# FUEL-OXIDIZER MIXTURES: THEIR STABILITIES AND BURN CHARACTERISTICS

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A survey of the stability and performance of 11 solid oxidizers and eight fuels was performed by differential scanning calorimetry (DSC), simultaneous differential thermolysis (SDT), and hot-wire ignition. Fuels used in the study were sugars and alcohols as well as sulfur and charcoal; all but charcoal melted below 200°C. The goal of the study was to determine whether the oxidizer or fuel controls the essential properties of the mixture. Several general observations were made: (1) There was wide variability in DSC results, even using the same batch of a mixture. (2) SDT traces often differed markedly from those of DSC. (3) At 50 wt % sugar, decomposition generally occurred as soon as the fuel melted. (4) With only 20 wt % sucrose, many of the oxidizer/fuel mixtures still exhibited the first exotherm immediately after the melt of the fuel. This behavior was so general that we have classified the decomposition of the fuel-oxidizer mixtures as fuel or oxidizer controlled. Oxidizer-controlled mixtures were those made with KClO<sub>4</sub>, KNO<sub>3</sub>, or NH<sub>4</sub>ClO<sub>4</sub>; they did not exhibit substantial exotherms until the oxidizer underwent a phase change or decomposition. A fuel-controlled mixture meant decomposition of the mixture ensued immediately after the fuel change or decomposition. A fuel-controlled mixture meant decomposition of the mixture ensued immediately after the fuel change or decomposition. A fuel-controlled mixture meant decomposition of the mixture ensued immediately after the fuel change or decomposition. A fuel-controlled mixture meant decomposition of the mixture stude with KClO<sub>3</sub>. Fuel-controlled oxidizer/fuel mixes exhibited lower decomposition temperatures than oxidizer-controlled mixtures.

KEY WORDS: explosives, FOX, inorganic oxidizers, thermal stability, burn

# 1. INTRODUCTION

Inorganic oxidizers find applications ranging from oxygen sources to sources of energy and propulsion. Examples include ammonium perchlorate with hydroxy-terminated polybutadiene for rocket fuel and ammonium nitrate with fuel oil for commercial mining. Many of these formulations have also found illicit use [1]. Herein, a number of solid oxidzers, with varying oxidizing power, were tested on a laboratory scale in mixtures with a variety of fuels. The objective was to assess their hazard and threat potential and to allow assessment of the usefulness of small-scale tests. Many of the oxidizers were oxy halide salts. These anions, with the highly oxidized central atoms, tend to be useful oxidizing agents which work most effectively in acidic solutions. The potassium, rather than the sodium, salts were used, since formulations with potassium cation tend to be less hygroscopic than those of sodium. The ammonium salts have different chemical behavior than potassium salts of the same anion because they carry and use, if required, their own fuel. The choice of fuels, like oxidizers, was limited to solids: polyalcohols, sulfur, and charcoal. The solid alcohols, some classed as sugars, melt at relatively low temperatures. Most fuels were combined with the oxidizers at a 50/50 wt % level. These fuel-rich mixtures are typical for pyrotechnic formulations. In addition, oxidizer/sucrose 80/20 mixtures were examined and compared to the 50/50 mixtures. For purposes of comparison, one nonalcohol, but low-melting fuel, sulfur, and a nonmelting fuel, charcoal, were examined.

# 2. EXPERIMENTAL

Eleven oxidizers and eight fuels were employed. All materials were reagent grade with the exception of the charcoal, which was purchased locally. The oxidizer/fuel mixtures were examined fuel rich at 50/50 wt % and closer to stoichiometric at 80/20 wt %. Actual stoichiometric ratios are shown in Table 1. Individual components with larger particle sizes (i.e., sugars and most oxidizers) were ground with a mortar and pestle prior to mixing. Those materials that were already fine powders, such as sulfur, were

		Stoichiome	etric mixtu	res ( wt %	o oxid	lizer)					
	KIO <sub>4</sub>	KMnO <sub>4</sub>	KBrO <sub>3</sub>	KClO <sub>3</sub>	KC	$r_2O_7$	KIO <sub>3</sub>				
Sucrose	80.1	81.6	79.6	74.1	87	7.3	83.3				
Lactose	80.1	81.6	79.6	74.1	87	7.3	83.3				
Fructose	79.3	80.8	78.8	73.1	86	5.7	82.6				
Glucose	79.3	80.8	78.8	73.1	86	5.7	82.6				
PE	83.5	84.8	83.1	78.3	89	9.6	86.3				
ET	80.9	82.3	80.4	75.1	87	7.8	84.0				
Sulfur	78.2	79.8	77.6	71.8	85	5.9	81.6				
Charcoal	90.5	91.3	90.3	87.2	94	4.2	92.2				
	KClO <sub>4</sub>	KNO <sub>3</sub>	KNO <sub>2</sub>	NH <sub>4</sub> Cl	$0_4$	NH	4NO <sub>3</sub>				
Sucrose	70.8	73.9	79.9	76.7		8	34.9				
Lactose	70.8	73.9	79.9	76.7	76.7		34.9				
Fructose	69.8	72.9	79.1	75.8		8	84.2				
Glucose	69.8	72.9	79.1	75.8		84.2					
PE	75.3	78.1	83.3	80.6		87.6					
ET	71.9	74.9	80.7	77.6		85.5					
Sulfur	68.4	71.6	78.0	74.6		8	83.3				
Charcoal	85.2	87.1	90.4	88.7		9	93.0				

