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# Synthesis and structural characterization of CO<sub>2</sub>-soluble oxidizers [Bu<sub>4</sub>N]BrO<sub>3</sub> and [Bu<sub>4</sub>N]ClO<sub>3</sub> and their dissolution in cosolvent-modified CO<sub>2</sub> for reservoir applications†

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CO<sub>2</sub> utilization in upstream oil and gas applications requires CO<sub>2</sub>-soluble additives such as polymers, surfactants, and other components. Here we report the facile synthesis of CO<sub>2</sub>-soluble oxidizers composed of judiciously selected organic cations paired with oxidizing anions. [Bu<sub>4</sub>N]BrO<sub>3</sub> and [Bu<sub>4</sub>N]ClO<sub>3</sub> are prepared using a double displacement synthetic strategy, whereby the crystalline product is readily obtained in high yield and structurally characterized using single-crystal X-ray diffraction. The facility of the approach is demonstrated through the preparation of several additional alkylammonium bromate compounds. Static solubility studies using a high-pressure cell with viewing windows showed that tetrabutylammonium compounds could be solubilized using cosolvent-modified CO<sub>2</sub>. Using 4 mol% ethanol as cosolvent, >3 mM [Bu<sub>4</sub>N]BrO<sub>3</sub> could be dissolved in CO<sub>2</sub>, while ~0.75 mM [Bu<sub>4</sub>N]ClO<sub>3</sub> could be dissolved in the same solvent system. The solubility properties of [Bu<sub>4</sub>N]BrO<sub>3</sub> along with its thermal stability up to ~200 °C suggest that it is a promising oilfield oxidizer that can be utilized in subterranean CO<sub>2</sub> applications.

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## Introduction

As the global demand for reducing CO<sub>2</sub> emissions continues to rise, the need for better methods to sequester, utilize, and convert CO<sub>2</sub> also continues to increase. Injecting CO<sub>2</sub> in subterranean rock formations is an important technology under development that can ultimately store large quantities of CO<sub>2</sub>.<sup>1</sup> Meanwhile CO<sub>2</sub> utilization in the energy sector for enhanced oil recovery (EOR)<sup>2,3</sup> or shale fracturing operations<sup>4,5</sup> may lead to some CO<sub>2</sub> uptake while also providing a means of reducing valuable groundwater consumption. Hydraulic fracturing in shale reservoirs with extended reach horizontal drilling and multistage fracturing can consume tens of millions of gallons of water in a single well. Using CO<sub>2</sub> for fracturing, however, is very challenging due to its low viscosity and poor dissolving power for the hydrophilic fracturing fluid additives that have been developed over the decades. Advances in nonfluorinated CO<sub>2</sub>-soluble polymers and surfactants suggests that CO<sub>2</sub>-based

hydraulic fracturing is attainable.<sup>6</sup> However no examples of complementary CO<sub>2</sub>-soluble oxidizers have been reported. These components are vitally important in fracturing fluid systems for breaking polymer chains to reduce viscosity at a specified time during the well operation and to aid in clean-up. Typical oxidizing salts used in aqueous fracturing fluids have negligible solubilities in liquid or supercritical CO<sub>2</sub>. Therefore, preparing oxidizers with solubility and reactivity properties suitable for use in CO<sub>2</sub> media are needed.

We turned our attention to bromate-based oxidizing salts, which have seen consistent application in subterranean stimulation fluids.<sup>7,8</sup> Their usage is partially due to the convenient overlap in the temperature range over which they are active toward relevant reductants and the typical bottom hole static temperature of reservoirs. Bromate-containing fluids injected from the surface into rock formations experience an inherent delay before activation due to the time required to heat the fluid to reservoir temperatures and thereby activate the bromate. *In situ* pH changes can also be used to alter the reactivity of bromate after a specified amount of time. Not only does the thermal stability of bromate lend to its usefulness in subsurface applications but also its high electron per mole oxidizing capacity (6e<sup>-</sup> to form the reduced species Br<sup>-</sup>) if all oxidizing equivalents are utilized.<sup>9</sup> Other common oxidizers used in these applications such as persulfate, chlorite, perborate, and peroxide are able to receive as low as 2e<sup>-</sup> per mole and/or have limited thermal stability. In some cases, many of these oxidizers

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† Electronic supplementary information (ESI) available: Detailed synthetic procedures, crystallographic data for compounds 1–2 and 6–7, TGA-DSC, melting points for tetrabutylammonium salts, CO<sub>2</sub> solubility test results. CCDC 2039678–2039681. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0ra09563j



also produce reduced species with the potential to generate scale, namely divalent salt precipitate, which may block hydrocarbon flow in pore spaces or propped fractures.

