

SUPPORTING INFORMATION

Synthesis and Structural Characterization of CO₂-Soluble Oxidizers [Bu₄N]BrO₃ and [Bu₄N]ClO₃ and Their Dissolution in Cosolvent-Modified CO₂ for Reservoir Applications

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Instrumentation:

- Thermo Scientific Barnstead Smart2Pure water purification system having a resistivity of 18.2 MΩ.cm was used to generate the de-ionized water (DI-H₂O) for all experimental procedures.
- A Lauda programmable recirculating silicone oil bath was used to perform the hydrothermal syntheses in the Ace Glass Pressure tubes.
- The polished samples were imaged both before and after oxidation at 1 keV using a ZEISS SIGMA VP SEM equipped with a Bruker Xflash Energy-Dispersive Spectrometer. Collection and processing of data were done using Bruker Espirit 2.1 software. EDS acquisition was performed in analytical mode with 5 nA probe current, 15 kV operating potential, 10.1 mm working distance, and 100 kcps (counts per second).
- Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA Instruments SDT Q600. Samples were heated at a rate of 10 °C min⁻¹ under nitrogen.
- Fourier transform infrared (FTIR) spectroscopy analysis of **1-7** was performed on an Agilent Cary 630 FTIR Spectrometer.
- Melting points of **1-4** were determined using a VWR Basic Digital Melting Point Apparatus (#75840-104).

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. Summary of chemical compounds/starting reagents used in this study.

Chemical Name	Formula	Vendor / Catalog #
potassium chlorate	KClO ₃	Alfa Aesar / A17075
sodium bromate	NaBrO ₃	Fritz Industries / OB-3N
barium bromate	Ba(BrO ₃) ₂	Alfa Aesar / A11008
barium chlorate	Ba(ClO ₃) ₂	Aldrich / 244554
tetramethylammonium sulfate	(Me ₄ N) ₂ SO ₄	TCI / T1240
tetrabutylammonium sulfate	(Bu ₄ N) ₂ SO ₄	Alfa Aesar / 41723
tetrabutylammonium perchlorate	(Bu ₄ N) ₂ ClO ₄	Beantown Chemical / 213960
tetrabutylammonium chloride	(Bu ₄ N) ₂ Cl	Millipore Sigma / 814645
bis(triphenylphosphine)iminium chloride	[PPN]Cl	Beantown Chemical / 141410
tributylamine	Bu ₃ N	TCI / T0357
dibutylamine	Bu ₂ NH	Acros / 103524-894

butylamine	BuNH ₂	Alfa Aesar / L03575
carbon dioxide, industrial	CO ₂	Praxair / CD50S
ethanol	CH ₂ OH	Decon Labs / 2701
acetone	(CH ₃) ₂ CO	VWR / BDH1101
ethyl acetate	CH ₃ CO ₂ CH ₂ CH ₃	J.T. Baker / 9280-01
ethyl lactate	CH ₃ CHCO ₂ CH ₂ CH ₃	TCI / L0003

Synthetic Methods:

Tetrabutylammonium bromate, [Bu₄N]BrO₃ (1). Compound 1 is prepared in high yield (99%) from the reaction of tetrabutylammonium sulfate and barium bromate. In a typical preparation, 100 mL of DI H₂O in a 250 mL Erlenmeyer flask were added 0.9 g of Ba(BrO₃)₂ (2.29 mmol), and the mixture was stirred. To this was added 2.66 g of a 50% w/w tetrabutylammonium sulfate solution (2.29 mmol). The mixture instantly turned a milky white and was allowed to stir for 3 h and then allowed to stand for 20 h before filtering to remove the BaSO₄. Yield 1.66 g (99% yield). IR (cm⁻¹), ν = 2950 (vs), 2905 (vs), 2840 (vs), 2740 (w), 2100 (w, br), 1650 (s), 1480 (vs), 1385 (s) 1290 (w), 1250 (w), 1170 (m), 1100 (s) 1060 (s) 1020 (m), 880 (s), 800 (vs). m.p. 54 °C.

