], we studied this system in more detail. CAN (1 mmol) was dissolved in the ionic liquid [C$_2$mim][TfO] (10 mmol), and benzyl alcohol (0.5 mmol) was added under nitrogen atmosphere after dissolution of the cerium(IV) salt. The reaction mixture was kept at 100 °C, and the progress of the reaction was monitored by gas chromatography. Nearly quantitative conversion of benzyl alcohol to benzaldehyde was observed after 6 h. GC-MS measurements revealed that traces of benzyl nitrate and benzoic acid were formed as side products (Scheme 2). The reaction temperature is an important parameter to control the selectivity of the oxidation of benzyl alcohol by CAN in the triflate ionic liquid. When the reaction temperature was lowered from 100 to 75 °C (keeping the other reaction parameters constant), only 70% yield of benzaldehyde was obtained (Figure 2). On the other hand, the reaction was complete after heating for 20 min at 125 °C.

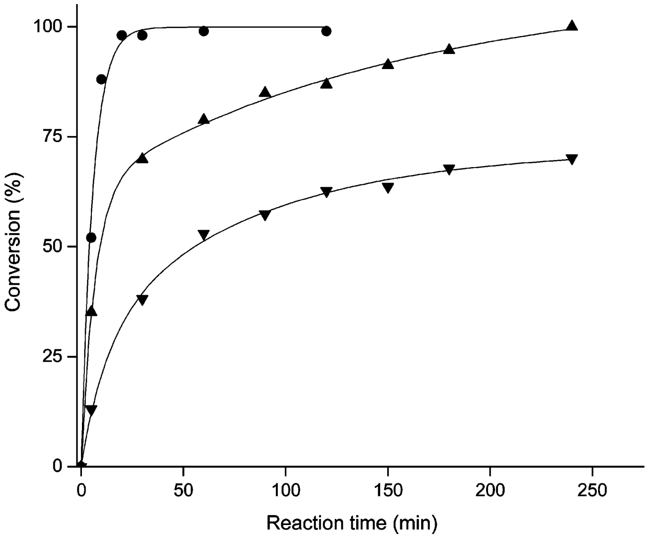


FIGURE 2. Time dependence of the conversion of benzyl alcohol (0.5 mmol) by oxidation with $(NH_4)_2[Ce(NO_3)_6]$ (1 mmol) in [C$_2$mim]-[TfO] (10 mmol) at 75 (▼), 100 (▲), and 125 °C (●).

Formation of benzyl nitrate and benzoic acid as side products during oxidation of benzyl alcohol in the [C$_2$mim][TfO] ionic liquid at 100 °C could be clearly observed by ^{13}C NMR investigation of reaction mixtures using ^{13}C-labeled benzyl alcohol, Ph^{13}CH$_2$OH (Figure 3). Compared to the compounds with natural ^{13}C abundance, ^{13}C-labeled benzyl alcohol, with a carbon-13 atom at the alcoholic position, allows detection of intermediates at much lower concentrations.[56] The proton-decoupled ^{13}C{^{1}H} NMR spectra were run at 75.47 MHz (on a 300 MHz NMR spectrometer) at room temperature on samples that were taken from the reaction mixture. It should be noted that NMR spectra of the neat ionic liquid reaction mixture could be recorded without the need of deuterated solvents. This also supports the observations by Giernoth and co-workers that high-resolution NMR spectra of solutes can be obtained in neat ionic liquid solvents.[57,58] Five minutes after addition of benzyl alcohol, the characteristic resonance peak of benzaldehyde at 195 ppm appeared. The only other product that could be observed in the NMR spectrum was benzyl alcohol, and no intermediates were detected. The other resonances observable in the NMR spectrum belong to the [C$_2$mim][TfO] ionic liquid and the aromatic carbons of benzyl alcohol (Figure 3). A peculiarity of the spectrum is the broad benzyl alcohol peak. As all other

