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Iodine-Rich Imidazolium Iodate and Periodate Salts: En Route to Single-Based Biocidal Agents

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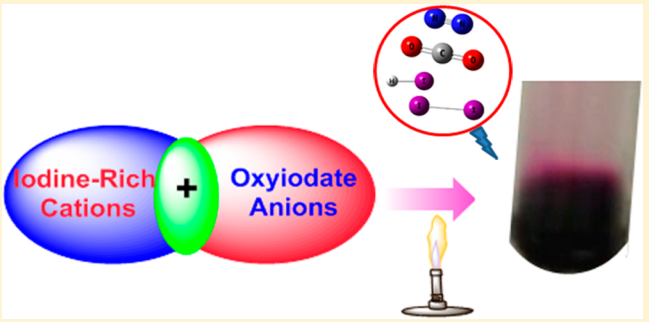
Supporting Information

ABSTRACT: Two classes of iodine-rich salts that consist of iodine-rich cations and iodate (IO_3^-) or periodate (IO_4^-) anions were synthesized. The synthesis of analogous $I_3O_8^-$ salts was more difficult because of poor solubility and hydrolytic instability. All iodine-rich salts were fully characterized by infrared, ^1H nuclear magnetic resonance, and ^{13}C nuclear magnetic resonance spectroscopy as well as elemental analyses. The molecular structures of compounds **15** and **24** were elucidated by X-ray single-crystal diffraction. Additionally, the heats of formation were calculated with Gaussian 03. The detonation properties and biocidal efficiency were calculated and evaluated using CHEETAH 7.



INTRODUCTION

To defeat a biological weapon effectively, it is necessary not only to eliminate the weapon of mass destruction (WMD) in the target but also to ensure that there are no viable biological agents in the plume that may cause collateral damage when released upon destruction of the target. The explosion of conventional warheads generates transient thermal effects that have a limited destructive impact on biological agents, and the blast could also have the undesirable effect of airborne dispersal of those biological agents. Therefore, in recent years, agent defeat weapons (ADWs) were developed to destroy or neutralize the active agents in the plume by releasing large amounts of strong biocides upon detonation.[1] Iodine is an effective biocide; the destruction of certain bacteria, amoebic cysts, and viruses (a 99.999% kill in 10 min at 25 °C) may require I_2 residuals of 0.2, 3.5, and 14.6 ppm, respectively.[2]

However, because of the ready sublimation of iodine, it is not practical to use the element itself as an ingredient in ADWs. Iodine-rich compounds in which the iodine exists in the form of C−I, iodide, or iodate exhibit relatively better stability and, therefore, could be used as potential ingredients for ADWs. Over the past few years, iodine-rich salts such as $[NH_4]^+[IF_2O_2]^-$, $[C(NH_2)_3]^+[IF_2O_2]^-$,[3] and tris[2-(*N*,*N*,*N*-trimethylammonium)ethyl]amine tripentaiodide[4] or molecular species such as 4,5-diiodo-1*H*-1,2,3-triazole,[5] tetraiodofuran,[6] and 1-diiodomethyl-3,4,5-triodopyrazole[7] were developed as potential ingredient candidates for ADWs (Figure 1). They are materials that produce nearly quantitative amounts of gaseous iodine (I_2) upon decomposition when formulated with oxidizers such as I_2O_5, HI_3O_8, HIO_3, and other components, but I_2O_5 and HI_3O_8 are hygroscopic and sensitive to moisture, making them readily hydrolyzable forming HIO_3 even under low-humidity conditions.[8]

Because energetic salts have the advantage of no or low vapor pressure, high thermal stability, and density and cations act as fuels while anions play a role as oxidizers in most cases,[9] the combination of an iodine-rich cation with IO_3^-, IO_4^-, or $I_3O_8^-$ as an anion in a prospective biocide should ensure a high iodine content and improve the oxygen balance, as well. This type of iodine-rich salt would provide an oxygen balance that approaches zero; therefore, these materials upon decomposition may find application as single-based biocidal agents.

We now describe a series of compounds comprised of an iodine-rich imidazolium cation and an iodate or periodate anion whose structures have been fully determined and whose properties have been investigated. Our efforts to synthesize iodine-rich imidazolium $I_3O_8^-$ compounds failed because of the poor solubility of $I_3O_8^-$ in organic solvents as well as their hydrolytic sensitivity.

RESULTS AND DISCUSSION

Synthesis. Imidazolium cations have been studied extensively in the field of ionic liquids.[10] They can be prepared readily by the reaction of an *N*-alkylimidazole with alkyl halide. To achieve a high iodine content and good oxygen balance, our first attempt was to prepare the 1,3-dimethyl-2,4,5-triiodoimidazolium cation by reacting 1-methyl-2,4,5-triiodoimidazole[5] with iodomethane. However, a mixture of compounds **2** and **3** (4:1 ratio) was obtained on the basis of proton nuclear magnetic resonance (NMR) integration (Scheme 1) probably

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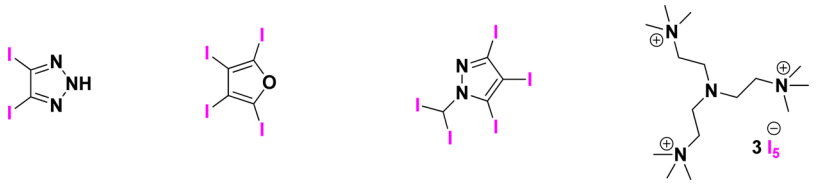
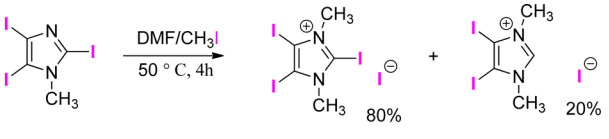


Figure 1. Promising iodine-rich ADW ingredients.