Tetrabutylammonium chlorate, [Bu₄N]ClO₃ (2). To 100 mL of DI H₂O in a 250 mL Erlenmeyer flask were added 0.76 g of Ba(ClO₃)₂ (2.29 mmol), and the mixture was stirred. To this was added 2.66 g of a 50% w/w tetrabutylammonium sulfate solution (2.29 mmol). The mixture instantly turned a milky white and was allowed to stir for 3 h and then allowed to stand for 20 h before filtering to remove the BaSO₄. The solution was then brought down to dryness *in vacuo*. Yield 0.73 g (98% yield). IR (cm⁻¹), ν = 2960 (m), 2935 (m), 2875 (m), 1476 (w), 1472 (w), 1381 (w), 1650 (s), 954 (vs), 930 (vs), 881 (m), 800 (w), 740 (m). m.p. 116-118 °C.

Bis(triphenylphosphine)iminium bromate, [PPN]BrO₃ (3). 4.0 g of NaBrO₃ (26.5 mmol) were dissolved in 30 mL of deionized H₂O in a 120 mL glass tube. To this solution was added 1.0 g [PPN]Cl (1.86 mmol) and the solution heated at 100 °C for 15 minutes without stirring. Over the course of this time, a liquid formed and collected at the bottom of the tube. Upon cooling, this material crystallized and was isolated by filtration. Recrystallization of this material in 15 mL DI H₂O yielded 0.88 g of [PPN]BrO₃ (71% yield). IR (cm⁻¹), ν = 3170 (w) 3150 (w) 3040 (s) 3010 (s), 2990 (s) 2700 (w) 2600 (w) 2230 (w) 2100 (w), 2080 (w), 2050 (w) 2000 (w), 1900 (w), 1830 (w), 1800 (w), 1780 (w) 1670 (w) 1600 (vs), 1480 (vs), 1420 (vs) 1300 (vs, br), 1190 (vs) 1100 (vs), 1020 (vs), 1000 (vs) 930 (w), 840 (vs), 790 (vs). m.p. 236-238 °C (dec.).

Bis(triphenylphosphine)iminium chlorate, [PPN]ClO₃ (4). 0.9 g of KClO₃ (7.43 mmol) were dissolved in 25 mL of deionized H₂O in a 120 mL glass tube. To this solution was added 1.0 g [PPN]Cl (1.86 mmol) and the solution heated at 100 °C for 20 minutes. Upon cooling, the solution precipitated a large amount of white solid which was the isolated by filtration. This solid was recrystallized in 15 mL DI H₂O yielding 0.96 g of [PPN]ClO₃ (83% yield). IR (cm⁻¹), ν = 3180 (w), 3150 (w), 3090 (s), 3060 (s), 3020 (m), 2990 (m), 2970 (w), 2700 (w), 2230 (w), 2080 (w), 1990 (w), 1900 (m), 1840 (w), 1780 (w), 1680 (w), 1590 (s), 1480 (vs), 1440 (vs), 1330 (vs), 1240 (vs), 1190 (vs), 1105 (vs), 1020 (vs), 970 (vs), 850 (m), 810 (vs). m.p. 237 °C (dec.).

Tributylammonium bromate, $[\text{Bu}_3\text{NH}]\text{BrO}_3$ (5). To 20 mL of DI H_2O in a 125 mL Erlenmeyer flask was added 0.5 ml (2.1 mmol) of tributylamine. To this mixture was added 57 μl of 98% H_2SO_4 (1.1 mmol) and the resulting mixture sonicated for 5 minutes. Separately, 0.42 g (1.1 mmol) of barium bromate were added to 80 mL of DI H_2O and sonicated for 5 minutes to encourage dissolution. Then, the tributylammonium sulfate solution was added to the barium bromate solution with rapidity. The resulting mixture was sonicated for 30 minutes and vacuum filtered twice to give a clear solution from which the water was removed under vacuum. The product is a colorless liquid at room temperature. IR (cm^{-1}), $\nu = 3430$ (m, br), 2960 (st), 2935 (m), 2873 (m), 1722 (vw), 1628 (m), 1460 (m), 1381 (w), 1066 (w), 786 (vs, sh), 768 (vs), 740 (s, sh).