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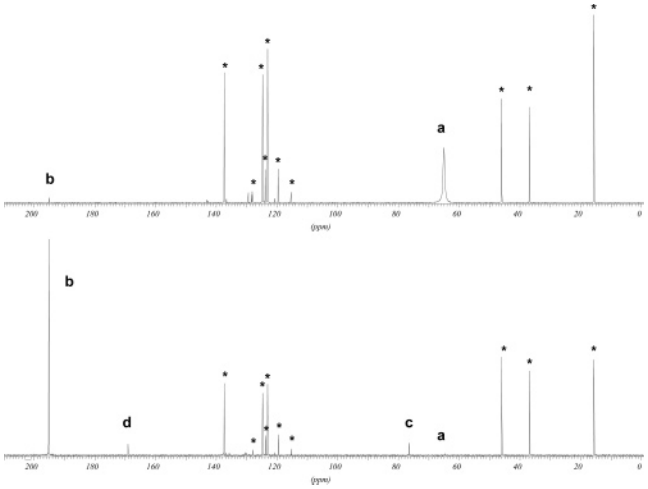

FIGURE 3. $^{13}C\{^1H\}$ NMR spectra of the oxidation of carbon-13-labeled $Ph^{13}CH_2OH$ to $Ph^{13}CHO$ by $(NH_4)_2[Ce(NO_3)_6]$ in neat [C_2mim]-[TfO]. The upper NMR spectrum was recorded after 5 min of reaction time and the lower NMR spectrum after 6 h of reaction. The labeled peaks are as follows: (a) benzyl alcohol, (b) benzaldehyde, (c) benzyl nitrate, and (d) benzoic acid. The resonances labeled by an asterisk (*) are due to the ionic liquid [C_2mim][TfO].

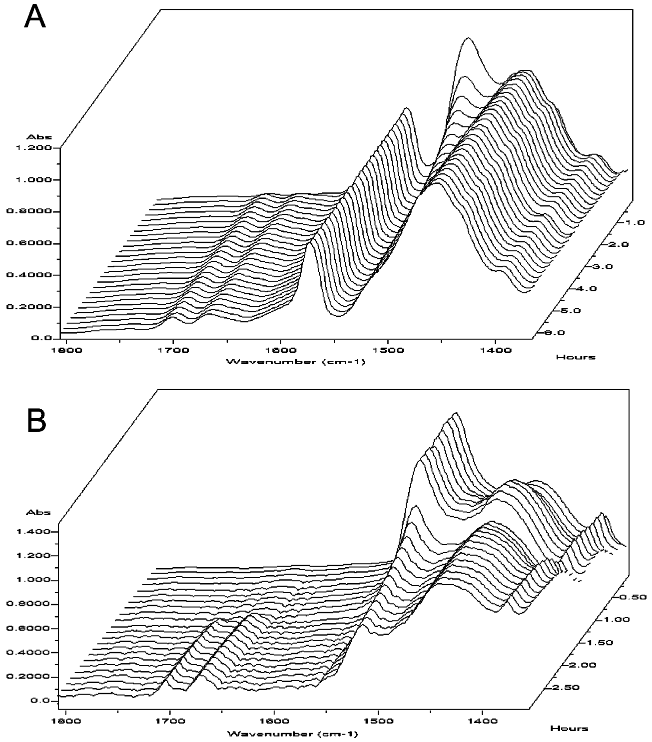

FIGURE 4. Monitoring the reaction between benzyl alcohol and $(NH_4)_2[Ce(NO_3)_6]$ by in-situ infrared spectroscopy in [C_2mim][TfO] (A) and CH_3CN (B).

resonances show natural line width, this phenomena can be due to a rapid exchange between free and cerium-coordinated benzyl alcohol. After 6 h, only trace amounts of benzyl alcohol remain; besides the main product benzaldehyde, small amounts of benzyl nitrate and benzoic acid were detected. The different compounds in the reaction mixtures were identified by their characteristic chemical shift values, but they were also compared to the values obtained in the NMR spectra of the pure products.