We recently demonstrated the use of two different bromate-based fluid systems for upstream well stimulation applications. The first fluid is composed of ammonium salts and sodium bromate where the ammonium is oxidized to generate mineral or organic acids depending upon the counteranion.<sup>10</sup> A second fluid system incorporating bromate was designed to fracture unconventional shale source rock by oxidizing the ductile polymeric organic matter dispersed on the fracture faces.<sup>11</sup> Both water-based stimulation fluids capture the effects of delayed oxidizer activation using natural reservoir heating as well as the high oxidizing power of bromate. Laboratory studies indicate that Br<sup>-</sup> ion, the fully reduced species, is the ultimate fate of the bromate system in the presence of hydrocarbon-bearing formation rocks such as carbonate and shale.

In order to bring the advantages of bromate oxidizer to CO<sub>2</sub>-based systems, a synthetic method was developed to replace the metal cation of a bromate salt with an organic cation to increase the overall hydrophobicity of the molecule. This approach is similar to the hydrophobic ion pairing (HIP) strategy that has been employed for drug delivery and protein solubilization in organic media where a charged hydrophilic molecule of interest is paired with a hydrophobic ion of opposite charge.<sup>12–16</sup> The bromate anion electrostatically coupled to an organic cation could potentially be solubilized in CO<sub>2</sub>. In general, CO<sub>2</sub> does not solubilize compounds that are high molecular weight, polar, or ionic to a significant extent. This solubility aspect handicaps the use of CO<sub>2</sub> as a solvent in most industrial applications for these types of compounds. However, it has been demonstrated that CO<sub>2</sub> can be modified with small amounts of polar cosolvent in order to drastically enhance the solubility of polar solutes and could potentially aid the solubility of ionic solutes given the proper choice of cation and anion. Recent studies on the solubility of light hydrocarbons in CO<sub>2</sub> demonstrated notable improvements when cosolvent was added to the fluid.<sup>17,18</sup> The current application requires that only small amounts of oxidizing salts be dissolved in CO<sub>2</sub>. For subterranean applications where oxidizers are utilized in aqueous fluids, concentrations are typically in the range of a few pounds per thousand gallons of fluid (<0.1 wt%).<sup>19,20</sup> The solubility of alkali salts of bromates in liquid or supercritical CO<sub>2</sub> is negligible, so enhancing the solubility through cation modification is highly desirable.

Here we report the preparation, structural characterization, and solubilization of bromate-based ionic compounds with hydrophobic character. A few structurally characterized examples of ionic compounds composed of bromate and organic cation exist, though the molecules were designed to be rich in reactive nitrogen sites for use as solid propellants.<sup>21</sup> We envisioned stable molecules where organic components are relatively inert to oxidation, such that the bromate would target an external source. Chlorate analogues were also prepared in order to demonstrate the utility of the general synthetic method for other oxidizing ionic liquids. Finally, the stability of the

prepared compounds was investigated through thermogravimetric analysis, and their solubility in CO<sub>2</sub> was examined.

## Experimental

### Chemical reagents and materials

All chemicals and solvents used in the preparation of the compounds described herein were of reagent grade and used without further purification (Table S1†). (WARNING: This series of reactions should be handled with extreme caution.)