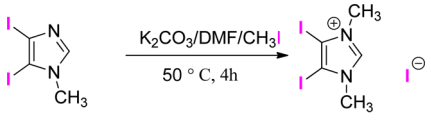
Scheme 1. Quaternization of 1



1 2 3

because of the electron donating effect of the methyl groups that cause the C−I in position 2 to be a very good leaving group. When 1-methyl-4,5-diiodoimidazole was used as the starting material, the reaction with iodomethane under similar reaction conditions gives **3** as a single product in good purity (Scheme 2).

Scheme 2. Synthesis of Compound 3



3

The introduction of methylene and ethylene bridges has the advantage of improving the thermal stability;[11] therefore, methylene- and ethylene-bridged 4,5-diioimidazole cations (**6** and **7**, respectively) were prepared by reacting 4,5-diiodoimidazole with KOH and diiodomethane or 1,2-dibromoethane in DMF in the presence of tetraethylammonium bromide as a phase transfer catalyst, followed by the reaction with iodomethane (Scheme 3).

To improve the energy content, cations containing one or two N-NH_2 groups (**9** and **12**, respectively) were prepared on the basis of a procedure similar to that described in the literature.[12] 1-Methyl-4,5-diiodoimidazole or 1-amino-4,5-diiodoimidazole in acetonitrile was treated with freshly prepared *O*-tosylhydroxylamine in dichloromethane to precipitate the corresponding tosylate salt. The tosylate salt reacts with a stoichiometric amount of aqueous hydrobromic acid, resulting in the bromide salt (Schemes 4 and 5). The amination of compounds **4** and **5** failed because of their poor solubility in acetonitrile, which precluded the reaction with *O*-tosylhydroxylamine.

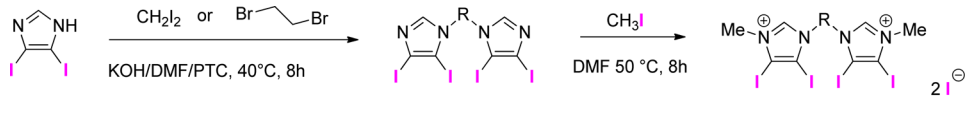
Silver iodate, $AgIO_3$, or silver periodate, $AgIO_4$, was readily prepared by treating $NaIO_3$ or $NaIO_4$, respectively, with $AgNO_3$ in aqueous solution; AgI_3O_8 was prepared according to the literature method.[13] With the pure iodine-rich imidazolium iodide or bromide and $AgIO_3$ or $AgIO_4$ materials available, the iodine-rich salts (**14**−**23**) were easily prepared via metathesis reactions of the corresponding iodide or bromide compounds with $AgIO_3$ or $AgIO_4$ in aqueous solution at 50 °C for 1 h. The solid AgI was removed by filtration, and the water in the filtrate was removed under vacuum to produce the desired compounds (Scheme 6). To prepare compound **13**, a mixture of compounds **13** and **14** was obtained initially by reacting the mixture of **2** and **3** with $AgIO_3$. The mixed products were washed with water to leave a solid residue that was found to be pure **13** in low yield (32.4%). The reaction of **9** with AgI_3O_8 in water results in compound **24** as a hydrolysis product; its structure was confirmed by X-ray single-crystal diffraction (Figure S4).

Spectroscopy. All NMR spectra were recorded in dimethyl sulfoxide-d_6 (DMSO-d_6). NMR data for compounds **13** and **21** could not be obtained because of their poor solubility in DMSO. Compounds with the same cation exhibit almost the same chemical shifts in the spectra. In the ^{1}H NMR spectra for the imidazole ring, CH is found at δ 9.42−9.92 (s), the amino group at δ 6.73−6.79 (s), and the methyl group at 3.79−3.92 (s). In the ^{13}C NMR spectra, the resonance for CH appears at δ ∼142 (s) and the chemical shift for C−I is at δ ∼95.

X-ray Crystallography. Suitable crystals of **15** for single-crystal X-ray diffraction were grown from water; three water molecules of crystallization are present in the crystal structure (Figure 2). The crystallographic data and refinement details as well as the packing diagrams are listed in the Supporting Information. The torsion angles [I1−C3−C4−N1 = −178.6(3)°, N2−C3−C4−I2 = 174.5(3)°, C5−N3−C7−I3 = −179.2(3)°, and I4− C6−C7−N3 = −173.2(3)°] show that the C−I bond is almost planar with the imidazole ring. The O4 atom in an anion forms two hydrogen bonds with the CH moieties in each of the two imidazole rings as shown in Figure 2.

