

Chemical Oxidants

Ranking Oxidant Sensitiveness: A Guide for Synthetic Utility

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Abstract: Common oxidants used in chemical synthesis, including newly developed perruthenates, were evaluated in the context of understanding (and better appreciating) the sensitiveness and associated potential hazards of these reagents. Analysis using sealed cell differential scanning calorimetry (scDSC) facilitated Yoshida correlations, which were compared to impact sensitiveness and electrostatic discharge experiments (ESD), that enabled sensitiveness ranking. Methyltriphenylphoshonium perruthenate (MTP3, 8), isoamyltriphenylphosphonium perruthenate (ATP3, 7) and tetraphenylphosphonium perruthenate (TP3, 9) were found to be the most sensitive followed by 2-iodoxybenzoic acid (IBX, 2) and benzoyl peroxide (BPO, 10), whereas the most benign were observed to be Oxone (12), manganese dioxide (MnO₂, 13), and N-bromosuccinimide (NBS, 17).

Chemical oxidants are indispensable reagents utilized in the course of undertaking a wide variety of synthetic transformations, of which alcohol oxidation is arguably the most common.^[1] A subset of alcohol oxidation is the controlled onestep oxidation of a primary alcohol to the important aldehyde functional group.^[2] Not surprisingly, an extensive range of onestep oxidation methods are now available,^[1-3] although it seems practitioners remain wedded to a handful of systems encompassed by sulfur activation protocols (e.g., Corey-Kim),^[4] the hypervalent iodides^[5] [e.g., Dess-Martin periodinane (DMP, 1),^[6] IBX (2)],^[7] the nitroxyl radicals [e.g., TEMPO (3)],^[8] and the Ley-Griffith reagent^[9] tetra-*n*-propylammonium perruthenate {(*n*Pr₄N)[RuO₄]; TPAP (**4**)}.^[10]

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The popularity of these systems is due to the mild conditions required to promote oxidation, proven wide functional group tolerance,^[11] and limited toxicity. However, in the case of IBX it has been known to explode,^[12] and although a stabilized version (SIBX, 5) is available,^[13] other oxidants also fall into the category of being impact and/or thermally sensitive. For example, organic peroxides^[14] [e.g., meta-chloroperoxybenzoic acid (mCPBA) (6)]^[15] and the nitroxyl radical ANBO.^[16] In addition, in the course of developing perruthenates ATP3 (7) and MTP3 (8),^[17] which are much more bench stable compared to TPAP, we discovered that they were impact sensitive. This aspect provided substantial inspiration to investigate and rank the sensitiveness of a range of common oxidants used in both academic and industrial settings.

Herein, we report the impact, thermal and electrostatic analysis of seventeen common oxidants (Figure 1) by using sealed



Figure 1. Oxidants commonly used in chemical synthesis as ranked according to electrostatic discharge energy (expressed in J) sensitiveness levels. Those oxidants highlighted in red indicated a sensitiveness in the hammer test.

cell differential scanning calorimetry (scDSC),^[18] which underpinned Yoshida correlations,^[19] hammer^[20] and electrostatic discharge (ESD) tests.^[21] When combined the results enabled an oxidant sensitiveness ranking to be formulated.

A hammer test was first performed to provide an indication of impact sensitiveness. While the hammer test is only a preliminary test, it is still useful to provide an indication of impact sensitiveness and requires far less material than more quantitative methods.^[22] The two possible outcomes of the hammer test are: 1) a go event, defined as the observation of any one of the following: audible report, flame or visible light, evidence of smoke, or definite evidence of discoloration of the sample due to decomposition; or 2) a no-go event, which is the absence of any of the above.^[19b] Although most oxidants were insensitive to hammer strikes, six compounds produced go events. These were phosphonium perruthenates ATP3 (7), MTP3 (8), and TP3 (9), which all produced black smoke and sometimes flame, benzoyl peroxide (BPO, 10), and IBX (2) which both produced a loud popping noise, and cerium(IV) ammonium nitrate (CAN, 11), which changed color from bright orange to pale yellow. IBX required the most force to produce a go event, whereas perruthenates and BPO required only a light tap indicating that they are extremely impact sensitive, with the latter being well known and widely reported.^[23] CAN (11) also required only a light tap to produce a color change, however this was not accompanied by any sound, flame, or smoke. The color change may be attributable to decomposition to CeO₂, which is pale yellow.^[24]