### General procedure to prepare compounds 1–8

The general strategy for the synthesis of alkylammonium bromates and chlorates is through a double-displacement reaction of [R<sub>x</sub>N<sub>4-x</sub>]<sub>2</sub>SO<sub>4</sub> with Ba(XO<sub>3</sub>)<sub>2</sub> to yield two equivalents of [R<sub>x</sub>N<sub>4-x</sub>]<sub>2</sub>XO<sub>3</sub> and one equivalent of BaSO<sub>4</sub> (R = alkyl; X = Br, Cl). Experimental preparations of [Bu<sub>4</sub>N]BrO<sub>3</sub> (1), [Bu<sub>4</sub>N]ClO<sub>3</sub> (2), [Bu<sub>3</sub>NH]BrO<sub>3</sub> (5), [Bu<sub>2</sub>NH<sub>2</sub>]BrO<sub>3</sub> (6), [BuNH<sub>3</sub>]BrO<sub>3</sub> (7) (Bu = Butyl), and [Me<sub>4</sub>N]BrO<sub>3</sub> (8) were carried out using this double displacement technique. The sulfate salts of [Bu<sub>3</sub>NH]<sup>+</sup>, [Bu<sub>2</sub>NH<sub>2</sub>]<sup>+</sup>, and [BuNH<sub>3</sub>]<sup>+</sup> salts were prepared by the reaction of the respective amine (Bu<sub>3</sub>N, Bu<sub>2</sub>NH, and BuNH<sub>2</sub>, respectively) with sulfuric acid. The synthesis of bis(triphenylphosphine)iminium, [PPN]<sup>+</sup>, bromate (3) and chlorate (4) was performed by reacting [PPN]Cl and alkali salts of XO<sub>3</sub><sup>-</sup> where X = Br, Cl. Detailed synthetic methods for each of compounds 1–8 along with their yields and characterization are provided in the ESI.†

### X-ray crystallography

Single crystal X-ray diffraction analysis was performed on 1–4 using either a Bruker PHOTON-II or Bruker APEX-II diffractometer. Details of the measurements are provided in the ESI.†

### CO<sub>2</sub> solubility tests

The solid sample was placed in a 450 mL high-pressure autoclave composed of corrosion-resistant Hastelloy metal alloy with see-through windows on two sides of the vessel as shown in Fig. S4.† Typical concentrations of solute ranged from 1.5–5 mM (e.g., 0.10 g [Bu<sub>4</sub>N]BrO<sub>3</sub> in ~170 g liquid CO<sub>2</sub>). Optionally, cosolvent was also added along with the solid oxidizer with the concentration of cosolvent ranging from 1–5 mol% relative to the amount of CO<sub>2</sub>. After combining solute and cosolvent, the autoclave was sealed and charged with liquid CO<sub>2</sub> to a specified mass. Most experiments were conducted with 170 g of liquid CO<sub>2</sub> such that the top level of the liquid was viewable through the see-through window. A propeller was used to stir the CO<sub>2</sub>-cosolvent-oxidizer mixture while monitoring through the window to determine whether the oxidizer is soluble, slightly soluble, or insoluble.

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA Instruments SDT Q600 Simultaneous DSC-TGA. The samples were placed in a tared alumina ceramic crucible and were



submitted to a non-oxidative (nitrogen) atmosphere under a flow rate of 100 mL min<sup>-1</sup> under standard temperature and pressure conditions. They were heated from ambient temperature to 1000 °C at a rate of 10 °C min<sup>-1</sup>. For each experiment, approximately 10–15 mg of solid material was placed in the crucible of the thermobalance.

## Results and discussion

### Overview

Common cations utilized in ionic liquids were considered for their compatibility with bromate and chlorate oxidizing anions such as tetraphenylphosphonium [Ph<sub>4</sub>P]<sup>+</sup>, imidazolium [Im]<sup>+</sup>, pyridinium [Pyr]<sup>+</sup>, pyrrolidinium [Pyr]<sup>+</sup>, and tetraalkylammonium [R<sub>4</sub>N]<sup>+</sup> as shown in Scheme 1. The most closely reported, related structure in the literature is that of guanidinium bromate.<sup>22</sup> No structures have been reported of these common ionic liquid cations with bromate or chlorate. [Pyr]<sup>+</sup>, [Pyr]<sup>+</sup>, and [Im]<sup>+</sup> were each considered as potential cations for pairing with bromate. The relative accessibility of the oxidizable N atoms suggested that the compounds, if formed, may not be stable. A systematic study was performed and will later be discussed to assess the stability of bromate in the presence of N with variable degree of substitution. A second consideration regarding cation selection is the relative cost as this is a significant factor for contemplating scalability for oilfield application. In this respect, [Pyr]<sup>+</sup>, [Pyr]<sup>+</sup>, and [Im]<sup>+</sup> are much more expensive than the alternative options.