Dibutylammonium bromate, $[\text{Bu}_2\text{NH}_2]\text{BrO}_3$ (6). To 20 mL of DI H_2O in a 125 mL Erlenmeyer flask was added 0.5 ml (3.3 mmol) of dibutylamine. To this mixture was added 88 μl of 98% H_2SO_4 (1.6 mmol) and the resulting mixture sonicated for 5 minutes. Separately, 0.64 g (1.6 mmol) of barium bromate were added to 80 mL of DI H_2O and sonicated for 5 minutes to encourage dissolution. Then, the dibutylammonium sulfate solution was added to the barium bromate solution with rapidity. The resulting mixture was sonicated for 30 minutes and vacuum filtered twice to give a clear solution from which the water was removed under vacuum. The product is a colorless liquid at room temperature. IR (cm^{-1}), $\nu = 3430$ (m, br), 2960 (st), 2935 (m), 2873 (m), 1722 (vw), 1628 (m), 1617 (m), 1460 (m), 1381 (w), 1066 (w), 915 (w), 780 (vs), 727 (vs). m.p. 4 °C.

Butylammonium bromate, $[\text{BuNH}_3]\text{BrO}_3$ (7). To 20 mL of DI H_2O in a 125 mL Erlenmeyer flask was added 0.33 ml (3.3 mmol) of butylamine. To this mixture was added 88 μl of 98% H_2SO_4 (1.6 mmol) and the resulting mixture sonicated for 5 minutes. Separately, 0.64 g (1.6 mmol) of barium bromate were added to 80 mL of DI H_2O and sonicated for 5 minutes to encourage dissolution. Then, the butylammonium sulfate solution was added to the barium bromate solution with rapidity. The resulting mixture was sonicated for 30 minutes and vacuum filtered twice to give a clear solution from which the water was removed under vacuum. Yield: 0.65 g (97%). IR (cm^{-1}), $\nu = 3041$ (st, br), 2960 (st), 2935 (m), 2875 (m), 1606 (m), 1600 (m), 1570 (s), 1174 (m), 1077 (m), 915 (m), 830 (s), 768 (vs), 757 (vs).

Tetramethylammonium bromate, $[\text{Me}_4\text{N}]\text{BrO}_3$ (8). To 100 mL of DI H_2O in a 250 mL Erlenmeyer flask was added 0.9 g of $\text{Ba}(\text{BrO}_3)_2$ (2.29 mmol), and the mixture was stirred. To this was added 0.559 g (2.29 mmol) tetramethylammonium sulfate dissolved in 5 mL DI water. The mixture instantly turned a milky white and was allowed to stir for 3 h and then allowed to stand for 20 h before filtering to remove the BaSO_4 . Yield 0.62 g (97% yield).

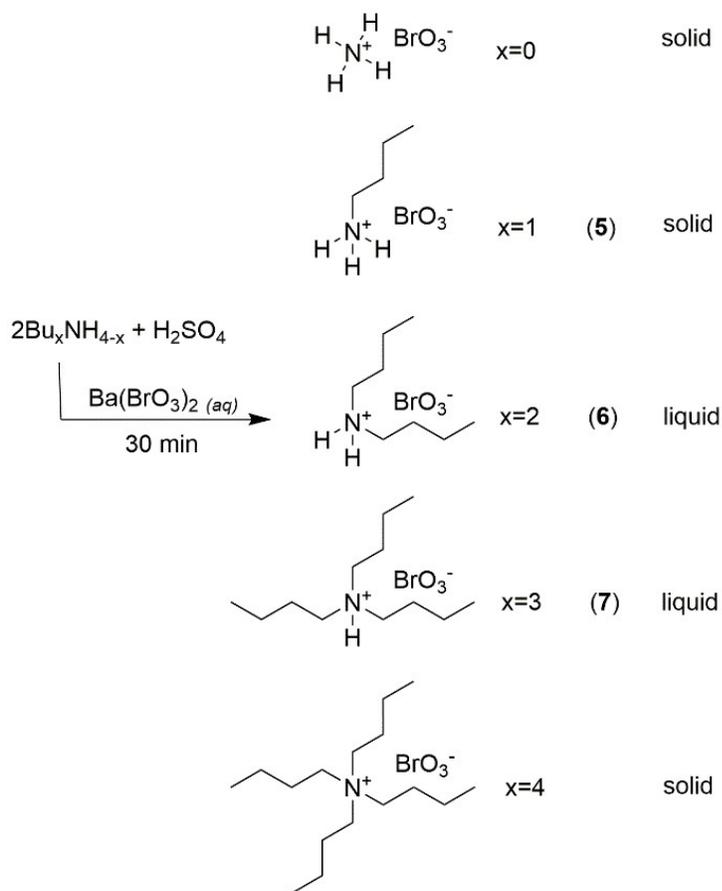
X-ray Diffraction:

An arbitrary sphere of data was collected on each crystal on either a Bruker PHOTON-II or Bruker APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [1]. Data were corrected for absorption and polarization effects [2] and analyzed for space group determination [1]. The structures were solved by dual-space methods and expanded routinely [3]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections [4]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent

isotropic displacement parameter of the atom to which they are bonded ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl, $1.2U_{\text{eq}}(\text{C})$ for all others). Disorder in the butyl chain and chlorine position in the anion for compound 4 was treated routinely, with locations for the minor component disorder atoms model on locations observed in difference Fourier maps. In the final model, the occupancies of the two components were summed to unity yielding ratios of 0.88:0.11 and 0.87:0.13 for the butyl chain and chlorine sites, respectively. The minor component atoms sites were modeled with isotropic displacement parameters. Modeling this disorder improved the overall structural model.

Table S2. Crystallographic data for 1-4.

	1	2	3	4
Formula	$\text{C}_{16}\text{H}_{38}\text{BrNO}_4$	$\text{C}_{16}\text{H}_{36}\text{ClNO}_3$	$\text{C}_{36}\text{H}_{30}\text{BrNO}_3\text{P}_2$	$\text{C}_{36}\text{H}_{30}\text{ClNO}_3\text{P}_2$
FW [g mol ⁻¹]	388.38	325.91	666.46	622.00
T [K]	120(2)	120(2)	120(2)	120(2)
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
<i>a</i> [Å]	9.8000(4)	12.0476(16)	9.4724(4)	9.4093(11)
<i>b</i> [Å]	12.7411(5)	24.535(3)	19.7442(9)	19.713(2)
<i>c</i> [Å]	16.7622(6)	14.501(2)	16.8171(7)	16.8064(19)
α [°]	90	90	90	90
β [°]	100.0239(13)	114.010(2)	103.8180(13)	103.680(4)
γ [°]	90	90	90	90
<i>V</i> [Å ³]	2061.03(14)	3915.4(9)	3054.2(2)	3028.9(6)
<i>Z</i>	4	8	4	4
ρ_{calc} [g cm ⁻³]	1.252	1.106	1.449	1.364
μ [mm ⁻¹]	2.010	0.205	1.489	0.270
<i>F</i> (000)	832	1440	1368	1296
Color / Habit	colorless, block	colorless, block	colorless, block	colorless, tablet
Size [mm]	0.343 × 0.159 × 0.134	0.251 × 0.241 × 0.145	0.281 × 0.092 × 0.078	0.221 × 0.194 × 0.054
θ Min-Max [°]	2.019 - 28.273	1.660 - 28.349	1.618 - 28.213	1.619 - 28.319
Dataset	-13:13; -16:16; -22:22	-16:16; -32:32; -19:19	-12:12; -26:26; -22:22	-12:12; -26:25; -22:22
Reflections collected	40837	75236	61375	60453
Independent reflections	5101 [$R_{\text{int}} = 0.0380$]	9754 [$R_{\text{int}} = 0.0341$]	7529 [$R_{\text{int}} = 0.0456$]	7533 [$R_{\text{int}} = 0.0544$]
Completeness to $\theta = 25.242^\circ$	100.0%	100.0%	100.0%	100.0%
Absorption correction	Numerical	Numerical	Numerical	Numerical
Max and min transmission	1.0000 and 0.6902	0.7844 and 0.7012	0.9871 and 0.7891	1.0000 and 0.9372
Data / restraints / parameters	5101 / 0 / 211	9754 / 0 / 443	7529 / 0 / 388	7533 / 0 / 388
Goof	1.026	1.025	1.049	1.109
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0244$, $wR_2 = 0.0538$	$R_1 = 0.0447$, $wR_2 = 0.1113$	$R_1 = 0.0307$, $wR_2 = 0.0663$	$R_1 = 0.0486$, $wR_2 = 0.1078$
R indices (all data)	$R_1 = 0.0325$, $wR_2 = 0.0571$	$R_1 = 0.0602$, $wR_2 = 0.1210$	$R_1 = 0.0393$, $wR_2 = 0.0701$	$R_1 = 0.0604$, $wR_2 = 0.1130$
Extinction coefficient	n/a	n/a	n/a	n/a
Largest diff. peak, hole [$e^- \text{Å}^{-3}$]	0.320, -0.256	0.703, -0.368	0.449, -0.447	0.532, -0.404
CCDC	2039678	2039679	2039680	2039681