**TABLE 1:** Calculated stoichiometric weight percent of oxidizer with specified fuels

used as received. Materials used to make the 80:20 sucrose mixtures were sieved to 50–100 mesh. Mixtures were generated by either gently stirring the fuel and oxidizer together in a ceramic dish with a wooden stick (earlier mixes), or by mixing them in a Resodyn LabRAM acoustic mixer for 2 min (50% intensity, frequency set to automatic). Mixture sizes ranged from 100 mg to 1 g, depending on the analyses to be performed.

A TA Q100 differential scanning calorimeter (DSC) was used, and samples were scanned at 20°/min. Samples of about 0.25 mg were flame sealed in glass capillaries (borosilicate 0.06 in. ID, 0.11 in. OD) held on a liquid-nitrogen-cooled metal post to ensure that decomposition did not occur during the sample preparation process. To ensure the integrity of the capillary sealing (i.e., no leaks), capillaries were weighed before and after DSC analysis. A TA Instruments Q600 simultaneous TGA/DSC (SDT) was used with unsealed samples held in ceramic crucibles. Empty crucibles were placed in the SDT, where they were weighed by the internal balance and about 5 mg of sample was added. Ceramic caps (i.e., not tightly sealed) were placed on the crucibles for samples which might eject material or on highly volatile samples, e.g., sulfur mixtures. The SDT was used because of its extended temperature range (1000°C vs 450°C for DSC). However, the thermograms obtained with sealed DSC did not perfectly match those observed with the unsealed ceramic pans used on SDT. The open pans allowed for the sample to volatilize as compared to the sealed scenario, where there is considerable pressure buildup. Differences for SDT included somewhat smaller exotherms, some smaller exotherms became endotherms, and larger exotherms were sometimes split by an endotherm. For this reason the sealed DSC tube results were reported for temperatures below 450°C; if temperatures above that are reported, they are SDT results.

Samples were usually run in triplicate, but where marked variations in the thermograms were apparent, up to seven samples were run. Because multiple endotherms and exotherms were often observed in the DSC and SDT traces and because many of the exotherms covered a wide temperature range (in a few cases up to  $100^{\circ}$ C), the major exotherm of a trace is usually reported with the initial temperature at which a deviation from baseline was visually detected followed by the temperature(s) at which "peak maxima" were observed, with the highest in bold, followed by the energy density of the mixture (J/g) calculated from the peak area using baselines established by the operator (Table 3).

For burn tests the oxidizers and sucrose were dried overnight in a vacuum oven at  $50^{\circ}$ C and then ground and sieved to 50–100 mesh. Pyrotechnic-grade (median particle size 23 µm) aluminum powder (Obron) was used. Samples were mixed with a Resodyn LabRAM acoustic mixer at 50% intensity for 2 min. Approximately 0.25 g samples were placed in a pile on a ceramic plate over a loop of 22 gage nichrome wire (30 cm long for power requirements of 150 W) attached to a variable autotransformer (set to 20 V) with a 25 amp internal fuse for the burn. Light output was recorded with a DET36A detector (Thor Labs) and recorded using a National Instruments USB-6210 data acquisition module. Light data was recorded at 10–100 kHz by measuring voltage

across a 350 ohm resistor. The detector was unfiltered for mixtures producing low levels of light (e.g. 80/20 or 50/50 oxidizer/sucrose). To resolve the brightest events (e.g. 80/20 oxidizer/aluminum powder), a 90% neutral density filter (ND10A, optical density of 1.0) was applied behind an iris (6.33 mm diameter opening, Iris SM1D12). The data acquisition card was set to a sampling rate of at least 10 kHz, with a pretrigger of 50–100 ms.

# 3. RESULTS AND DISCUSSION

#### 3.1 Neat Species

Oxidizers were restricted to solids of various oxidizing power. Oxidizing power itself is variously rated. Intrinsic oxidizing ability, given by standard reduction potential (1 M aq solution against  $H_2$  as zero) in volts, is a meaningful approach to quantifying oxidizing power. This is given below starting with the species having the most positive potential, noting that actual potentials depend on the pH of solutions and final products:

 $\begin{array}{l} H_2O_2 > IO_4^- > MnO_4^- > BrO_3^- > MnO_4^- > ClO_3^- > Cr_2O_7^- > ClO_4^- > IO_3^- > NO_3^- \\ > NO_2^- \\ 1.8 > 1.7 \\ -1.6 > 1.7 \\ -1.5 > 1.5 \\ -1.4 > 1.5 > 1.5 \\ > 1.4 \\ -1.3 > 1.4 \\ -1.2 > 1.2 \\ -1.1 > 1.0 \\ -0.8 > -0.46 \end{array}$ 

 $NO_3^- \rightarrow NO, HNO_2, NH_4^+, NO_2 0.96, 0.94, 0.87, 0.80$ , respectively

An alternative approach to rating oxidizing power is a burn test. The U.N. Manual of Tests and Criteria rates an oxidizer by comparing its burn rate in an admixture with cellulose (2:3 and 3:7 ratios) to mixtures of potassium bromate/cellulose [2]. In our burn tests 250 mg, instead of 30 g, and sucrose or aluminum powder were used instead of cellulose. Fuel-oxidizer burn rates are shown in Table 2.