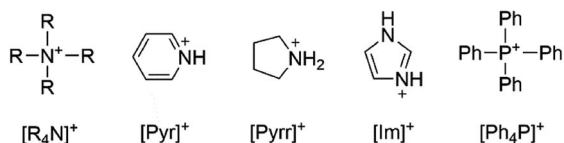
Tetraalkylammonium and tetraalkylphosphonium cations are frequently used in ionic liquids due to their high chemical and thermal stability.<sup>23</sup> The sterically protected N means that the cations have low susceptibility to oxidation. Tetraalkylphosphonium cations are less preferred for oilfield chemistry applications as any degradation of the cation to form phosphate ions could be detrimental to the reservoir environment where divalent scaling can plug pore throats or fractures. By contrast, tetraalkylammonium salts are already used in the oilfield for clay stabilization<sup>24</sup> or biocidal purposes, so scaling new products for field application may be accelerated. These salts are routinely added to fluids for subterranean application in clay-bearing shales where there is strong potential for water swelling<sup>25</sup> and hence destabilization of the formation surface. Therefore, adding the new tetraalkylammonium bromate/chlorate compounds to existing aqueous or CO<sub>2</sub>-based fluid formulations offers a dual benefit.

Literature precedent exists for dissolving CO<sub>2</sub> in alkylammonium-based ionic liquids. For example, tributylmethylammonium methylsulfate was demonstrated to dissolve

CO<sub>2</sub> and did so even to a greater extent than the imidazolium analogue 1-butyl-3-methyl-imidazolium methylsulfate.<sup>26</sup> Similarly, a tetraalkylammonium-based poly(ionic liquid) exhibited particularly high dissolution of CO<sub>2</sub>, absorbing as much as 77% of its weight in CO<sub>2</sub>.<sup>27</sup> The solubility of alkylammonium salts in CO<sub>2</sub> is less well understood. There is precedent for dissolving ionic compounds by fluorinating either the cation or both the cation and anion.<sup>28</sup> Fluorinated alkylammonium cations are expected to be moderately soluble, but the scale of the application would prevent widespread adoption due to the cost prohibitive nature of fluorinated compounds. There is some evidence for improving the solubility of salts in CO<sub>2</sub> by exchanging alkali cations for tetraalkylammonium cations. The solubility of the tetrabutylammonium salt of diethyldithiocarbamate was 2.7 times more soluble than the sodium salt.<sup>29</sup> Though this is an ionic compound, the anion has favorable solubility in CO<sub>2</sub> so the oxyhalides of the present application are expected to be more challenging to dissolve.

Alkylated ammonium compounds are frequently used as phase transfer catalysts. Their solubilities and ion pairing attributes in water and organic solvents has been studied thoroughly, though limited information is available about their solubilities in CO<sub>2</sub>. In water, tetraalkylated ammonium cations pair more readily with larger halide anions based on the cation–anion radial distribution function predicted by molecular dynamics.<sup>30</sup> Tetramethylammonium behaves as a harder cation, though the softer structures of tetraethylammonium and tetrapropylammonium allow some water to penetrate.<sup>30</sup> Tetramethylammonium salts are known to have very low solubility in chloroform,<sup>31</sup> so they are unlikely to dissolve in CO<sub>2</sub>. Though the solubility of similar salts increases with the length of the alkyl chain, there may be a reverse at high chain lengths.<sup>31</sup> Tetrahexylammonium ions appear to create large pockets where solvent is excluded and large anions can be housed.<sup>32</sup> Pairing an oxidizing anion with an alkylammonium cations with long alkyl chains may ultimately hinder the anion's reactivity with substrates.

Tetrabutylammonium may serve as an ideal intermediate cation size with both sufficient hydrophobicity to encourage solubility in CO<sub>2</sub> while also allowing reactivity between the anion and substrate. Tetrabutylammonium cations are one of the most ubiquitous cations used for phase transfer catalysis and their structures, ion–ion interactions, and transport across liquid/liquid interfaces have been studied in detail.<sup>33,34</sup> Their salts have good solubility in both aqueous and organic phases and are a good target for a subterranean application where miscibility with reservoir fluids including both water and hydrocarbons is desirable. Tetrabutylammonium cations have been used as phase transfer catalysts for oxidation reactions.<sup>35</sup> For example, tetrabutylammonium hypochlorite can be generated *in situ* and transferred to an organic phase where benzyl alcohol is oxidized to aldehyde.<sup>36–38</sup> Tetrabutylammonium cation has also been paired with bromite<sup>39</sup> or dichromate<sup>40</sup> to name a couple more examples. The synthesis of [Bu<sub>4</sub>N]BrO<sub>3</sub> and [Pr<sub>4</sub>N]BrO<sub>3</sub> by bubbling chlorine gas through a solution of the tetraalkylammonium bromide was reported, though the compounds isolated were yellow or orange in color suggesting the formation of the tribromide salts or bromine contamination.<sup>41</sup>



Scheme 1 Cations commonly used in ionic liquids.