Scheme S2. Synthesis of butylammonium bromates series.

Thermogravimetric Analysis:

[PPN]BrO₃ and [PPN]ClO₃ were stable while heating to 238 °C and 279 °C, respectively, where an abrupt ~14% mass loss was accompanied by a strong exotherm for each. The spectra are shown in Figures S2 and S3. The resultant products were stable upon further heating to ~350 °C, where further decomposition initiated and continued until approximately 70% additional mass loss occurred. Final masses for each were in the range of 10-15% after heating to 1000 °C. The exotherms suggest the oxidation of PPN's nitrogen atom to NO_x and concomitant gas evolution. Given the anaerobic conditions, it is unlikely that triphenylphosphine oxide forms during this exothermic reaction, particularly since evaporation is not observed at its melting point of 360 °C. Triphenylphosphonium bromide/chloride formation is also ruled out as it can be thermolyzed at relatively low temperature in refluxing xylene (140 °C).⁶² While heating [PPN]BrO₃ in a capillary tube in the melting point apparatus, an orange color is observed just before reaching 240 °C, suggesting formation of bromine as the bromate reacts and is reduced.

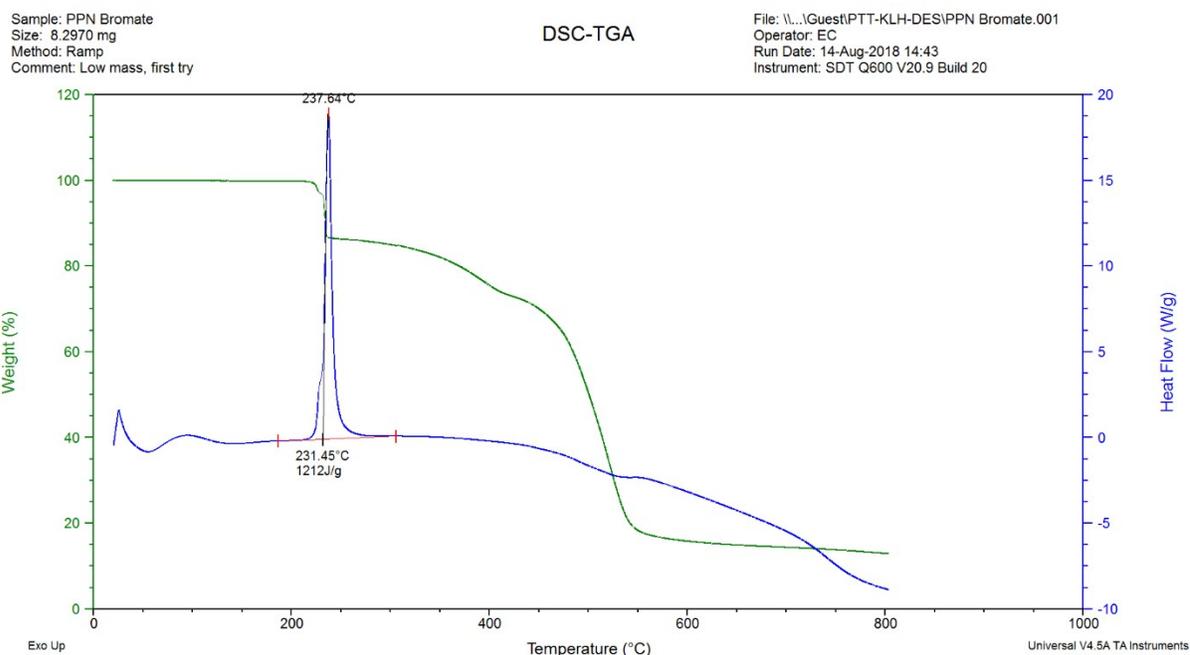


Figure S2. TGA of [PPN]BrO₃

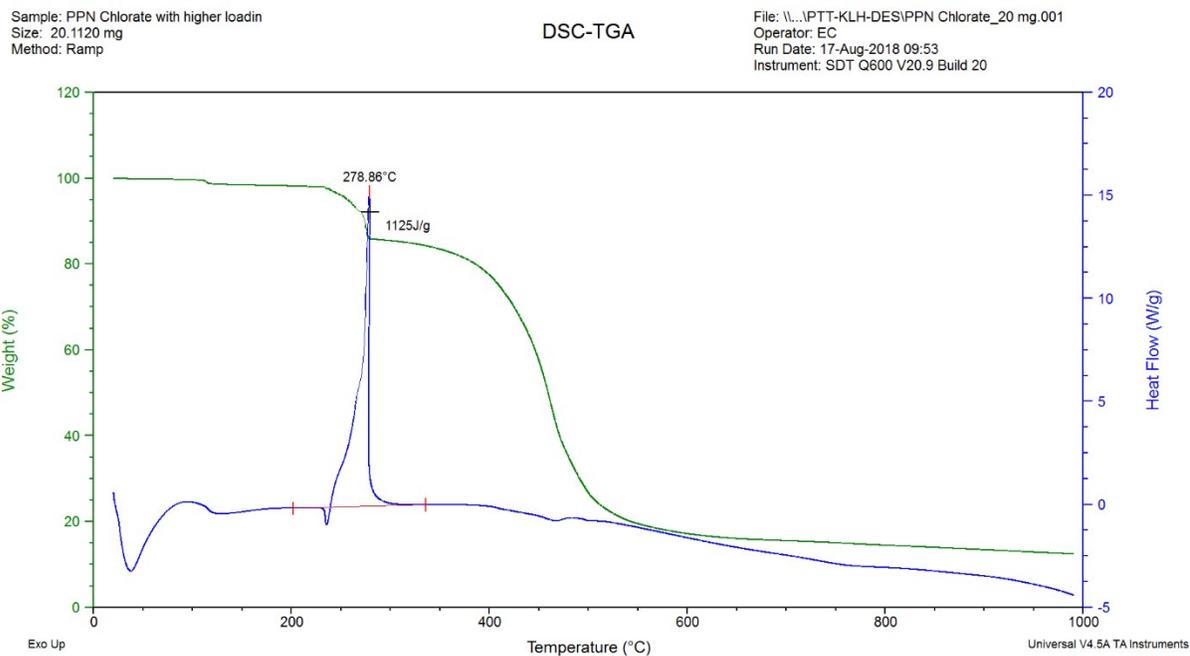


Figure S3. TGA of [PPN]ClO₃

Table S3. Melting points of [Bu₄N]X salts.

Anion, X	m.p. (°C)
BrO ₃ ⁻	54
F ⁻	58-60
Cl ⁻	83-86
Br ⁻	103
ClO ₃ ⁻	116-118
I ⁻	141-143
H ₂ PO ₄ ⁻	151-154
HSO ₄ ⁻	168-172
PF ₆ ⁻	244-246