Oxidation of benzyl alcohol by CAN in [C_2mim][TfO] was also studied by in-situ FTIR spectroscopy (Figure 4A). This is a valuable technique for monitoring oxidation reactions in ionic liquids because oxidation reactions are accompanied by functional group transformations that give rise to noticeable differences in the infrared absorption spectra. The proof-of-principle of in-situ monitoring of reactions in ionic liquids by infrared spectroscopy have been demonstrated by some of us for Friedel−Crafts reactions.[59] However, in-situ infrared spectroscopy can be applied to follow up other types of organic reactions. A disadvantage of this technique is its relative insensitivity, so that some reaction intermediates are difficult to detect.[60] CAN and [C_2mim][TfO] were mixed together in a reaction vessel equipped with an FTIR probe. The reaction mixture was heated to 100 °C, and IR measurement was started. The pale orange suspension became a deep red solution upon rapid dissolution of the cerium salt. When benzyl alcohol was added to the mixture, the intensity of the absorption band at 1516 cm^{-1} decreased with the concomitant appearance of new bands at 1699 and 1666 cm^{-1}. These bands were assigned on the basis of several experiments performed in [C_2mim][TfO] and/or CH_3CN. When CAN was dissolved in CH_3CN at 80 °C, the IR also showed a very strong band at 1516 cm^{-1} due to CAN (Figure 4B). After addition of benzyl alcohol the color of the orange solution turned red and the intensity of this band decreased, as expected, and two bands appeared at 1703 and 1671 cm^{-1}, similarly to the previous experiments in [C_2mim][TfO]. The band at 1703 cm^{-1} can be assigned to the product benzaldehyde since the IR of benzaldehyde either in CH_3CN or [C_2mim][TfO] show bands at 1703 or 1699 cm^{-1}, respectively. The band at 1671 cm^{-1} is due to dissolved HNO_3, evidenced by the appearance of the same IR band by adding a few drops of a liquid prepared and distilled off from the mixture of KNO_3 and excess H_2SO_4. A similar band was observed at 1666 cm^{-1} when HNO_3 was added to [C_2mim][TfO].

Anhydrous versus Hydrated Cerium(IV) Triflate. Reaction of benzyl alcohol with anhydrous cerium(IV) triflate in triflate ionic liquids like [C_2mim][TfO] yielded dibenzyl ether and only a small amount of benzaldehyde (as confirmed by GC-MS analysis). However, when anhydrous cerium(IV) triflate was replaced by commercially available hydrated cerium(IV) triflate, $Ce(TfO)_4 \cdot xH_2O$, oxidation of benzyl alcohol did yield benzaldehyde as the main product. These results indicate that anhydrous cerium(IV) triflate acts as a dehydrating agent in ionic liquids, whereas hydrated cerium(IV) triflate acts as an oxidant under these same conditions (Scheme 3).

This difference in selectivity between anhydrous and hydrated cerium(IV) triflate looked astonishing at first instance, but earlier studies on oxidation of benzylic compounds by cerium(IV) triflate showed that the water content has a marked influence on the oxidation ability.[61] In those studies, commercial samples were found to have a higher oxidation power than freshly prepared samples, which could be traced back to a higher water content in the commercial samples than in the freshly prepared samples. Rehydration of the freshly prepared samples led to a similar activity as that of commercial samples. In our opinion, the influence of the water content of rare-earth-containing

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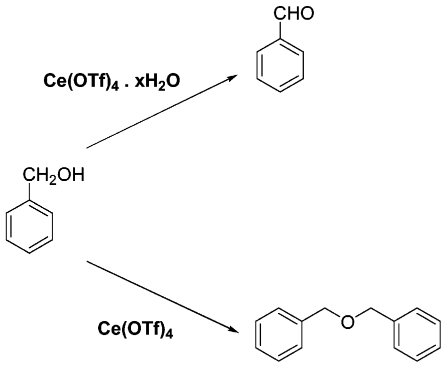
SCHEME 3. Different Reaction Products for Reaction of Benzyl Alcohol with Hydrated or Anhydrous Cerium(IV) Triflate in the Ionic Liquid [C_2mim][TfO][a]