Physicochemical Properties. The thermal behavior of compounds **13**−**23** was investigated by performing differential scanning calorimeter scans at a heating rate of 5 °C/min. Densities were obtained at 25 °C using a gas pycnometer. All compounds decompose without melting in the range from 92.3 °C (**20**) to 187.0 °C (**14**). Densities range between 2.86 g cm^{-3} (**21**) and 3.20 g cm^{-3} (**18**). The replacement of a methyl group with an amino group leads to an increase in density. The IO_4

Scheme 3. Preparation and Quaternization of Methylene- and Ethylene-Bridged 4,5-Diiodoimidazoles



4: -CH_2-
5: -CH_2-CH_2-

6: -CH_2-
7: -CH_2-CH_2-

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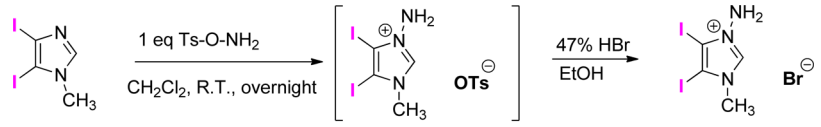
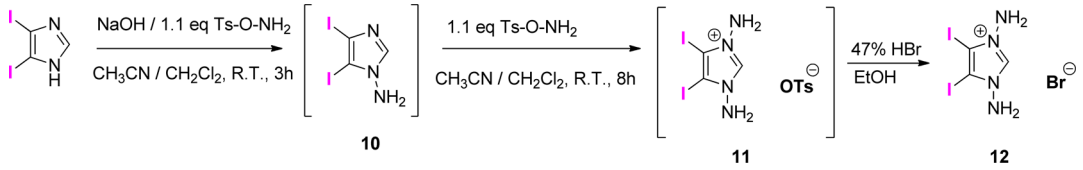
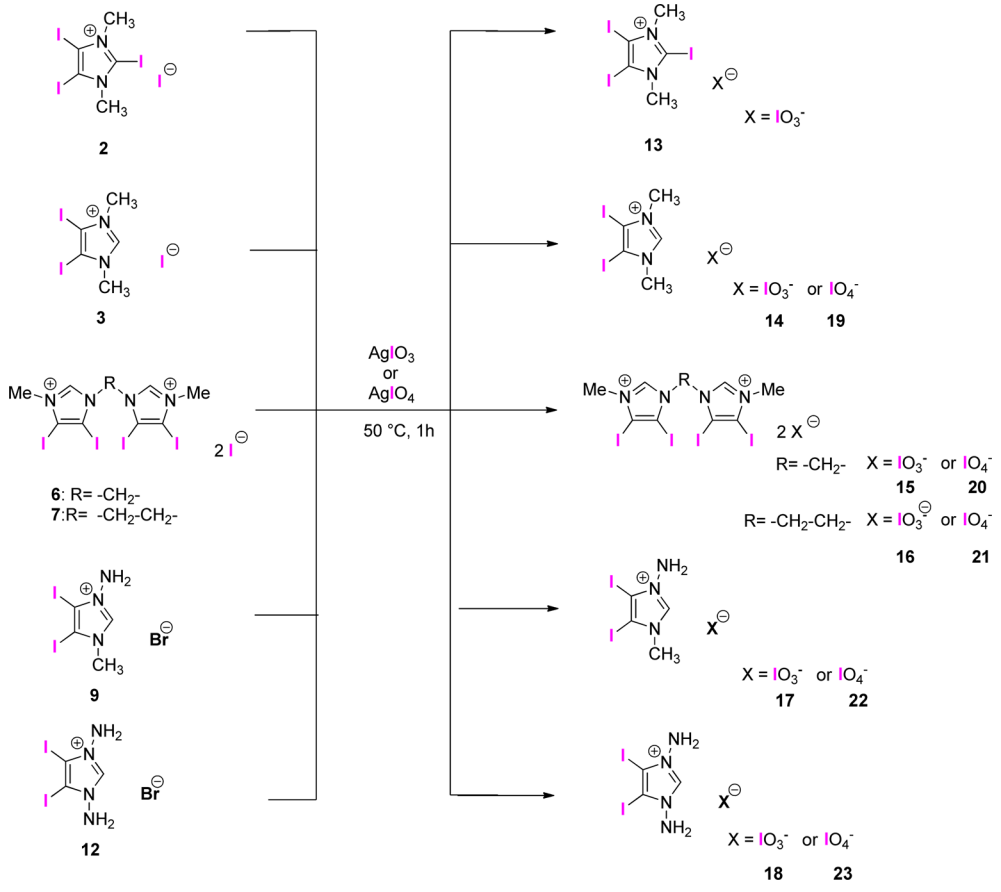
Scheme 4. Preparation of 1-Amino-3-methyl-4,5-diiodoimidazolium Bromide (9)



Scheme 5. Synthesis of 1,3-Diamino-4,5-diiodoimidazolium Bromide (12)



Scheme 6. Preparation of Salts with IO_3^- or IO_4^- Anions via Metathesis Reactions



anion-containing compounds are slightly less dense than their IO_3 analogues.

The heats of formation of all the compounds were calculated using the Gaussian 03 (revision E.01) suite by isodesmic reactions.[14] For iodine-rich cations, the (15s, 11p, 6d) basis of Stromberg et al.[15] was augmented with another p shell and the five valence sp exponents were optimized, resulting in a [5211111111, 411111111, 3111] contraction scheme in conjunction with 6-31+G** for first- and second-row elements. Single-point energy (SPE) refinement on the optimized geometries was performed with the use of the MP2/6-311++G** level. The heats of formation for the IO_3^- and IO_4^- anions were obtained by using the G2ECP (ZPE=MP2) method. The heats of formation for the salts were calculated by employing the Born−Haber cycle. Heats of formation for compounds **13**−**23** are in the range from −1412.3 kJ mol^{-1} (**21**) to −24.7 kJ mol^{-1} (**18**). The presence of additional amino groups in the molecules results in higher heats of formation.