Thermal stability was assessed by the temperature at peak maximum of the DSC exotherm. The higher the exotherm temperature, the more thermally stable the species. Some salts decomposed with an exclusively endothermic response (Table 3). Among salts releasing heat (i.e. exothermic response), the amount of heat varied dramatically from more than 1000 J/g for mixtures of ammonium salts, which can undergo self-oxidation, to a few hundred joules per gram for other mixtures. The thermal traces of the oxidizers alone were not simple. They included phase change(s), decompositions, and heats of fusion (i.e. melts) of the decomposition product. Some salts EO<sub>4</sub><sup>-</sup> underwent intraconversion with a related oxide EO<sub>3</sub><sup>-</sup>, E = Cl or I. In the case of the periodate/iodate pair, periodate decomposed to iodate at about 330°C and thereafter their thermograms were identical [3–7].

Ammonium perchlorate (AP,  $NH_4ClO_4$ ) alone did not melt but exhibited an endotherm around 245°C (~70 J/g) as a result of an orthorhombic-to-cubic phase change.

		1		1						1											
$KNO_2$	-0.46	78%	0/ 07	212		1777	$KNO_2$		2.5	0.6	1	I	Bubbled			$KNO_2$	_	1.3		0.3	32
$NH_4NO_3$		20%	0/07	176		2084	$NH_4NO_3$		18.2	1.6		1	Bubbled			$\rm NH_4NO_3$		18.1		2.7	
$KNO_3$	1.0 - 0.8	70%	% <b>0</b> t	396		1108	$KNO_3$		3.8	0.7	I	I	Bubbled			$KNO_3$		2.5		0.7	I
$KIO_3$	1.2–1.1	270%	0/ 77	182		939	KIO <sub>3</sub>		7.5	2.1	I	I	Bubbled			$KIO_3$		1.6		0.4	I
KClO <sub>4</sub>	1.4–1.2	16%	0/0 <del>1</del>	540		735	KClO <sub>4</sub>		Too fast	Too fast	2736	11	Bright	flash		$KClO_4$		2.5		0.4	11
NH <sub>4</sub> ClO <sub>4</sub>		3.10%	0,40	484		1342	NH4CIO4		4.3	1.0	144	73	Bright	flash,	strobes	$NH_4CIO_4$		4.6		0.8	3
$K_2Cr_2O_7$	1.4–1.3	16%	10/0	231		157	$K_2Cr_2O_7$		Too fast	Too fast	140	54	Bright	flash		$K_2 C r_2 O_7$		4.9		1.7	
KClO <sub>3</sub>	1.5	30%	0/ 20	180		3195	KClO <sub>3</sub>		Too fast	Too fast	1129	286	Bright	flash		KClO <sub>3</sub>		1.0		0.4	104
$KBrO_3$	1.5 - 1.4	<b>70</b> %	0/ 67	186		1511	$KBrO_3$		Too fast	Too fast	1113	437	Bright	flash		$KBrO_3$		Too fast			346
$KMnO_4$	1.7–1.5	75%	0/ C7	236		1741	$KMnO_4$		Too fast	Too fast	2360	297	Bright	flash		$KMnO_4$		1.9		0.2	25
KIO <sub>4</sub>	1.7–1.6	78%	0/ 07	187		1681	$KIO_4$		Too fast	Too fast	2564	232	Bright	flash		$KIO_4$		Too fast			56
Oxidizer	Anion potential 1	М аq. п <sub>2</sub> U V Wt % оууден in	oxidizer	Decomp °C 8/2	oxidizer/sucrose	J/g heat relea- sed	Burn test 8:2	oxidizer:Al	Avg. burn time by eye (s)	Std. dev.	Avg. peak light signal (mV)	Std. dev.	Notes			Burn test 8:2	oxidizer:sucrose	Avg. burn time	by eye (s)	Std. dev	Avg. peak light