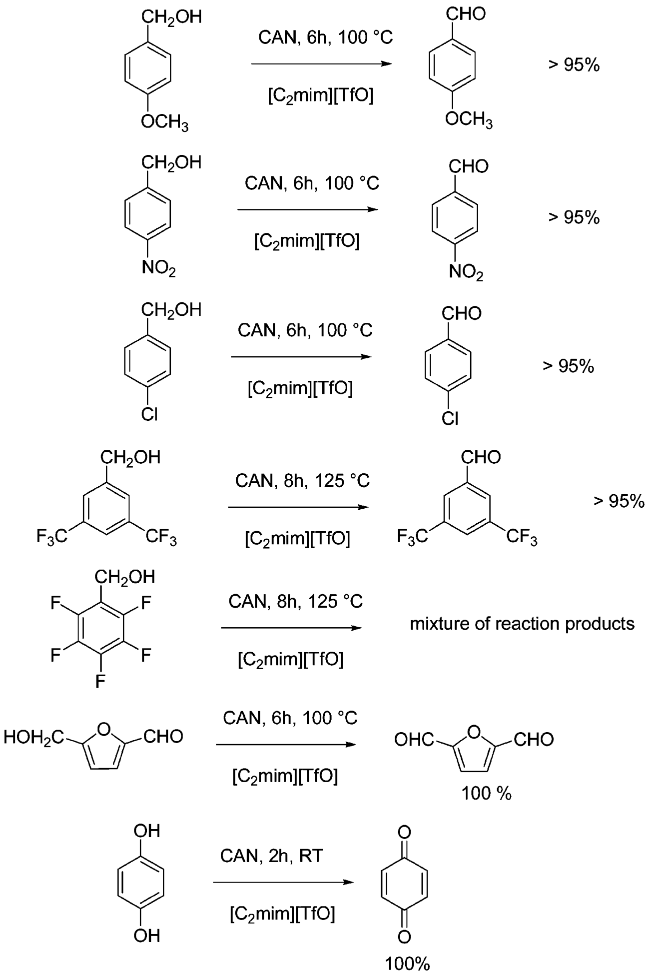


[a] The reaction mixture was heated for 6 h at 100 °C.

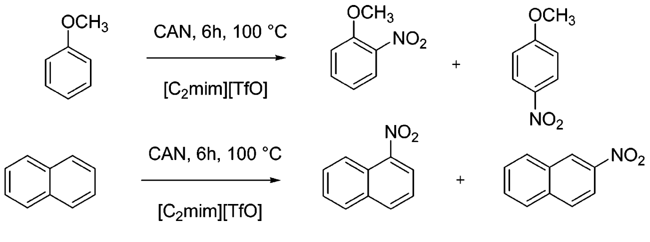
reagents on the selectivity of organic reactions should be studied more in detail. Of course, reproducible preparation of rare-earth salts with a given water content will be a challenge, especially because many rare-earth salts are moderately to very hygroscopic. It should be noted that if one wants to observe the dehydrating action of cerium(IV) triflate, the ionic liquid needs to be carefully dried. When an ionic liquid is left to equilibrate with the atmosphere, considerable amounts of water will be absorbed by the ionic liquid.[62]