The composition of the decomposition products for the iodine-rich compounds is an important parameter in evaluating their ability to destroy or neutralize an active agent. The higher the iodine (I_2) concentration in the products generated, the more efficient the compound is as a biocide. The decomposition products were predicted using CHEETAH 7 under Chapman−Jouguet conditions. The products were converted to standard atmospheric conditions at 298 K and 1 atm (Table 1). As shown in Figure 3, most of the compounds release more than 70 wt % of I_2 upon decomposition. Compound **13** exhibits

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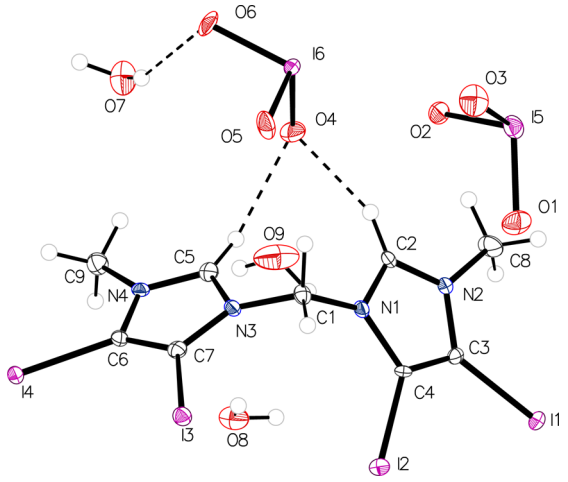

Figure 2. Crystal structure of **15**·3H_2O.

Table 1. Predicted Major Decomposition Products with CHEETAH 7

compd	N_2(g)	I_2(g)	HI(g)	C(s)	CH_4(g)	CO_2(g)
13	4.31	77.14	0.10	3.73	3.67	10.14
14	5.35	71.59	1.10	4.05	5.32	12.58
15	5.43	72.81	1.00	4.11	3.85	12.78
16	5.36	71.78	1.05	4.63	4.56	12.60
17	8.01	71.48	1.07	2.33	4.54	12.56
18	10.66	71.38	1.03	0.60	3.77	12.53
19	5.19	69.44	1.09	2.82	5.16	16.28
20	5.27	70.60	1.00	2.86	3.73	16.53
21	5.20	69.62	1.04	3.38	4.42	16.31
22	7.77	69.35	1.06	1.15	4.41	16.25
23	10.34	67.76	2.52	0	3.29	15.34

the best biocidal capability. The IO_3^--containing compounds show biocidal activity that is more promising than that of the corresponding IO_4^--containing compounds upon decomposition.

Detonation velocities and pressures were calculated with the CHEETAH 7 code. All of the iodine-rich iodate and periodate salts exhibit low detonation properties (Table 2). Compound **18** possesses the best detonation properties (D = 4558 m s^{-1}; P = 13.79 GPa) among the new iodo compounds. The impact sensitivities are found to be in the range of 3−6 J, which is comparable with that of the IO_2-substituted compounds we reported previously.[5] While improved iodine content for compounds **13**−**23** ranging from 70.3 to 78.1% was observed, the oxygen balances are from −4.4 to −16.8%; their high iodine content and good oxygen balance give rise to good candidates for use as single-based biocidal agents.

CONCLUSIONS

In conclusion, a series of compounds consisting of iodine-rich imidazolium cations and IO_3^- or IO_4^- anions were prepared and fully characterized. The structure of compound **15** was determined by single-crystal X-ray diffraction. All of the compounds have high densities, high iodine contents, desirable detonation properties, and acceptable oxygen balances that make them good candidates as single-based biocidal agents. To achieve desirable impact sensitivities, the treatment with coating agents will be needed for their future applications.

EXPERIMENTAL SECTION

Caution: *All of the oxyiodate salts presented in this paper are sensitive to impact and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and handling them.*

General Methods. Reagents were purchased from Aldrich and Acros Organics and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively. DMSO-d_6 was used as a solvent and locking solvent. Chemical shifts in the ^{13}C spectra are reported relative to Me_4Si. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q20) at a heating rate of 5 °C/min. IR spectra were recorded using KBr pellets for solids on a Bio-Rad model 3000 FTS spectrometer. Densities were determined at 25 °C by employing a Micromeritics AccuPyc 1330 gas pycnometer. Elemental analyses were conducted using an Exeter

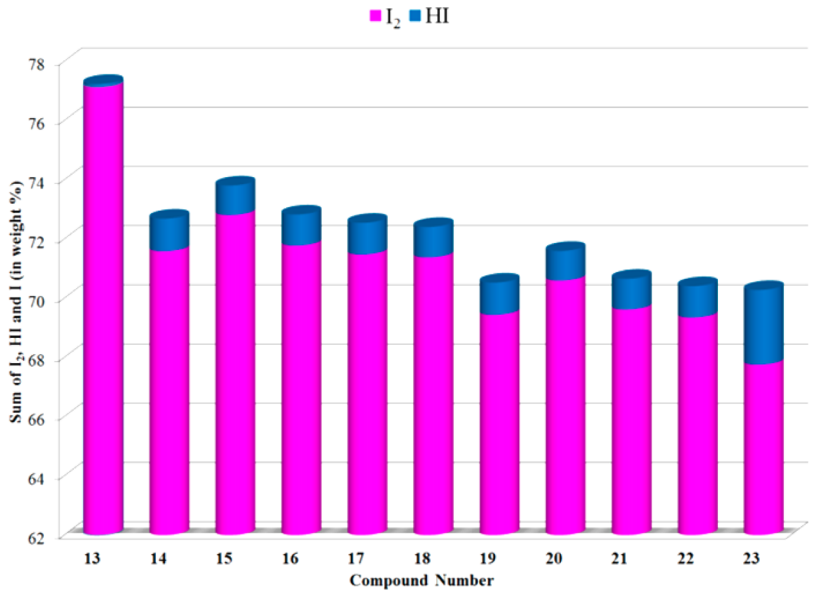

Figure 3. Sum of I_2 and HI in the decomposition products (weight percent).