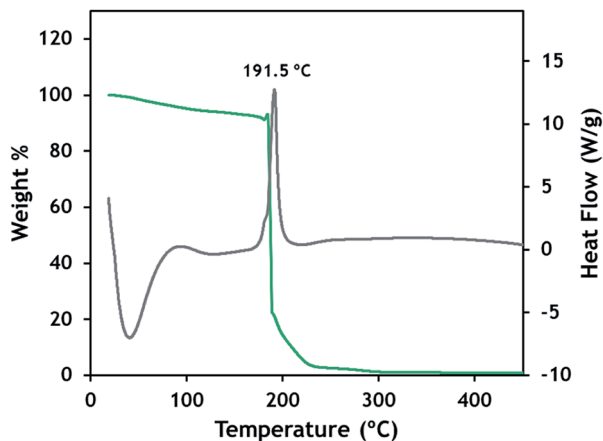


Fig. 3 TGA-DSC of 1 while heating from room temperature to 400 °C.

Compounds 5–7 were readily synthesized by protonating the respective amine with sulfuric acid to form the alkylammonium salt. A double displacement reaction between the alkylammonium sulfate and  $\text{Ba}(\text{BrO}_3)_2$  was then performed to yield the alkylammonium bromate series. Scheme S2† illustrates the reaction sequence. The stability of the resulting compounds changed sharply as the number of butyl substituents on the alkylammonium cation was reduced. Dibutyl- and tributylammonium bromates were each isolated as liquids and are stable during manipulation. Monobutylammonium bromate was isolated as a clean solid that was stable during manipulation and storage for several days. However, after approximately 10 days, the material decomposed with rapid gas evolution. Compounds 1–2 have been observed to be stable indefinitely (>6 months) while stored in a sealed container.

The reactivity and thermal decomposition of 1 follows a straightforward sequence as shown in Fig. 3. Heating the solid at 10 °C per minute resulted in a gradual mass loss of 7–8% while heating to nearly 200 °C, consistent with the complete evaporation of water from the solid. When the temperature reaches 192 °C, a large exotherm is generated accompanied by abrupt and complete mass loss. Interestingly, 1 has a notably lower melting point (54 °C) than other tetrabutylammonium salt derivatives as shown in Table S3.† This observation can be rationalized by the hydrate crystal structure, where bromate-water linkages form throughout the lattice. The low melting point and high decomposition temperature means that this compound has a large stable liquid temperature range of ~138 °C. This may open additional applications for this chemistry such as gas hydrate removal. The melting point depression through hydrate or other lattice modification may also provide an approach for ionic liquid-based  $\text{CO}_2$  capture technologies that are often limited due to their high melting points.

### $\text{CO}_2$ solubility

In order to test the solubility of the newly prepared 1 in  $\text{CO}_2$ , an autoclave with see-through windows as shown in Fig. S4† was used in order to visualize the dissolution process and determine

whether each solute could dissolve in the  $\text{CO}_2$ . A static view cell apparatus has previously been reported for other  $\text{CO}_2$  solubility studies.<sup>46</sup> Addition of liquid  $\text{CO}_2$  to either 1 or 2 in the see-through autoclave (1.5 mM) resulted in opaque fluid indicating that the solids were either insoluble or sparingly soluble. 2 separates as a white solid while 1 separates from the mixture as an oily liquid, consistent with its low melting point (54 °C) under atmospheric conditions. A limited number of polar solutes have been directly dissolved in  $\text{CO}_2$ , but adding a small amount of polar cosolvent has been shown to enhance the solubility significantly by changing the thermodynamic properties of the system.<sup>47,48</sup> For example, aspirin solubility in  $\text{CO}_2$  was enhanced five times with acetone cosolvent and 14 times with methanol or ethanol cosolvent.<sup>49</sup> Typical cosolvents used with  $\text{CO}_2$  to enhance the solubility of various solutes include ketones, alkanes, and alcohols.<sup>47</sup> Alcohols can act as hydrogen-bonding acceptors and donors, while ketones are only able to act as hydrogen-bonding acceptors. Alkanes are nonpolar and can only interact with solutes molecules *via* van der Waals interactions. Cosolvents are typically added up to 5 mol% though in some cases reach 10 mol%.<sup>50</sup>