Substrates Other than Benzyl Alcohol. Although major parts of our work have focused on oxidation of benzyl alcohol by cerium(IV) salts in ionic liquids, we also tested other substrates. For these reactions, CAN was chosen as the oxidizing agent and [C_2mim][TfO] as the ionic liquid. After dissolution of CAN, substrate was added and the reaction mixture was kept for 6 h at 100 °C under nitrogen atmosphere. Under these conditions, quantitative conversion of 4-chlorobenzyl alcohol, 4-methoxybenzyl alcohol, and 4-nitrobenzyl alcohol to the corresponding aldehyde was observed (Scheme 4). Incomplete conversion to a mixture of reaction products was found for 3,5-bis(trifluoromethyl)benzyl alcohol at 100 °C even after prolonged heating, but increasing the reaction temperature to 125 °C resulted in nearly quantitative conversion of bis(trifluoromethyl)benzyl alcohol into bis(trifluoromethyl)benzaldehyde after 8 h (Scheme 4). This example also illustrated that an increase in reaction temperature leads not only to a faster reaction but also to a higher yield of the desired reaction product. Even after prolonged heating at 125 °C, no more than about 70% of 2,3,4,5,6-pentafluorobenzyl alcohol was converted into reaction products, which consisted mainly of 2,3,4,5,6-pentafluorobenzaldehyde and smaller amounts of 2,3,4,5,6-pentafluorobenzoic acid (Scheme 4). 5-(Hydroxymethyl)furfural was quantitatively converted to 2,5-furandicarboxaldehyde (Scheme 4). Quantitative conversion of 1,4-hydroquinone to 1,4-quinone was observed even at room temperature (Scheme 4). CAN in 1-ethyl-3-methylimidazolium triflate caused ring nitration of anisole, although only 75% conversion of anisole was observed in the ionic liquid after 6 h at 100 °C (Scheme 5). The ratio of ortho: para isomer was 3:5. Naphthalene underwent ring nitration as well (85% conversion under the given reaction conditions) (Scheme 5). The ratio of 1-nitronaphthalene to 2-nitronaphthalene was 9:1.

SCHEME 4. Oxidation Reactions with $(NH_4)_2[Ce(NO_3)_6]$ (CAN) in [C_2mim][TfO]



SCHEME 5. Nitration Reactions with $(NH_4)_2[Ce(NO_3)_6]$ (CAN) in [C_2mim][TfO]



The observation that heating the reaction mixture at higher temperatures (125 °C) not only increases the reaction rate, but also often has a beneficial influence on the product yield is interesting. The potential of ionic liquid to carry out reactions at high temperatures has not received much attention yet, although it already was realized a long time ago that high-temperature molten salts can be for some types of organic reactions a very good reaction solvent.[63−65]

Oxidative Stability of Triflate Ionic Liquids. We also tested the stability of the triflate ionic liquids [C_2mim][TfO] and [C_6mim][TfO] against the oxidizing power of CAN at elevated temperatures. For these tests, 0.25 mmol of CAN and 2.5 mmol

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of the ionic liquid were placed in small vials that were closed with a septum. Solutions of CAN in the ionic liquid were heated for 6 h at 125 and 150 °C under a nitrogen atmosphere. No evolution of brown gases was observed. No decomposition products could be detected by ^{1}H and ^{13}C NMR after reaction. These results indicate that the triflate ionic liquids have a good stability against oxidation by CAN under the conditions at which the CAN-mediated organic transformations are being performed. However, decomposition of the ionic liquid by CAN could be observed at high CAN concentration and high temperatures: when 1 mmol of CAN and 2 mmol of the ionic liquid were heated to 150 °C, formation of brown nitrogen dioxide gas could be observed. In the ^{1}H and ^{13}C NMR spectra of the ionic liquid, decomposition products could be detected after reaction with CAN.

Conclusions

Thus far a limited number of oxidation reactions in ionic liquids have been published, and most of these studies are about the use of mild oxidizing agents.[36,66] Although many ionic liquids have a wide electrochemical window, one has to take the possibility of decomposition of the ionic liquid components by strong oxidants into account. The general applicability of imidazolium ionic liquids in oxidation reactions still has to be proven.

This study shows that imidazolium ionic liquids can be used as solvents for cerium(IV)-mediated oxidation reactions, but careful selection of both the cerium(IV) salt and the ionic liquid is necessary in order to overcome solubility and stability problems. In our case, the best cerium(IV) salts are cerium(IV) ammonium nitrate (CAN) and cerium(IV) triflate. 1-Alkyl-3-methylimidazolium triflates are preferable as the ionic liquid solvent. Cerium(IV) salts have a poor solubility in 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imides. 1-Alkyl-limidazolium ionic liquids are not suitable as solvent for CAN-mediated oxidation reactions because the ionic liquid is decomposed by CAN under formation of nitrogen dioxide gas. Our results show that good yields can be obtained for oxidation of benzyl alcohols to benzaldehydes and oxidation of 1,4-hydroquinone to 1,4-quinone, although it must be admitted that no major advantages are offered at this stage by using ionic liquids instead of conventional solvents.