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Table 2. Physicochemical Properties of Compounds 13−23

compd	T_d[a] (°C)	d[b] (g/cm^3)	$\Delta H_f°$[c] (kJ/mol)	D[d] (m/s)	P[e] (Gpa)	% iodine	OB[f] (%)	IS[g] (J)
13	177.4	3.17	−232.3	3173	6.0	78.1	−12	5
14	187.0	2.96	−300.1	3532	7.0	72.7	−17	6
15	124.7	2.96	−704.0	3166	5.4	73.8	−12	6
16	164.0	2.93	−749.8	3199	5.4	72.8	−15	6
17	148.4	3.12	−164.6	4132	10.4	72.5	−12	4
18	149.0	3.20	−24.7	4558	13.8	72.4	−8	4
19	130.4	2.92	−634.8	3383	5.8	70.5	−13	4
20	92.3	2.91	−1378.2	2958	4.2	71.6	−9	5
21	109.8	2.86	−1412.3	2959	4.1	70.6	−12	5
22	130.5	2.98	−495.4	3877	8.4	70.4	−9	3
23	143.1	3.03	−354.4	3433	11.1	70.3	−4	3
TNT	295	1.65	−31.7	6881	19.5	0	−25	15

[a]Decomposition temperature (onset). [b]Measured density at 25 °C. [c]Calculated heat of formation. [d]Detonation velocity calculated with CHEETAH 7. [e]Detonation pressure calculated with CHEETAH 7. [f]Oxygen balance for $C_aH_bO_cN_dI_e$: OB = $1600(c - b/2 - a)$/MW. [g]Impact sensitivity measured via the BAM method.

CE-440 elemental analyzer. Impact sensitivity measurements were taken using a standard BAM Fallhammer.

Iodination of 1-Methyl-2,4,5-triiodoimidazole. To a solution of 1-methyl-2,4,5-triiodoimidazole (0.92 g, 2 mmol) in DMF (5 mL) was added iodomethane (0.34 g, 2.4 mmol) dropwise. The mixture was stirred at 50 °C for 4 h. The solid formed was collected by filtration and washed with ethanol (3 × 5 mL) and then cold water (5 mL), resulting in a mixture of compounds **2** and **3** (0.81 g). Because they are poorly soluble in organic solvents, separation was not possible. The **2**:**3** ratio was 4:1 on the basis of proton NMR integration.

1,3-Dimethyl-4,5-imidazolium Iodide (3). Pure **3** was prepared as follows. To a suspension of 4,5-diiodoimidazole (0.96 g, 3 mmol) and potassium carbonate (0.56 g, 4 mmol) in DMF (10 mL) was slowly added iodomethane (1.28 g, 9 mmol). The reaction mixture was stirred at 50 °C overnight. The precipitate was filtered and washed with ethanol (3 × 5 mL) and diethyl ether (5 mL). Yield: 0.89 g, 62.4%. T_{dec}: 252.4 °C. IR: ν = 3106, 3018, 2939, 1652, 1553, 1489, 1433, 1235, 1204, 1192, 1166, 1101, 1084, 942, 829, 800, 771, 698, 655, 611 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.42 (1H, s, CH), 3.83 (6H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 38.82, 94.03, 140.75. Elemental analysis of $C_5H_7I_3N_2$ (475.83). Calcd: C, 12.62; H, 1.48; N, 5.89. Found: C, 12.66; H, 1.27; N, 5.72.

Bis(4,5-diiodo-1*H*-imidazol-1-yl)methane (4). A mixture of 4,5-diiodoimidazole (1.6 g, 5 mmol) and potassium hydroxide (0.28 g, 5 mmol) in DMF (4 mL) was stirred at room temperature for 30 min. Tetraethylammonium bromide (TEAB) (0.12 g) was added, followed by diiodomethane (0.67 g, 2.5 mmol). The reaction mixture was heated for 10 h at 50 °C, cooled to room temperature, and poured into cold water (10 mL). The resulting precipitate was collected by filtration and washed with water (3 × 5 mL) and ethanol (3 × 3 mL). Air drying gave a pale yellow solid. Yield: 1.42 g, 87.4%. T_{dec}: 252.4 °C. IR: ν = 3101, 1629, 1483, 1443, 1391, 1347, 1311, 1225, 1153, 1072, 977, 937, 814, 775, 752, 652, 610, 440 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 8.07 (2H, s, CH), 6.24 (2H, s, CH_2). ^{13}C NMR (DMSO-d_6): δ 59.8, 84.2, 98.6, 143.4. Elemental analysis of $C_7H_4I_4N_4$ (651.75). Calcd: C, 12.90; H, 0.62; N, 8.60. Found: C, 12.92; H, 0.59; N, 8.40.

Bis(4,5-diiodo-1*H*-imidazol-1-yl)ethane (5). A method similar to that for **4** was used. Yield: 1.42 g, 85.3%. T_{dec}: 285.4 °C. IR: ν = 3101, 2959, 2778, 1639, 1541, 1479, 1470, 1425, 1375, 1285, 1270, 1229, 1203, 1179, 1163, 1142, 1074, 955, 937, 878, 818, 654, 617, 563, 446 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 7.62 (2H, s, CH), 4.34 (4H, s, CH_2CH_2). ^{13}C NMR (DMSO-d_6): δ 48.8, 85.8, 96.5, 141.9. Elemental analysis of $C_8H_6I_4N_4$ (665.78). Calcd: C, 14.43; H, 0.91; N, 8.42. Found: C, 14.60; H, 0.92; N, 8.19.