**TABLE 2:** Burn time (seconds) of a 4:1 oxidizer:sucrose mix

	$KNO_2$	12	Yellow	flame	KNO <sub>2</sub>	2.6		1.1	43		13	Dim	yellow	flame	$KNO_2$		2.1		0.5	160		88	Orange	flame
	$NH_4NO_3$	Ι	Dim yel-	low flame	NH4NO3	21.4		4.8	I		1	No light,	black	snake	$NH_4NO_3$		28.7		6.2	14		4	Yellow	flickering
	KNO <sub>3</sub>	I	Charring,	no flame	KNO <sub>3</sub>	0.9		0.1	43		13	Dim yel-	low flame		KNO <sub>3</sub>		4.5		1.8	91		33	Orange	flame
	KIO <sub>3</sub>	I	Charring,	no flame	KIO <sub>3</sub>	0.6		4.2	I		1	Dim yel-	low flame		KIO <sub>3</sub>		4.9		1.2	221		35	White	flickering
	$KCIO_4$	4	Purple	flame	KClO <sub>4</sub>	8.1		1.1	58		13	Dim	yellow	flame	$KCIO_4$		4.5		0.6	737		304	White	w mue
	$NH_4CIO_4$	1	Yellow	flame	$NH_4CIO_4$	9.2		1.2	10		2	Dim yel-	low flame		$NH_4CIO_4$		6.3		1.0	226		45	Br yellow	flame
	$K_2Cr_2O_7$	I	Charring,	no flame	$K_2Cr_2O_7$	15.9		1.7	I		I	Dim yel-	low flame		$K_2Cr_2O_7$		16.0		1.6	26		8	Yellow	flame
	KClO <sub>3</sub>	43	Purple	flame	KClO <sub>3</sub>	2.6		0.8	128		41	Purple	flame		KClO <sub>3</sub>		4.4		1.7	762		104	Br	yellow flame
	$KBrO_3$	86	Purple	flame	KBrO <sub>3</sub>	Too fast		Too fast	430		164	Purple	flame		$KBrO_3$		Too fast		Too fast	2228		228	Bright	flash
	$KMnO_4$	9	Orange	flame	KMnO <sub>4</sub>	10.4		2.1	8		7	Dim	yellow	flame	$KMnO_4$		3.0		0.8	147		22	Orange	flame
ued	$KIO_4$	23	Purple	flickering	$\mathrm{KIO}_4$	3.1		0.5	I		1	No light,	black	snake	$KIO_4$		1.6		0.5	1413		331	Bright	flash
TABLE 2: Contin	Oxidizer	Std. dev.	Notes		Burn test 5:5 oxidizer:sucrose	Avg. burn time by	eye (s)	Std. dev.	Avg. peak light	signal (mV)	Std. dev.	Notes			Burn test 8:2	oxidizer:benzoic acid	Avg. burn time by	eye (s)	Std. dev.	Avg. peak light	signal (mV)	Std. dev.	Notes	

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				$KIO_4$	KN	$\Lambda nO_4$	KI	$3rO_3$
	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Ex
hase cha	nge		IS	DT only				
Ielt			544-571-611		240 lit start		413(60)	
			(436)		peak			
<b>Ielt KX</b>			675(54)		541(59)		729(488)	
ecompos	se			334- <b>350</b> (85)		305(145)		4
ucrose	173-190-201	257- <b>297</b> -334	<b>65</b> 150(30),	<b>65a</b> 153-171(1698),	36 187(20)	36 189-235-	<b>91</b> 180(66),	6
	(148), 238(26)	(206)	675 (25)	<b>293-348</b> (198) sdt,		269-306(1214)	730(22)	<u>ב</u>
				442(328) sdt				sd
ucrose			76 675(32)	76 155-167- <b>187</b>	75 191(43)	<b>75 221-236-</b>	79 180(66),	79
0%0				(1681), 297(24) sdt,		272-303-355	792	<u> </u>
				349(183), 441-460		(1741) dsc, 603-		37.
				(469) sdt		693(308) sdt		
actose	151(132), 208(68)	282- <b>299</b> (419)						
ructose	88- <b>128</b> -162	268(233)	66 675(24)	<b>66 132</b> (780), <b>348</b>	37 108(94),	<b>37</b> 131- <b>178</b> -	92 115(55),	92
	(263)			(37), 434(230)	391(15), 434(27)	<b>256</b> -296(1608)	730(11)	372
Hucose	165(198), 233(73)	305(333)						
entae- vthritol	191(311), 263 (32) 350(81)							
rythri-	124(385).		67a 600(4).	67a 137-188	46 110(26)	<b>46</b> 114- <b>161</b> -258	93 190(50).	<u>93 2</u>
, l	330(547) bp		662(24)	244(1059), 351(7),		(1931), 355(152)	730(46)	260-
				435(28)				600
urfur	108-115-121		89 114(17),	<b>89</b> 236- <b>262-284</b> -	86 114(19)	86 259-310-		
	(70), 180(8), 315		578(2)	<b>298</b> (1269)		<b>380</b> (808)		
harcoal		150						