The reactions in this study made use of stoichiometric quantities of cerium(IV) salts. It would be desirable if cerium(IV) could be regenerated in the ionic liquid because this would allow full recycling of the ionic liquid and of the cerium reagent. The obvious method of choice to regenerate cerium(IV) is electrochemical oxidation of the dissolved cerium(III) salts. Although the observation of anodic oxidation peaks in preliminary cyclic voltammetry experiments indicates that electrochemical oxidation of cerium(III) in ionic liquids is in principle possible, scaling up to carry out bulk electrolysis is a major challenge. Electrochemical regeneration of cerium(IV) in acidic aqueous solution has been illustrated by Kreh et al.[14]

An interesting observation is that anhydrous cerium(IV) triflate acts as a dehydrating agent toward benzyl alcohol in dry ionic liquids, whereas hydrated cerium(IV) triflate acts under the same reaction conditions as an oxidant. The advantage of performing organic reactions in ionic liquids at higher temperatures has been stressed. In the case of the cerium-mediated oxidation reactions of alcohols, higher reaction temperatures lead to smaller amounts of byproducts.

Experimental Section

Synthesis of 1-Methylimidazolium Nitrate, [Hmim][NO$_3$].[67] A dilute nitric acid solution (5.059 g of nitric acid (65 wt %) in 20 mL of water) was added to an aqueous solution of 1.05 equiv of *N*-methylimidazole (4.089 g, 49.79 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. Water was removed by sweeping compressed air above the solution at 80 °C. Upon cooling the liquid down to room temperature, a white solid formed. This was powdered, washed with diethyl ether, and dried in vacuo at 40 °C. The yield was quantitative. The white solid became yellow at temperatures above 100 °C. The ionic liquid could be decolorized by refluxing the aqueous solution in the presence of active charcoal.

Synthesis of 1-Methylimidazolium Hydrogensulfate, [Hmim][HSO$_4$]. A solution of 1-methylimidazole (9.21 g, 112 mmol) in 30 mL of dichloromethane was slowly added to an aqueous solution of sulfuric acid (96 wt %, 11.6 g, 114 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature, and the aqueous phase was separated and washed with dichloromethane. Water was removed by sweeping compressed air at 80 °C over the liquid. The ionic liquid was dried in vacuo at room temperature. The yield was quantitative. Anal. Calcd for $C_4H_8N_2O_4S$: C, 26.66; H, 4.48; N, 15.55. Found: C, 26.00; H, 4.64; N, 15.17. ^{1}H NMR (300 MHz, DMSO-*d*$_6$, δ/ppm): 12.87 (s, 2H), 9.48 (s, 1H), 8.14 (s, 1H), 8.07 (s, 1H), 4.36 (s, 3H). ^{13}C NMR (75.47 MHz, DMSO-*d*$_6$, δ/ppm): 136.1, 123.6, 120.1, 35.7.

Synthesis of 1-Methylimidazolium Trifluoromethanesulfonate, [Hmim][TfO].[68] A solution of 1-methylimidazole (4.355 g, 53 mmol) in dichloromethane (15 mL) was slowly added to a solution of trifluoromethanesulfonic acid (TfOH) (7.960 g, 53 mmol) in dichloromethane (15 mL) at 0 °C under nitrogen. A white solid precipitated. It was filtered, washed with dichloromethane, and dried in vacuo at 40 °C. The yield was quantitative.