1,1′-Methylenebis(4,5-diiodo-3-methyl-1*H*-imidazolium) Diiodide (6). To a 50 mL round bottom flask containing bis(4,5-diiodo-1*H*-imidazol-1-yl)methane (0.65g, 1 mmol) suspended in DMF (2 mL) was added iodomethane (0.42 g, 3 mmol). The flask was sealed with a stopper and then heated slowly to 50 °C overnight. After cooling to room temperature, the solid was collected by filtration, washed with methanol (3 × 3 mL), and air-dried. Yield: 0.73 g, 76.8%. T_{dec}: 255.6 °C. IR: ν = 3026, 2984, 2927, 1655, 1546, 1499, 1437, 1391, 1359, 1309, 1182, 1094, 1043, 826, 792, 689, 629, 604, 490 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.65 (2H, s, CH), 6.56 (2H, s, CH_2), 3.91 (6H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 63.94, 94.0, 97.1, 142.1. Elemental analysis of $C_9H_{10}I_6N_4$ (935.63). Calcd: C, 11.55; H, 1.08; N, 5.99. Found: C, 11.55; H, 1.20; N, 5.99.

1,1′-Ethylenebis(4,5-diiodo-3-methyl-1*H*-imidazolium) Diiodide (7). A method similar to that for **6** was used. Yield: 0.68 g, 71.6%. T_{dec}: 266.2 °C. IR: ν = 3126, 3077, 3006, 2889, 2082, 1653, 1553, 1532, 1503, 1438, 1390, 1361, 1324, 1297, 1195, 1180, 1151, 1102, 1070, 943, 769, 614 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.68 (2H, s, CH), 4.63 (4H, s, CH_2CH_2), 3.86 (6H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 39.45, 50.96, 95.84, 141.04. Elemental analysis of $C_{10}H_{12}I_6N_4$ (949.65). Calcd: C, 12.65; H, 1.27; N, 5.90. Found: C, 12.86; H, 1.24; N, 5.89.

1-Methyl-3-amino-4,5-diiodoimidazolium Bromide (9). To a solution of 1-methyl-4,5-diiodoimiazole (0.67 g, 2 mmol) in acetonitrile (8 mL) was added freshly prepared *O*-tosylhydroxylamine (2.2 mmol) in dichloromethane (10 mL) while the mixture was being stirred at room temperature. Stirring was continued for 8 h. The precipitate was filtered, air-dried, and then dissolved in a minimal amount of ethanol. Hydrobromic acid (47%, 0.40 g) was added. After the mixture had been stirred for 30 min, diethyl ether (60 mL) was added. The resulting solid was filtered and air-dried to yield 0.45 g (52.3%) of **9**. T_{dec}: 221.0 °C. IR: ν = 3265, 3184, 3102, 3052, 1610, 1538, 1499, 1432, 1395, 1192, 1174, 1115, 1106, 1083, 995, 806, 778, 606, 536 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.46 (1H, s, CH), 6.78 (2H, s, -NH_2), 3.79 (3H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 57.35, 93.90, 99.41, 141.21. Elemental analysis of $C_4H_6BrI_2N_3$ (429.82). Calcd: C, 11.18; H, 1.41; N, 9.78. Found: C, 11.68; H, 1.30; N, 9.60.

1,3-Diamino-4,5-diiodoimidazolium Bromide (12). To sodium hydroxide (0.08 g, 2 mmol) in acetonitrile (8 mL) was added 4,5-diiodoimidazole (0.64 g, 2 mmol). The mixture was stirred for 30 min at room temperature, and freshly prepared *O*-tosylhydroxylamine (2.2 mmol) in dichloromethane (8 mL) was added slowly. The mixture was stirred for 3 h at room temperature, followed by adding a second equivalent of *O*-tosylhydroxylamine (2.2 mmol) in dichloromethane (8 mL). The mixture was stirred for 8 h. The resulting solid was filtered, air-dried, and then dissolved in a minimal amount of ethanol, followed by the addition of hydrobromic acid (47%, 0.40 g). After the mixture had been stirred for 30 min, diethyl ether (60 mL) was added, and the formed solid was filtered and air-dried to yield 0.25 g (35.2%) of **12**. T_{dec}: 199.7 °C. IR: ν = 3249, 3111, 3064, 3004, 1636, 1526, 1416, 1351, 1274, 1201, 1176, 1069, 1022, 836, 784, 598, 565, 416 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 9.54 (1H, s, CH), 6.74 (2H, s, -NH_2). ^{13}C NMR (DMSO-d_6): δ 95.34, 134.72. Elemental analysis of

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$C_4H_5BrI_2N_4$ (430.81). Calcd: C, 8.36; H, 1.17; N, 13.00. Found: C, 8.29; H, 1.06; N, 11.86.

General Procedure for Preparing Imidazolium Iodate and Periodate Salts. The iodide or bromide salt (0.2 mmol) was suspended in water (5 mL), and $AgIO_3$ or $AgIO_4$ (0.4 mmol) was added. The reaction mixture was protected from light and stirred at 50 °C for 3 h. The precipitate was removed by filtration, and the product was obtained by removing solvent and drying under vacuum. The $AgIO_3$ or $AgIO_4$ was prepared by reacting the corresponding sodium salt with $AgNO_3$. For compound **13**, a mixture of compound **2** and **3** was reacted with $AgIO_3$. After the reaction, the solid mixture obtained from the filtrate was washed with water (3 × 3 mL), and the residue was air-dried and found to be pure **13** on the basis of elemental analyses.