TABLE	3: Continued							
	K	CIO <sub>3</sub>	K <sub>2</sub> C	$r_20_7$	ΉN	$_4$ ClO $_4$	KC	IO4
	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm
Phase					248(62)		307(85)	
change								
Melt	<b>58</b> (116)		398				613(115)	
Melt KX	767(177)		757(10)		767(177)		757(10)	
Decom-		417(9), 584-619				<b>404</b> (1081)		653(266)
pose		(446)						
Sucrose		14 153-164-215-	95 187(13)	95 244(83),	28 165(66),	<b>28</b> 175- <b>185</b> -209	26 181(66),	26 280(142),
		249-256(1955)		403(15),	246(24),	(181), 266-280-	307(36), 765(7)	427- <b>494</b> (1206)
				491(32)	759(79)	340-424(1843)		sdt
Sucrose	5 766(123)	73, 5 162-180-	94 193(34)	94 225-244-	71 173(35),	71 484(1342)	74 187(32),	need DSC
20%		236(3195),		268(159)	245(54),	dsc, 318 sdt, 394	304(85),	74 540(735),
		338(61)			758(6)	sdt	787(170)	620(223)
Lactose	15 150(60)	15 182-200-241-						
		253-270(1684)						
Fructose	17 123(11),	<b>17</b> 125- <b>175-</b>	96 101(50)	96 187(130)	29 118(117),	29 180(300), 284-	27 128(29), 311	27 511(931)
	767(29)	242-276(2955)			244(10)	340-420(2285)	(45), 767(16)	
Glucose	16 155(19)	16 158-175,						
		240-283(2193)						
Pentae-	<b>31</b> 191(176),	31 209-237-265						
rythritol	767 (91)	(2111), 617(45)						
Eryth-	<b>30b</b> 120(260)	<b>30b</b> 195-216-	<b>97</b> 193(24),	97 404(89)	44 108(45),	44 262-298-340-	45 118(200),	<b>45 329-355</b>
ritol		259-280(2339)	398(123)		246(53),	438-452(3196)	306(18),	(438), 503-575-
							768(52)	644(213)
Surfur	38a 115(33),	38a 142-180			85 114(37),	85 389-421	84 115, 120(54),	<b>84</b> 424- <b>470</b>
	317(7),	(829)			245(25),	(1493)	307(36),	-486(1384),
	440(17)				670(11)		765(14)	597(154)
Charcoal	42	42 334(1541)	98 395(23)	<b>98</b> 401(61)	69 244(20)	69 344(2000)	54, 70 307(43),	70 449-524
							766(14)	(1100)
	K	CIO <sub>3</sub>	$K_2C$	$r_2O_7$	HN	4 CIO4	KC	$10_4$

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TABLE:	3: Continue	ł						
	P	d0 <sub>3</sub>	KNC	03	Z	$H_4NO_3$	R	NO2
	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm	Endotherm	Exotherm
<b>Phase</b> change	nothir	ıg in DSC	132(53), 222(3)		55(22), 130(40)		45(13)	
Melt	553d(609)		330(29)		167		424(82)	
Melt KX	680(75)							
Decom-	831-900(275)		702(433)			261-316-336	517(2),	930(176)
pose						(1407)	903(17)	
Sucrose	<b>62</b> 152(19),	<b>62</b> 156- <b>187</b>	<b>18</b> 137(22),	<b>18</b> 219- <b>265</b>	22 54(16),	<b>22</b> 147- <b>176</b>	55 192(57)	55 212-239-
	678(8)	(1736), 438(137)	181(73), 219(14)	(298), 359- <b>393</b>	127(15)	(2627), 296(513)		290(1618)
		sdt		(400 or 1269)				
Sucrose	77 160(39)	77 163-182(939)	72 131(45),	72 381-396-	68 56(14),	<b>68 151-176</b> ,	78 172(41),	78 177-212-222-
20%		dsc, <b>434</b> (207)	173(20)	413-453(1108)	129(33)	202(2084), 283-	940(21)	251(1777), 323-
		sdt				295-333(1010)		333(65)
Lactose			<b>19</b> 132(9),	19 271(300),	23 55(10),	23 160-182-209, 221		
			151(70), 212(9)	379 <b>-394</b> (800)	107(110)	(1493), 311(183)		
Fructose	<b>63</b> 123(27),	<b>63</b> 128-156	21 122(72)	21 230-314-380	25a 55(15),	25a 150-170(3475),		56 136-170-218
	678(10)	(1491), 430(117)		(244), <b>409</b> (550)	130(80)	336(607)		(944)
Glucose			20 133-152-165	20 271-305	24 54(11),	24 153-188(2400),		
			(140)	(370), <b>392</b> (414)	107(90)	309(318)		
Pentae-			(23), 190(139),	440, 470(1467),	33 54(13), 126	33 242-265(2008)		
rythritol			354(164), 687(849)	765, 842, 940	(38), 175(9)			
Eryth-	<b>64</b> 123(119),	<b>64</b> 178(931)	34 113(125),	34 298(30),	35 86(59),	35 255-261(1653)	57 116(43)	57 250-318-357
ritol	608(2), 668(15)		130(32)	<b>416</b> (2695)	119(11)			(1041)
f	(01)000	00 010 100	40-115 110	10 - 200 227	30 11 ((10)	20 100 21E(0220)		00 251 204
Suriur	<b>55</b> 114,	<b>88</b> 2/0- <b>303</b> - 100/2411)	40a 115, 119,	40a 300-327-	<b>39</b> 116(40)	<b>39</b> 198- <b>21</b> 7(2379)		<b>8/ 251-294</b>
	119(28)	400(2411)	131(65), 189(12)	420(1092)				310(1962)
Charcoal			<b>43</b> 129(22), 332(47)	<b>43 461</b> (2182)		<b>41 221</b> (1472)		
	R	ci0 <sub>3</sub>	KNC	)3	Z	H <sub>4</sub> NO <sub>3</sub>	K	NO <sub>2</sub>