Thermal and electrostatic stimuli are also known to initiate decomposition reactions of sensitive compounds; thus, the oxidants were evaluated under these conditions to facilitate further ranking. Thermal behavior was examined by using scDSC, and this also provided data for Yoshida correlations, which can be used to predict the potential of compounds to be both impact sensitive and explosive.^[19] By plotting the onset temperature (T_{DSC}) against the total energy (Q_{DSC}) of the exotherm, predictions can be made based on whether the compound appears above or below the threshold energy level for each property. The left-limit temperature, and more conservative energy threshold, were used in this study as recommended by Sperry et al.^[19b] Sealed crucibles were necessary to prevent the loss of oxidant through vaporization or sublimation. Loss of sample material results in inaccurate energy measurements for Yoshida correlations, and some oxidants lost all mass before any exotherm was observed in open crucibles [e.g., TEMPO (3), Figure 2]. The scDSC heat flow curves of all compounds can be found in the Supporting Information (Figures S1-S21).

Hypervalent iodides DMP (1) and IBX (2) underwent exothermic decomposition with onset temperatures of 116 and 186 °C, respectively. The decompositions were highly exothermic and both oxidants were flagged by Yoshida correlations. Newly developed perruthenates ATP3 (7) and MTP3 (8) had onset temperatures of 95 and 80 °C, respectively. The perruthenates 7 and 8, and IBX, all displayed a vertical onset, and an unusual hook in the heat flow curve, which is hypothesized to result from thermal lag; that is, due to the relatively thick crucible walls, the instrument was not able to accurately record the ex-



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Figure 2. TGA/DSC and scDSC data for TEMPO (3), an exemplar demonstrating loss of sample mass (red trace) and an exotherm when the cell was sealed (dashed line).

tremely rapid thermal decomposition of these oxidants, which is evidenced by the vertical onset. To better evaluate the decomposition of these compounds the heating rate was lowered from 5 to 1° Cmin⁻¹. The heat flow curves of ATP3 and MTP3 were improved, revealing that the initial decomposition of each consists of two separate exothermic events, however the onset temperatures lowered to 75 and 68 °C, respectively. When heated at 1° Cmin⁻¹ IBX retained the vertical onset and hook, suggesting that the thermo-decomposition was still very rapid at the slower heating rate.

In contrast to MTP3 and ATP3, perruthenates TPAP (**4**) and TP3 (**9**) showed normal heat flow curves at 5 °C min⁻¹ suggesting that their thermal decomposition was not as rapid as that of ATP3 and MTP3. TPAP showed a two-step initial decomposition, whereas TP3 showed only one initial decomposition peak. The onset temperatures were higher than those of the other perruthenates, at 108 and 157 °C, respectively. However, the thermal decompositions were large (i.e., -599 and -406 cal g⁻¹), flagging both as potentially impact sensitive and explosive.

SIBX (5) was designed to be stabilized against impact and thermal stimuli compared to pure IBX,^[13a] and this was supported by a no-go event in the hammer test as well as scDSC results. An endotherm was observed with a peak of 114 °C, which may be due to melting of benzoic acid (m.p. = 122 °C)^[25] followed by a large exotherm with an onset of 191 °C, similar to that of pure IBX, and Q_{DSC} of -540 cal g⁻¹. Interestingly, SIBX also flagged as potentially explosive and impact sensitive according to Yoshida calculations; however, the heat flow curve was a normal shape at 5 °Cmin⁻¹, indicating that thermo-decomposition was slower than that of pure IBX.