Beyond pharmaceutical examples such as aspirin, naproxen,<sup>51,52</sup> and acetaminophen,<sup>53</sup> many other examples exist for solubilizing polar compounds in  $\text{CO}_2$  through polar cosolvent addition. Caffeine can be extracted from green tea using ethyl lactate, ethyl acetate, and ethanol where ethyl lactate showed the strongest effects upon solubilization due to its ability to hydrogen bond through both hydroxyl and carbonyl groups.<sup>54</sup> Benzoic acid and salicylic acid solubilities are improved with methanol and ethanol due to hydrogen bonding between the solute and cosolvent.<sup>55,56</sup> Acetic acid and methyl acetate are each suitable cosolvents for stearic acid, though acetic acid has a much stronger effect on solubility.<sup>57</sup> A combination of cosolvents also aids in the solubilization of stearic acid in  $\text{CO}_2$ , though the effect of binary cosolvent was observed to be intermediate to the two individual cosolvents.<sup>58</sup> Perhaps most relevant to the present study is an ionic compound composed of an alkylated ammonium salt. Acid Red 57, an anionic dye, can be ion paired with dodecyltrimethylammonium cation and solubilized in  $\text{CO}_2$  with 10 mol% methanol as cosolvent.<sup>59</sup>

Solubility experiments were then conducted on 1 in the presence of cosolvents. A wide range of cosolvents were tested including acetone, ethyl acetate, ethyl lactate, ethanol, and acetic acid. The results of dissolution tests performed with 4 mol% cosolvent in the presence of 1.5 mM 1 solute are shown in Fig. 4. Very little, if any, solute is dissolved in  $\text{CO}_2$  modified with either acetone or ethyl acetate, even after stirring for a few hours. On the other hand,  $\text{CO}_2$  modified with either ethyl lactate or ethanol yielded fully homogenous solutions with no visible solute. The positive effect of these two cosolvents is likely attributed to their hydrogen-bond donating capabilities and not to their dipole moments, because ethanol has a low dipole moment relative to both acetone and ethyl acetate.

Increasing the concentration of 1 two-fold to 3 mM while maintaining the concentration of cosolvent distinguished the dissolution effects of ethanol from ethyl lactate. Fig. 5(a) shows the results of the two tests. While 3 mM of 1 with 4 mol% ethyl



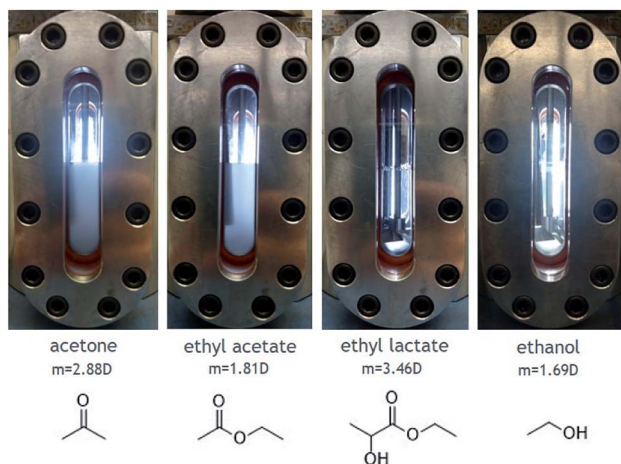


Fig. 4 Dissolution tests of **1** (1.5 mM) in carbon dioxide (20 °C, ~800 psi) with 4 mol% cosolvent.