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[Ammonium chlorate is thermally unstable and has been reported to spontaneously ignite at temperatures as low as 100°C [8]. For this reason it was not used in this study.] Continued heating of AP in sealed DSC ampules resulted in a single exotherm which began around 350°C and reached a maximum at about 400°C ( $\sim$ 1300 J/g). The SDT results appeared quite different. Immediately after the 245°C phase change, a small exotherm ( $\sim$ 360 J/g) at  $\sim$ 318°C was observed with a second endotherm centered around 435°C following it (Fig. 1). This apparent difference in AP behavior has been explained by the sublimation of AP above 350°C competing with its decomposition. In the sealed DSC ampule, AP did not sublime. It has been reported that the competition between AP sublimation and AP decomposition was dramatically affected by pressure [9]. [As heating of the open pan in the SDT was continued, a small endotherm at 757°C was observed, the melt of KCl.]

An advantage of the SDT thermal analysis was that it allowed scanning to higher temperatures. Since the crucibles were not sealed, thermal traces differed markedly from sealed DSC thermal analysis. For example, the exotherm in the ammonium nitrate (AN,  $NH_4NO_3$ ) thermal trace at 316°C in SDT became an endotherm at 292°C due to the volatilization of the AN. This same observation was made with a number of compounds and formulations. Sulfur, in the open pans, exhibited an exotherm at around 400°C. This was evidently a reaction with oxygen in air, since no exotherm was observed when the samples were scanned under nitrogen.

The fuels, mostly alcohols, melted below 200°C; only charcoal did not exhibit a melt. The monosaccharrides, glucose and frutose, and the disaccharides, sucrose (glucose and fructose) and lactose (glucose and galactose), were examined in mixture with 11 oxidizers. The disaccharrides and glucose exhibited an endotherm at around 150–176°C, while for frutose the endotherm was earlier at 128°C. Pentaerythritol and erythritol not only had melting points in the temperature range of the other sugars (191°C and 124°C, respectively), but both of them boiled before 300°C. These endothermic events ensured that thermal scans in open pans would be markedly different than in sealed pans. In addition to solid alcohols, sulfur and charcoal were used as fuels. Although sulfur had a low-melting endotherm, charcoal did not. Upon heating in air, sulfur exhibited an exotherm attributed to oxidation.

# 3.2 Oxidizer/Fuel Mixtures

#### 3.2.1 Periodate

A number of kinetic and mechanistic studies have been done on the oxidizing power of periodate [10, 11]. For example, it has been reported that  $KIO_4$  oxidized glucose to formaldehyde and formic acid through a cyclic diester of periodic acid. The DSC thermograms of  $KIO_4$  mixed with either 20 or 50 wt % sucrose were similar [cf. Figs. 2(a) and 3(a)]. Immediately after the melt of sucrose, a single large exotherm was observed.



FIG. 1: Ammonium perchlorate DSC vs SDT.

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**FIG. 2:**  $KIO_4 + 50\%$  sucrose (mix 65)—DSC vs SDT.



**FIG. 3:**  $KIO_4 + 20\%$  sucrose (mix 76)—2 DSC traces.

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The SDT of the same mixtures had a different appearance, with a small exotherm immediately after the sucrose melted and additional exotherms around 293°C and 348°C, with a sharp exotherm at 442°C [Fig. 2(b)]. Figure 3(b), which was taken from the same batch as Fig. 3(a), shows the occasional variablity encountered in thermal scans. This one may be a result of a leak with partial loss of the fuel component. With 50 wt % fructose or erythritol, the exotherm also began immediately after the melt of the fuel, but the melt came at lower temperatures for fructose ( $\sim$ 103°C) or for erythritol ( $\sim$ 121°C). Sulfur melted at 115°C and exhibited another slight endotherm at around 180°C. An exothermic decomposition of the periodate/sulfur mix began at about 235°C and rose to a maximum at around 300°C. Figure 4 shows both the DSC and SDT of this event.

# 3.2.2 Iodate

The DSC thermogram of both the 50/50 and 80/20  $\text{KIO}_3$ /sucrose mixtures exhibited large exotherms immediately after the melt of sucrose. Figure 5 shows substantial differences between DSC and SDT. The heat release in the SDT was significantally less than in the DSC (Fig. 5), likely a result of heat of vaporization countering overall heat release. The DSC traces of iodate with 50 wt % fructose or erythritol were similar to those of sucrose, initiating an exothermic reaction immediately after the melt [11].

#### 3.2.3 Bromate

Among the oxo-halides, bromate is among the least studied. Nevertheless, the kinetics of the neat salt KBrO<sub>3</sub> have been studied by isothermal and dynamic TGA and its oxidation of alcohols reported [12, 13]. The exotherm of KBrO<sub>3</sub>/sucrose mixtures started immediately after the sugar melted. However, the initial endotherm was not easily observed. It was visible in the mix with 20% sucrose but barely detected in the 50% sucrose mix (Fig. 6). The difference between the DSC and SDT traces was considerable. The DSC exhibited a single exotherm around 206°C; the SDT trace showed that exotherm and a second one at ~374°C. The melt of fructose or erythritol initiated their decomposition with bromate. The same difference between the DSC and the SDT was also observed when the fuel was erythritol—DSC had one exotherm 211–304°C and SDT had at two 234°C and 379°C (Fig. 7).