*1,3-Dimethyl-2,4,5-triiodoimidazolium Iodate (**13**).* T_{dec}: 177.4 °C. IR: ν = 3264, 2933, 1669, 1560, 1501, 1473, 1432, 1384, 1313, 1093, 783, 751, 629, 548, 543, 444 cm^{-1}. No NMR data were obtained because of its poor solubility in DMSO. Elemental analysis of $C_5H_6I_4N_2O_3$ (649.73). Calcd: C, 9.24; H, 0.93; N, 4.31. Found: C, 9.02; H, 1.09; N, 4.14.

*1,3-Dimethyl-4,5-diiodoimidazolium Iodate (**14**).* T_{dec}: 187.0 °C. IR: ν = 3314, 3166, 3136, 3016, 1629, 1560, 1514, 1448, 1384, 1322, 1188, 1105, 1044, 760, 616, 600, 577 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.44 (1H, s, CH), 3.83 (3H, s, -CH_3). ^{13}C NMR (DMSO-d_6): δ 140.73, 94.01, 38.82. Elemental analysis of $C_5H_7I_3N_2O_3$ (649.73). Calcd: C, 11.46; H, 1.35; N, 5.35. Found: C, 11.54; H, 1.24; N, 5.21.

*1,1′-Methylenebis(4,5-diiodo-3-methyl-1H-imidazolium) Diiodate (**15**).* T_{dec}: 124.7 °C. IR: $\tilde{\nu}$ = 3034, 1741, 1637, 1557, 1504, 1438, 1383, 314,1192, 1098, 759, 606 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.92 (2H, s, CH), 6.61 (2H, s, CH_2), 3.92 (6H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 63.90, 94.42, 97.56, 142.00. Elemental analysis of $C_9H_{10}I_6N_4O_6{\cdot}3H_2O$ (1031.62). Calcd: C, 9.96; H, 1.49; N, 5.16. Found: C, 9.98; H, 1.26; N, 4.97.

*1,1′-Ethylenebis(4,5-diiodo-3-methyl-1H-imidazolium) Diiodate (**16**).* T_{dec}: 159.6 °C. IR: ν = 3105, 3003, 2952, 1638, 1548, 1506, 1447, 1359, 1324, 1209, 1186, 1102, 760, 621, 457 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.50 (1H, s, CH), 4.65 (4H, s, CH_2), 3.88 (6H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 39.44, 50.94, 95.80, 141.01. Elemental analysis of $C_{10}H_{12}I_6N_4O_6$ (1045.65). Calcd: C, 11.49; H, 1.16; N, 5.36. Found: C, 11.50; H, 1.17; N, 5.20.

*1-Amino-3-methyl-4,5-diiodoimidazolium Iodate (**17**).* T_{dec}: 148.4 °C. IR: ν = 3265, 3188, 3113, 3054, 1610, 1543, 1499, 1432, 1394, 1325, 1193, 1175, 1115, 1083, 1024, 995, 758, 638, 607, 588, 536, 460 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.47 (1H, s, CH), 6.79 (2H, s, -NH_2), 3.80 (3H, s, -CH_3). ^{13}C NMR (DMSO-d_6): δ 57.35, 93.91, 99.42, 141.21. Elemental analysis of $C_4H_6I_3N_3O_3$ (524.82). Calcd: C, 9.15; H, 1.15; N, 8.01. Found: C, 9.13; H, 1.07; N, 7.79.

*1,3-Diamino-4,5-diiodoimidazolium Iodate (**18**).* T_{dec}: 149.0 °C. IR: ν = 3314, 3236, 3166, 3102, 3018, 1617, 1522, 1498, 1319, 1197, 1111, 965, 835, 791, 756, 632, 605, 571 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.56 (1H, s, CH), 6.73 (4H, s, -NH_2). ^{13}C NMR (DMSO-d_6): δ 95.35, 134.71. Elemental analysis of $C_3H_5I_3N_4O_3$ (525.81). Calcd: C, 6.85; H, 0.96; N, 10.66. Found: C, 6.98; H, 0.88; N, 10.45.

*1,3-Dimethyl-4,5-diiodoimidazolium Periodate (**19**).* T_{dec}: 130.4 °C. IR: ν = 3166, 3093, 2950, 1729, 1655, 1557, 1513, 1438, 1386, 326, 1187, 1104, 858, 826, 775, 761, 598, 504 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.42 (1H, s, CH), 3.82 (6H, s, -CH_3). ^{13}C NMR (DMSO-d_6): δ 38.84, 93.55, 140.86. Elemental analysis of $C_5H_7I_3N_2O_4$ (539.83). Calcd: C, 11.12; H, 1.31; N, 5.19. Found: C, 11.33; H, 1.29; N, 5.05.

*1,1′-Methylenebis(4,5-diiodo-3-methyl-1H-imidazolium) Diperiodate (**20**).* T_{dec}: 92.3 °C. IR: ν = 3154, 3117, 2946, 1733, 1638, 1552, 1508, 1439, 1191, 1104, 757, 616 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.66 (2H, s, CH), 6.56 (2H, s, CH_2), 3.91 (6H, s, CH_3). ^{13}C NMR (DMSO-d_6): δ 63.93, 94.44, 97.58, 142.01. Elemental analysis of $C_9H_{10}I_6N_4O_8$ (1063.63). Calcd: C, 10.16; H, 0.95; N, 5.27. Found: C, 9.96; H, 1.20; N, 4.91.