Synthesis of 1-Butylimidazolium Nitrate, [Hbim][NO$_3$].[67] A dilute nitric acid solution (3.72 g of nitric acid (65 wt %) in 20 mL of water) was added to an aqueous emulsion of 1.05 equiv of *N*-butylimidazole (4.40 g, 35.43 mmol) at 0 °C. The reaction mixture was allowed to warm to room temperature. The reaction mixture was extracted with hexane. Water was removed by sweeping compressed air above the solution at 80 °C. The ionic liquid was dried in vacuo at 40 °C. The yield was quantitative. The white liquid slowly solidified at room temperature and became a yellow liquid at temperatures above 100 °C. It could be decolorized by refluxing the aqueous solution in the presence of active charcoal.

Synthesis of 1-Butylimidazolium Trifluoromethanesulfonate, [Hbim][TfO]. 1-Butylimidazole was prepared by reacting imidazole with NaOH and BuBr in ethanol. Diethyl ether (20 mL) was added very slowly to trifluoromethanesulfonic acid (5.75 g, 38.3 mmol) at 0 °C under nitrogen atmosphere. The solution of 1-butylimidazole (5.00 g, 40.3 mmol) in 10 mL of diethyl ether was added dropwise to the cooled solution of trifluoromethanesulfonic acid under nitrogen at 0 °C. The white solid formed was filtered off, washed with diethyl ether, and dried in vacuo. The yield was quantitative. Anal. Calcd for $C_8H_{13}F_3N_2O_3S$: C, 35.03; H, 4.78; N, 10.21. Found: C, 34.57; H, 4.87; N, 10.07. ^{1}H NMR (300 MHz, DMSO-*d*$_6$, δ/ppm): 13.96 (s, 1H), 8.99 (s, 1H), 7.86 (s, 1H), 7.60 (s, 1H), 4.17 (broad signal, 2H), 1.74 (broad signal, 2H), 1.19 (broad signal,

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2H), 0.82 (broad signal, 3H). ^{13}C NMR (75.47 MHz, DMSO-d_6, δ/ppm): 135.3, 122.1, 120.9 (q, J = 321.5 Hz), 120.2, 48.6, 31.7, 19.0, 13.2.

Synthesis of 1-Hexyl-3-methylimidazolium Trifluoromethanesulfonate, [C$_6$mim][TfO]. The ionic liquid [C$_6$mim][TfO] was prepared by addition of 1.5 equiv of trifluoromethanesulfonic acid (10.00 g, 66.6 mmol) to a cooled and vigorously stirred solution of 1-hexyl-3-methylimidazolium bromide (10.66 g, 43.1 mmol) in 80 mL of dichloromethane. After addition of the acid, the reaction mixture was refluxed for 2 h and stirred overnight at room temperature. Excess ammonia gas was bubbled through the solution, and the precipitated white solid was filtered off. The solution of the ionic liquid in dichloromethane was washed with water until the pH of the washing water was neutral. The organic phase was dried over neutral alumina and filtered, and dichloromethane was removed on a rotary evaporator. Residual dichloromethane was removed in vacuo at 40 °C. Yield: 11.9 g (87%). Anal. Calcd for $C_{11}H_{19}F_3N_2O_3S$: C, 41.76; H, 6.05; N, 8.86. Found: C, 41.20; H, 6.17; N, 9.02. ^{1}H NMR (300 MHz, chloroform-d_3, δ/ppm): 9.24 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 4.49 (t, 2H, J = 7.1 Hz), 4.23 (s, 3H), 2.15 (broad signal, 2H), 1.56 (broad signal, 6H), 1.10 (broad signal, 3H). ^{13}C NMR (75.47 MHz, chloroform-d_3, δ/ppm): 135.6, 122.8, 122.0, 119.9 (q, J = 320.3 Hz), 48.8, 35.0, 30.0, 29.0, 24.7, 21.3, 12.7.