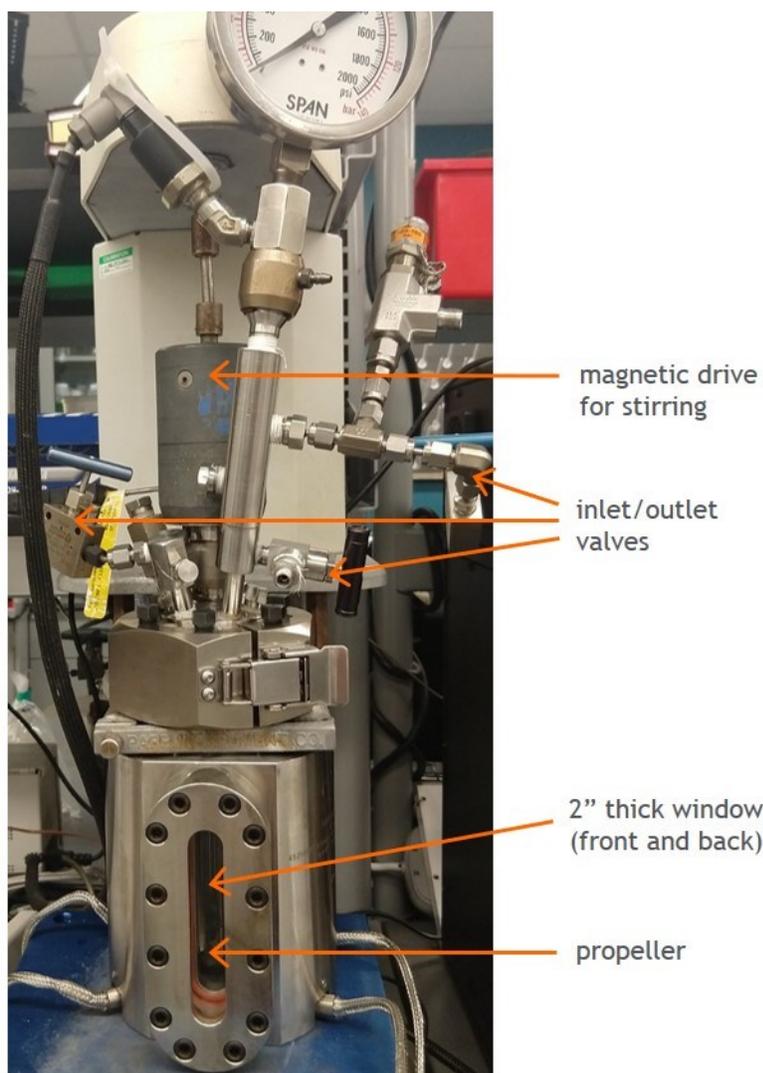


Figure S4. Parr reactor with see-through windows. The autoclave is equipped with Hastelloy wetted parts and can be operated up to 1900 psi and 200 °C.

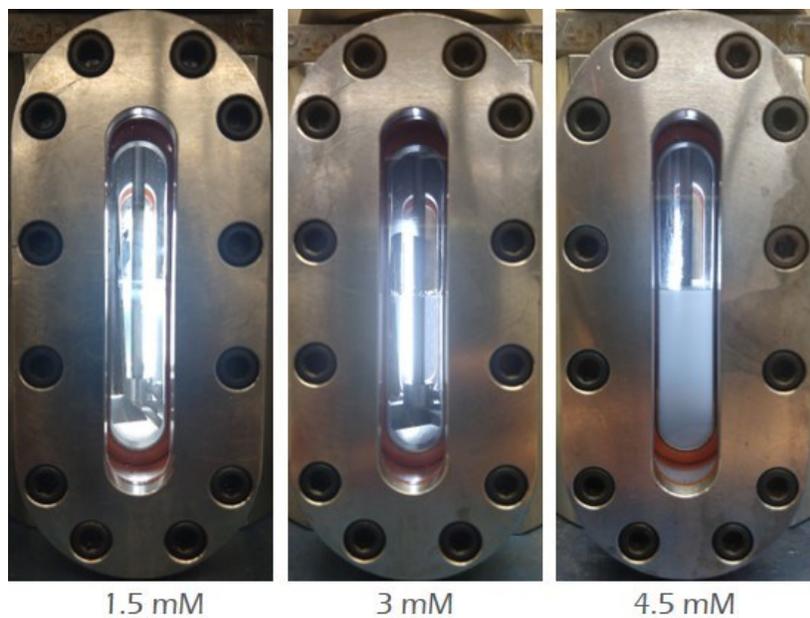


Figure S5. Solubility tests of varying concentrations of $[\text{Bu}_4\text{N}]\text{BrO}_3$ in CO_2 modified with 4 mol% ethanol.