Benzoyl peroxide (**10**) and *m*CPBA (**6**) are well known to be explosive, and consequently neither is available commercially in pure form. Although they have caused accidents in pilot plants and on industrial scales,^[15a,26] they are both commonly used in academic settings.^[1] The thermal decomposition of dry, recrystallized benzoyl peroxide is preceded by a melt with an

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exotherm onset temperature of 104 °C. This finding was similar to literature temperatures, although the Q_{DSC} in this study (-553 cal g⁻¹) was higher than reported.^[27] A T_{DSC} and Q_{DSC} for commercial 75% benzoyl peroxide has been reported, and the energy released was low enough that, when stabilized with 25% water, this oxidant is predicted by Yoshida correlations to be impact sensitive, but not explosive.^[28] Commercial *m*CPBA (77%) was used herein, and provided an onset temperature of 91°C with a Q_{DSC} value of -527 cal g⁻¹. The T_{DSC} was in accordance with literature values, but the Q_{DSC} was again higher than that reported.^[27,29] Unsurprisingly, both *m*CPBA and benzoyl peroxide flagged as potentially impact sensitive and explosive.

Cerium ammonium nitrate (11), which reacted to the hammer test with a change in color, had a high onset temperature of 224°C and a Q_{DSC} of -677 cal g⁻¹. Although, CAN had the second highest T_{DSC} of the oxidants tested, it also had the third highest Q_{DSC} , behind IBX and PCC (16), and flagged as potentially impact sensitive and explosive in Yoshida correlations.

Only four oxidants did not flag as potentially impact sensitive and explosive: Oxone (12), MnO_2 (13), DDQ (14), and sulfur trioxide pyridine complex (SO₃·pyr, 15). Of these, DDQ and MnO_2 did not show any exotherms below 300 °C with DDQ melting and MnO_2 not undergoing any thermal transitions. The MnO_2 sample appeared unchanged upon opening the crucible. Oxone and SO₃·pyr did display exotherms; however, their energy and onset temperatures were such that they are below the Yoshida energy thresholds.

The remaining oxidants—TEMPO (3), PCC (16), and NBS (17)—are all flagged by Yoshida correlations with T_{DSC} values of 182, 164, and 131 °C, and Q_{DSC} values of -464, -725, and -494 cal g⁻¹, respectively (Figure 3).

Electrostatic discharge (ESD) is the accidental stimulus that is most likely to occur in a laboratory setting from human static electricity (e.g., transferred through a metal spatula). ESD



Figure 3. Yoshida plot of oxidants which exhibited exotherms under scDSC analysis. All data was acquired with a heating rate of 5 °C min⁻¹. Oxidants above the blue line are considered potentially impact sensitive, with those above the orange line potentially explosive. Thresholds used are 25% lower than the original Yoshida thresholds to provide a more conservative prediction as recommended by Sperry et al.^[19b]

testing was carried out in accordance with established protocols, and three levels were tested: 0.045, 0.45, and 4.5 J.^[30] Briefly, a capacitor was charged to a defined potential (0.045, 0.45, or 4.5 J) and a pulse was applied to cause the potential of the selected capacitor to form across the sample spark gap. Typically values for the buildup of electrostatic energy on a person are within the range of 0.005-0.08 J, which is enough to set off some primary explosives.^[21,31] Phosphonium perruthenates ATP3 (7), MTP3 (8), and TP3 (9) all ignited at the lowest setting, whereas TPAP (4) did not ignite even at the highest setting of 4.5 J. Although the addition of stabilizing agents appears to lower the impact and thermal sensitiveness of IBX, both SIBX (5) and IBX (2) ignited at the second lowest setting (0.45 J) along with benzoyl peroxide (10) and DDQ (14). At the highest setting of 4.5 J, TEMPO (3), SO₃·pyr (15), PCC (16), and DMP (1) ignited. Of these oxidants, only SO₃·pyr did not flag in the Yoshida correlations, suggesting a slightly better safety profile than the others. Finally, with no ignitions at 4.5 J were mCPBA (6), CAN (11), oxone (12), MnO₂ (13), NBS (17), and TPAP (4).