Synthesis of 1-Ethyl-3-methylimidazolium Trifluoromethanesulfonate, [C$_2$mim][TfO].[69] 1-Methylimidazole (16.882 g, 206 mmol), distilled over KOH, was slowly added to freshly distilled ethyl trifluoromethanesulfonate (37.314 g, 209 mmol) in a Schlenk flask under nitrogen atmosphere at 0 °C. After addition was completed, the reaction mixture was allowed to warm to room temperature and stirred overnight. The excess ethyl trifluoromethanesulfonate was removed in vacuo at room temperature for 3 h; then the ionic liquid was further dried in high vacuum at 50 °C for 6 h. The yield was quantitative.

Synthesis of 1-(2-Ethoxyethyl)-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide, [C$_2$OC$_2$mim][NTf$_2$].[70] 1-Methylimidazole (8.042 g, 98 mmol) was mixed with 2-ethoxyethyl chloride (12.250 g, 113 mmol) in a Schlenk flask under nitrogen atmosphere. The mixture was stirred and heated at 105 °C for 48 h. The obtained brown viscous liquid was dissolved in 70 mL of distilled water and decolorized with charcoal. After removal of charcoal an aqueous solution of lithium bis(trifluoromethylsulfonyl)imide (33.61 g, 117 mmol in 30 mL of water) was added in one portion. The formed ionic liquid [C$_2$OC$_2$mim][NTf$_2$] gave a second phase which was separated. The aqueous phase was extracted with dichloromethane (3 × 150 mL); the organic phase was collected, washed with water (50 mL), and dried on $MgSO_4$. The solid was filtered off, dichloromethane was evaporated, and the ionic liquid was dried in high vacuum at 50 °C for 6 h. A 36.24 g amount of [C$_2$OC$_2$mim][NTf$_2$] was obtained (85%).

Oxidation of Benzyl Alcohol by CAN in [C$_2$mim][TfO]. Cerium ammonium nitrate (548 mg, 1 mmol) was placed in a Schlenk flask, and [C$_2$mim][TfO] (2.60 g, 10 mmol) was added. The Schlenk flask was sealed with a septum and then evacuated and flushed three times with nitrogen gas. Benzyl alcohol (54 mg, 0.5 mmol) was added under nitrogen atmosphere. The reaction mixture was placed in an oil bath at 100 °C and stirred for 6 h. The reaction mixture became a deep red solution immediately after placing the Schlenk flask in the oil bath. The color changed to light orange after 1 h, and 3 h later the solution was yellow. Benzaldehyde was extracted with toluene (5 × 5 mL) under nitrogen atmosphere. The organic phase was examined by GC, GC-MS, and NMR. Yield (95−97%) was determined by GC using dodecane as internal standard.

General Procedure for Reacting Benzyl Alcohol, Benzyl Alcohol Derivatives, and Aromatics with CAN in an Ionic Liquid. Cerium ammonium nitrate (1 mmol) and ionic liquid (10 mmol) were placed in a Schlenk flask. The Schlenk flask was sealed with a septum and then evacuated and flushed three times with nitrogen gas. The organic substrate (0.5 mmol) was added under nitrogen atmosphere. The reaction mixture was placed in an oil bath at 100 °C and stirred for 6 h. The reaction mixture became a deep red solution immediately after placing the Schlenk flask in the oil bath. The color changed to light orange after 1 h, and 3 h later the solution was yellow. In general, aluminum foil was wrapped around the reaction flask to exclude light from the reaction mixture. The product was extracted with toluene (5 × 5 mL) under nitrogen atmosphere. The organic phase was examined by GC, GC-MS, and NMR. The yield was determined by GC using dodecane as internal standard. For the oxidation of 1,4-hydroquinone, the reaction time could be reduced because the reaction was already complete after 2 h at room temperature.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of 1-methylimidazolium hydrogensulfate, [Hmim][HSO$_4$], 1-butylimidazolium trifluoromethanesulfonate, [Hbim][TfO], 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, [C$_2$mim][TfO], and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate, [C$_6$mim][TfO]; ^{19}F NMR spectrum of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, [C$_2$mim][TfO]. This material is available free of charge via the Internet at http://pubs.acs.org.

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