# 3.2.4 Chlorate

The exotherm of KClO<sub>3</sub>/sucrose mixes started with a sucrose melt, 180°C. With the 50/50 mix there was only partial separation of exotherms (Fig. 8); the combined heat release totaled about 2000 J/g. Chlorate with 20 wt % sucrose had a similar thermal trace, but the first peak ( $\sim$ 180°C) was smaller than the second peak ( $\sim$ 230°C). In some traces a second exotherm was observed at  $\sim$ 336°C, the temperature at which chlorate melts

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**FIG. 4:** KIO<sub>4</sub> + 50% sulfur (mix 89)—DSC vs SDTT.

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**FIG. 5:**  $KIO_3 + 50\%$  fructose (mix 63)—DSC vs SDT.



**FIG. 6:** KBrO<sub>3</sub> + 50% sucrose (mix 91) or 20% sucrose (mix 79).

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**FIG. 7:** KBrO<sub>3</sub> + 50% erythritol (30b)—DSC vs SDT.



**FIG. 8:** KClO<sub>3</sub> + 20% sucrose (mix 73) or 50% sucrose (mix 14).

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(Fig. 8). Variations in appearance of the DSC thermograms is likely a result of how thoroughly the oxidizer and fuel were mixed. However, the occasional difference among the DSC traces was not nearly as dramatic as the difference between the DSC and SDT thermograms of the same mixture (Fig. 9). A detailed examination of the reaction between KClO<sub>3</sub> and lactose noted the importance of liquid lactose and its solubilization of the chlorate; it also noted no disporportionation into perchlorate [14, 15]. The 50/50 mix of chlorate with glucose, fructose, or pentaerythritol (PE) also exhibited the exotherm as soon as the sugar melted. Interestingly, although erythritol melted at lower temperature than PE ( $124^{\circ}$ C vs  $191^{\circ}$ C), the exothermic reaction between erythritol and KClO<sub>3</sub> did not begin immediately after the erythritol melt; it was not observed to start until 195°C, almost the same temperature as the exothermic reaction between PE and KClO3. With the chlorate/charcoal 50/50 mix in a sealed DSC tube, the exotherm was initiated by the melt of KClO<sub>3</sub>. KClO<sub>3</sub> with sulfur had one of the lowest temperature exotherms of the oxidizers with sulfur. Sulfur alone had a small endotherm around 180°C, and the chlorate/sulfur exotherm immediatelly followed this. This mixture is prone to accidental ignition [16]. In general, low-melting fuels increase sensitivity.

#### 3.2.5 Perchlorate

Although there was a slight exothermic "hump" at around 280°C where sucrose itself decomposed, the main exotherm of the 50/50 sucrose/KClO<sub>4</sub> mixtures did not occur until almost  $\sim$ 500°C (Fig. 10) [15]. Neither the melt of sucrose or fructose nor the phase change of the perchlorate ( $\sim$ 305°C) instigated the exothermic decomposition of these mixtures, but when erythritol was mixed with KClO<sub>4</sub>, exothermic decomposition began immediately after 305°C where KClO<sub>4</sub> underwent a phase change.

The appearance of the thermograms after the erythritol melt depended on whether the sample was heated open or sealed. Both showed an endotherm for the erythritol melt around 123°C, but in the open SDT container there was a second endotherm at ~277°C which blended into the perchlorate phase change at 305°C (Fig. 11). This extra endotherm was due to the vaporation of the erythritol; thus it was unclear how much fuel remained or whether it was involved in the small exothermic decomposition observed at ~644°C. In the sealed tubes, the endothermic phase change of KClO<sub>4</sub> was followed by an exotherm. The melting endotherm of KCl was around 760°C. The volatilization of the fuel in the open-container SDT was also an issue with the perchlorate/sulfur mixtures. Nevertheless, the DSC trace showed several endothermic events for the melt of sulfur polymorphs as well as the melt of KClO<sub>4</sub>. The exothermic decomposition of the mixture was not observed until almost 470°C.

The chlorates and perchlorates behaved differently under heating. KClO<sub>3</sub> with 50 wt % sucrose (mix 14) produced a large exotherm initiated by the melt of sucrose ( $\sim$ 180°C) and spanning a large range of temperatures. In contrast, KClO<sub>4</sub> with 50 wt % sucrose (mix 26) survived the endothermic melt of sucrose and its own phase change (307°C).



**FIG. 9:** KClO<sub>3</sub> + 20% sucrose (mix 73)—DSC and SDT.

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**FIG. 10:** KClO<sub>4</sub> + 50% sucrose (mix 26)—DSC and SDT.

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**FIG. 11:** KClO<sub>4</sub> + 50% erythritol (mix 45)—DSC and SDT.