Combining the three sensitiveness test results clearly highlighted some oxidants as being more problematic than others. IBX, benzoyl peroxide, and the phosphonium perruthenates ATP3, MTP3, and TP3 are all sensitive to impact, as demonstrated by go events in the hammer test. All these oxidants displayed highly exothermic decomposition and ESD sensitiveness. In contrast, Oxone and manganese dioxide were benign in every test, giving no-go events in hammer test, no ignition at 4.5 J, and no (or small) exotherms in scDSC. These data enabled classification of these two oxidants as having the best safety profile of those tested.

To provide a ranked series (Table 1), the oxidants were scored according to their sensitiveness testing results. For the hammer test, a go event = 1 and a no-go = 0. For scDSC, being flagged = 1, whereas falling below the threshold is equivalent to 0. For ESD testing, no ignition = 0, ignition at 4.5 J = 1, ignition at 0.45 J=2, and ignition at 0.045 J=3. By using this method, a higher final score indicates that the oxidant shows increased sensitiveness and should be treated with more care. However, the specific hazards should always be considered before using any oxidant, for example mCPBA scores only 1, but has an onset temperature below 100 °C, so it should not be used when elevated temperatures are required. Furthermore, in terms of handling some of the tested oxidants, one must be mindful of potential sources of ignition that may be presemt in the synthetic laboratory. For instance, the use of earthed spatulas and conductive or antistatic containers may be one way to mitigate the potential ESD risk when handling oxidisers with low ESD sensitiveness; while the use of Tefloncoated spatulas and avoiding 'tapping' spatulas may be one way to mitigate risks when handling oxidants that exhibit impact sensitiveness.

In conclusion, the synthetic chemist relies heavily on a range of oxidants to perform a vast array of synthetic transformations. The sensitiveness data provided herein contributes to the understanding of the safety profile of some common oxidants, and can thus be used when selecting appropriate re-

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Table 1. Summary of oxidant sensitiveness testing and overall ranking from least to most sensitive.								
Compound	Hammer	$Q_{\rm DSC}$ [cal g ⁻¹]	$T_{\rm DSC}$ [°C]	Yoshida	ESD ignition [J] ^[b]	Score		
MnO ₂ (13)	no-go	n/a	n/a	n/a	n/a	0		
Oxone (12)	no-go	-88	135	n/a	n/a	0		
NBS (17)	no-go	-494	131	IS/EP	n/a	1		
TPAP (4)	no-go	-599	108	IS/EP	n/a	1		
<i>m</i> CPBA (6)	no-go	-527	91	IS/EP	n/a	1		
SO₃·pyr (15) ^[a]	no-go	-108	247	n/a	4.5	1		
CAN (11)	go	-677	224	IS/EP	n/a	2		
TEMPO (3)	no-go	-464	182	IS/EP	4.5	2		
PCC (16)	no-go	-725	164	IS/EP	4.5	2		
DMP (1)	no-go	-625	116	IS/EP	4.5	2		
DDQ (14)	no-go	n/a	n/a	n/a	0.45	2		
SIBX (5)	no-go	-540	191	IS/EP	0.45	3		
IBX (2)	go	-890	186	IS/EP	0.45	4		
BPO (10)	go	-553	104	IS/EP	0.45	4		
TP3 (9)	go	-406	157	IS/EP	0.045	5		
ATP3 (7)	go	-451	95	IS/EP	0.045	5		
MTP3 (8)	go	-781	80	IS/EP	0.045	5		
[a] Multiple exotherms, none were above the Yoshida threshold. [b] Lowest level at which ignition occurred.								

agents. A series of seventeen common oxidants has been ranked based on their sensitiveness to three stimuli commonly encountered in the laboratory—impact, thermal, and electrostatic discharge. The most sensitive were found to be phosphonium perruthenates MTP3 and TP3, whereas MnO₂ and Oxone were the least sensitive.

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Conflict of interest

The authors declare no conflict of interest.

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Ranking Oxidant Sensitiveness: A Guide for Synthetic Utility



Which one is the most sensitive? Seventeen common oxidants were evaluated in the context of impact, thermal and electrostatic sensitiveness, and ranked as a guide for synthetic utility and de novo reaction design.

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