lactate demonstrated low solubility in CO<sub>2</sub>, 3 mM **1** with 4 mol% ethanol was fully dissolved in the CO<sub>2</sub> solution. However, 4.5 mM of **1** with 4 mol% ethanol exhibited some cloudiness, indicating that the solubility limit is slightly less than that (Fig. S5†). In order to examine the role of the butyl chains in the solubility of this compound, the solubility of [Me<sub>4</sub>N]BrO<sub>3</sub> (**8**) was also examined. The results of 1.5 mM **8** dispersed in CO<sub>2</sub> with 4 mol% of either ethyl lactate or ethanol are shown in Fig. 5(b). As is evident in the images, **8** exhibits low solubility in CO<sub>2</sub> in the presence of either cosolvent, indicating that the longer butyl chains provide the requisite hydrophobicity to enhance the solubility of these compounds in nonpolar CO<sub>2</sub> solvent. Although **3** and **4** could be readily prepared in high yield and isolated as crystalline solids, their solubility in CO<sub>2</sub> was limited in the presence of any of the cosolvents examined.

Compound **2** exhibited much lower solubility than **1** with the various cosolvents. With 4 mol% of ethanol, ethyl lactate, ethyl acetate, or acetone, 1.5 mM of **2** in CO<sub>2</sub> is not fully dissolved. Decreasing the concentration of solute to 0.75 mM yielded full solubility in CO<sub>2</sub> with 4 mol% ethanol but still a significant undissolved fraction in CO<sub>2</sub> modified with 4 mol% ethyl lactate.

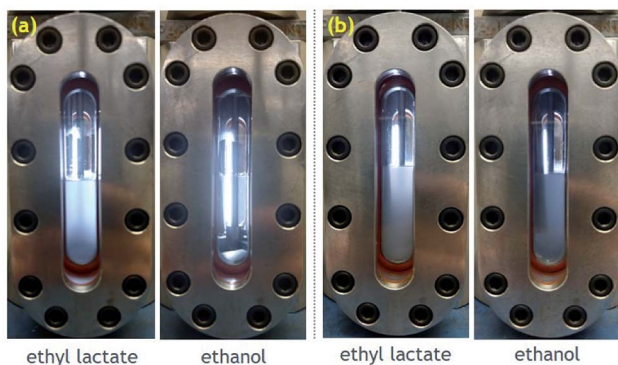


Fig. 5 Dissolution tests of (a) **1** (3 mM) and (b) **8** (1.5 mM) in carbon dioxide (20 °C, ~800 psi) with 4 mol% cosolvent.

Meanwhile, the commercially available [Bu<sub>4</sub>N]ClO<sub>4</sub> exhibited even lower solubility than **2**, where even 0.75 mM [Bu<sub>4</sub>N]ClO<sub>4</sub> in CO<sub>2</sub> modified with 4 mol% ethanol was sparingly soluble. The two solubility tests performed at 0.75 mM are shown in Fig. S6.† By contrast, [Bu<sub>4</sub>N]Cl exhibited solubility results very similar to **1** where 3 mM was fully dissolved but 4.5 mM is cloudy. The solubility trend of the [Bu<sub>4</sub>N]<sup>+</sup> salt series in CO<sub>2</sub> modified with 4 mol% ethanol follows the trend:



The higher solubility of the bromate salt is consistent with the bromate *versus* chlorate crystal structures. The bromate ions form a hydrogen-bonded chain with water molecules, while the chlorate salt is anhydrous. It has been shown that bromate exhibits both structure-making and structure-breaking properties in water, where the three oxygen atoms acts kosmotropically while the bromine atom behaves chaotropically.<sup>60</sup> In the current system, bromate may interact more favorably with the hydrogen-bond donating solvents than chlorate or perchlorate, yielding higher solubility. Notably, the solubility of [Bu<sub>4</sub>N]BrO<sub>3</sub> achieved (>12 wt%) with ethanol cosolvent significantly exceeds the typical concentrations utilized in the application (~0.03 wt%).

## Conclusions

Oxybromine chemistries continue to be actively explored for their utility in chemical transformations and their presence in aqueous environmental systems. The synthesis of oxidizers composed of bulky organic cations and oxybromine/oxychlorine anions is now reliably demonstrated. The oxidizers are prepared in high yield using a straightforward double displacement reaction method and isolated as crystalline solids whose structures were verified crystallographically. [Bu<sub>4</sub>N]<sup>+</sup> paired with bromate or chlorate is stable upon heating to ~200 °C, well above subterranean temperature conditions. Dissolution of **1** and **2** in cosolvent-modified CO<sub>2</sub> was achieved using ethanol and, to a lesser degree, ethyl lactate, demonstrating the utility of these compounds for potential field application.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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