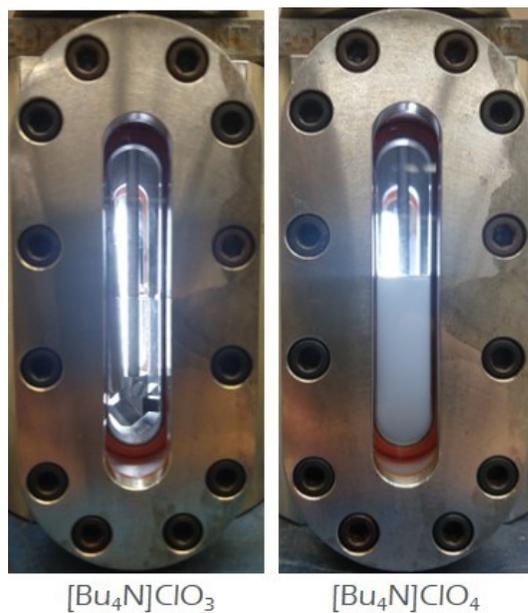


Figure S6. Solubility tests of 0.75 mM $[\text{Bu}_4\text{N}]\text{ClO}_3$ and 0.75 mM $[\text{Bu}_4\text{N}]\text{ClO}_4$ in CO_2 modified with 4 mol% ethanol.

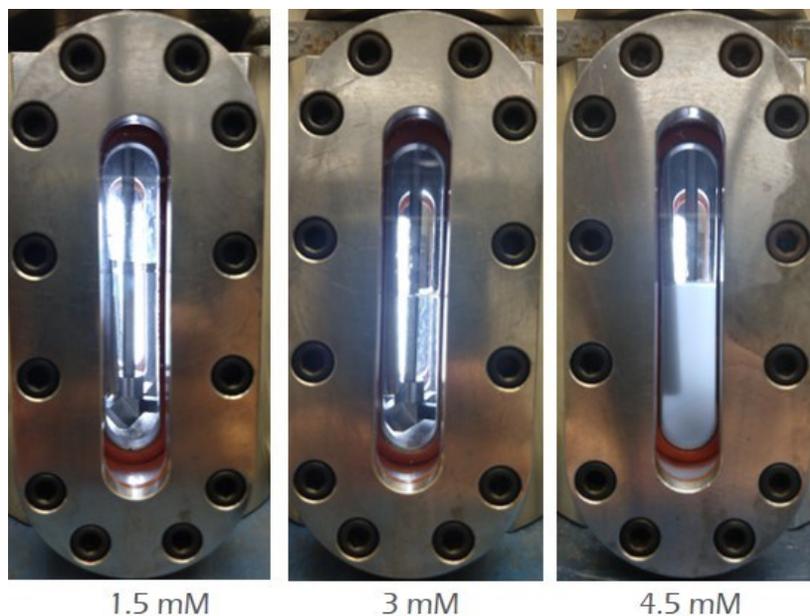


Figure S7. Solubility tests of varying concentrations of $[\text{Bu}_4\text{N}]\text{Cl}$ in CO_2 modified with 4 mol% ethanol.

References:

- [1] *APEX-3*. Bruker AXS. Madison, Wisconsin, USA. **2016**.
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- [3] G. M. Sheldrick. *Acta Crystallogr.*, **2015**, A71, 3.
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- [5] R. Salmasi, A. Salimi, M. Gholizadeh, M. Rahmani and J. C. Garrison, Symmetric quaternary phosphonium cation and perchlorate/chlorate anions: Crystal structure, Database study and Hirshfeld surface analysis, *J. Mol. Str.*, 2019, **1179**, 549–557.
- [6] R. P. Sharma, R. Bala, R. Sharma and V. Ferretti, Binding of inorganic oxo-anions to cationic cobaltamine: Synthesis, characterization, X-ray structures determination and DFT calculations of $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{ClO}_3)$, $[\text{Co}(\text{NH}_3)_6]\text{Br}_2(\text{ClO}_3)$ and $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2(\text{IO}_3)\cdot\text{H}_2\text{O}$, *Inorg. Chim. Acta*, 2005, **358**, 3457–3464.