*1,1′-Ethylenebis(4,5-diiodo-3-methyl-1H-imidazolium) Diperiodate (**21**).* T_{dec}: 109.8 °C. IR: ν = 3117, 3012, 2946, 1736, 1676, 1555, 1505, 1439, 1382, 1312, 1194, 1098, 757, 633, 604, 498 cm^{-1}. No NMR data were obtained because of its poor solubility in DMSO. Elemental analysis of $C_{10}H_{12}I_6N_4O_8$ (1077.65). Calcd: C, 11.15; H, 1.12; N, 5.20. Found: C, 11.33; H, 1.20; N, 5.10.

*1-Amino-3-methyl-4,5-diiodoimidazolium Periodate (**22**).* T_{dec}: 130.4 °C. IR: ν = 3262, 3157, 3118, 3054, 1630, 1544, 1500, 1438, 1193, 1115, 984, 773, 754, 620, 589 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.46 (1H, s, CH), 6.79 (2H, s, -NH_2), 3.79 (3H, s, -CH_3). ^{13}C NMR (DMSO-d_6): δ 57.32, 93.89, 99.42, 141.20. Elemental analysis of $C_4H_6I_3N_3O_3$ (540.82). Calcd: C, 8.88; H, 1.12; N, 7.77. Found: C, 9.03; H, 1.02; N, 7.31.

*1,3-Diamino-4,5-diiodoimidazolium Periodate (**23**).* T_{dec}: 143.1 °C. IR: ν = 3316, 3234, 3162, 3101, 3019, 1617, 1522, 1498, 1383, 1289, 1199, 1112, 962, 790, 769, 604, 570 cm^{-1}. ^1H NMR (DMSO-d_6): δ 9.58 (1H, s, CH), 6.74 (4H, s, -NH_2). ^{13}C NMR (DMSO-d_6): δ 95.30, 134.70. Elemental analysis of $C_3H_5I_3N_4O_3$ (541.81). Calcd: C, 6.65; H, 0.93; N, 10.34. Found: C, 6.75; H, 0.68; N, 10.54.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02195.

X-ray crystal diffraction data and crystal structures for compounds **15** and **24** and Gaussian calculations (PDF)
CCDC 1497391 (TXT)
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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Klapötke, T. M. *Chemistry of High-energy Materials*; De Gruyter: Berlin, 2011.

(2) Kaiho, T. *Iodine Chemistry and Applications*; John Wiley & Sons, Inc.: New York, 2015.

(3) Fischer, D.; Klapötke, T. M.; Stierstorfer, J. Synthesis and characterization of guanidinium difluoroiodate, $[C(NH_2)_3]^+[IF_2O_2]^-$ and its evaluation as an ingredient in agent defeat weapons. *Z. Anorg. Allg. Chem.* **2011**, *637*, 660−665.

(4) Chand, D.; He, C.; Hooper, J. P.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Mono- and diiodo-1,2,3-triazoles and their mono nitro derivatives. *Dalton Trans.* **2016**, *45*, 9684−9688.

(5) He, C.; Zhang, J.; Shreeve, J. M. Dense iodine-rich compounds with low detonation pressures as biocidal agents. *Chem. - Eur. J.* **2013**, *19*, 7503−7509.

(6) Chand, D.; Shreeve, J. M. Versatile polyiodopyrazoles: synthesis and biocidal promise. *Chem. Commun.* **2015**, *51*, 3438−3441.

(7) He, C.; Parrish, D. A.; Shreeve, J. M. Alkyl ammonium cation stabilized biocidal polyiodides with adaptable high density and low pressure. *Chem. - Eur. J.* **2014**, *20*, 6699−6706.

DOI: 10.1021/acs.inorgchem.6b02195
Inorg. Chem. 2016, 55, 12844−12850

(8) (a) Little, B. K.; Emery, S. B.; Nittinger, J. C.; Fantasia, R. C.; Lindsay, C. M. Physiochemical characterization of iodine(V) oxide, Part 1: Hydration rates. *Propellants, Explos., Pyrotech.* **2015**, *40*, 595−603. (b) Little, B.; Emery, S.; Lindsay, C. Physiochemical characterization of iodine (V) oxide Part II: Morphology and crystal structure of particulate films. *Crystals* **2015**, *5*, 534.
(9) Gao, H.; Shreeve, J. M. Azole-Based energetic salts. *Chem. Rev.* **2011**, *111*, 7377−7436.
(10) Zhang, Q.; Shreeve, J. M. Energetic ionic liquids as explosives and propellant fuels: A new journey of ionic liquid chemistry. *Chem. Rev.* **2014**, *114*, 10527−10574.
(11) Joo, Y.-H.; Shreeve, J. M. Energetic ethylene- and propylene-bridged bis(nitroiminotetrazolate) salts. *Chem. - Eur. J.* **2009**, *15*, 3198−3203.
(12) Klapötke, T. M.; Piercey, D. G.; Stierstorfer, J. The 1,3-diamino-1,2,3-triazolium cation: A highly energetic moiety. *Eur. J. Inorg. Chem.* **2013**, *2013*, 1509−1517.
(13) Xu, X.; Hu, C.-L.; Li, B.-X.; Yang, B.-P.; Mao, J.-G. α-AgI_3O_8 and β-AgI_3O_8 with large SHG responses: Polymerization of IO_3 groups into the I_3O_8 polyiodate anion. *Chem. Mater.* **2014**, *26*, 3219−3230.
(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision E.01; Gaussian, Inc.: Wallingford, CT, 2004.
(15) Strömberg, A.; Gropen, O.; Wahlgren, U. Gaussian basis sets for the fourth-row main group elements, In−Xe. *J. Comput. Chem.* **1983**, *4*, 181−186.

DOI: 10.1021/acs.inorgchem.6b02195
Inorg. Chem. 2016, 55, 12844−12850