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It did not exhibit an exotherm until near its own melting point about  $500^{\circ}$ C. It exhibited an endotherm at about  $760^{\circ}$ C, as did KClO<sub>3</sub>, the melt of KCl. Potassium perchlorate was particularly unaffected by its fuel, although for most fuels an exotherm could be observed above  $500^{\circ}$ C.

#### 3.2.6 Ammonium Perchlorate

NH<sub>4</sub>ClO<sub>4</sub> (AP) with 50 wt % sucrose (mix 28) or fructose (mix 29) began to exothermically decompose immediately after the sugar melted, but the heat released was small, only a few hundred joules per gram; this is likely partial decomposition of the sugar. Not until after an endotherm around 246°C, the phase change of AP, was a large exotherm (2300 J/g) observed. When there was only 20 wt % sucrose, there was no exotherm visible in the DSC trace until after the AP phase change (the SDT trace differed). Likewise, the mix of AP with erythritol did not exotherm until the AP phase change, but heat release was observed from immediately after the phase change ( $\sim 247^{\circ}$ C) to a maximum at around 438°C. In the thermograms of the AP/charcoal (mix 69) no exotherms were observed until after the AP phase change, at 247°C; however, where the first exotherms were observed depended on whether the sample was a sealed DSC sample or an open SDT sample. This observation was true for the AP sugars discussed above and the AP/sulfur (mix 85). For AP/charcoal a single sharp exotherm was observed around  $456^{\circ}C$  (~900 J/g) in the DSC trace but at  $343^{\circ}C$  (~2000 J/g) in the SDT trace (Fig. 12). This difference between the DSC and SDT traces was noted in other mixtures, but in those cases it was attributed to the volatilization of the fuel. However, with charcoal, fuel volatility was not a possible explanation. AP thermal decomposition is known to be particularly sensitive to pressure [9, 17].

#### 3.2.7 Nitrate

Although sucrose and KNO<sub>3</sub> underwent several endothermic events (melt of sucrose, phase change of KNO<sub>3</sub>), the decomposition of sucrose/KNO<sub>3</sub> mixtures did not begin until after the nitrate had melted ( $327^{\circ}$ C). Thus, with the sugars, erythritols, and charcoal, decomposition was not observed until almost 400°C (Figs. 13 and 14). With sulfur as the fuel, decomposition was observed at almost 100° lower temperature. (It should be noted with 50/50 sucrose/nitrate a small exotherm indicative of sucrose decomposition was often seen at around 265°C.)

#### 3.2.8 Nitrite

The DSC of KNO<sub>2</sub> with 50 or 20 wt % sucrose showed one large exotherm (about 1500 J/g) immediately after the melt of the sucrose. Examination of the SDT shows the same exotherm centered around 250°C, but a majority of the heat was released (about 955 J/g) at higher temperature,  $\sim$ 446°C (Fig. 15). Only with erythritol was the initial



FIG. 12: AP +50% charcoal (mix 69)—DSC and SDT.

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**FIG. 15:**  $KNO_2 + 20\%$  sucrose (mix 78)—DSC and SDT.

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exotherm above 200°C. In mix 57,  $\text{KNO}_2$ /erythritol, the exotherm centered at around 318°C, around the temperature of the melt of  $\text{KNO}_2$  and the boiling point of erythritol (Fig. 16).  $\text{KNO}_2$  with 50 wt % sulfur showed a sharp exotherm maximum at around 290°C (Fig. 17).

# 3.2.9 Ammonium Nitrate

AN, like AP, released substantial energy (~1500 J/g) without added fuel. The exothermic maximum of AN with all sugars was around 170°C; this could be the melt of the sugars or that of NH<sub>4</sub>NO<sub>3</sub>. The fact that with fructose the reaction does not occur when the fructose is completely molten, ~120°C, suggests the exothermic decomposition between AN and the sugars is facilitated when both species are molten (Figs. 18 and 19). In several of the thermograms with only 20% sucrose, heat release was not only observed at around 170°C, but also a significant, sometimes equal, exotherm at around 300°C. Despite various endotherms, the erythritols produced a single sharp exotherm at around 270°C, which is close to the normal decomposition temperature of AN. With sulfur (mix 39) and with charcoal (mix 41) the exothermic events occurred about 220°C, after the melting point of ammonium nitrate but earlier than its normal decomposition temperature (Figs. 20 and 21). The reaction with charcoal appeared at lower temperature than with any other oxidizer.



**FIG. 16:** KNO<sub>2</sub> + 50% erythritol (mix 57).

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**FIG. 20:** AN + 50% charcoal (mix 41).



# 3.2.10 Permanganate

Permanganate itself has a complex decomposition pattern [18]. As with many of the other oxidizers, the exotherm of the sugar permanganate mix started as soon as the sugar melted (sucrose, fructose, or erythritol) [19]. The exothermic region lasts through the melt of KMnO<sub>4</sub>. With fructose, decomposition also began as soon as the fructose melted, and the second exotherm occurred at the temperature where fructose decomposed  $\sim 260^{\circ}$ C (Fig. 22). The DSC of KMnO<sub>4</sub> with sulfur reached a maximum at around  $309^{\circ}$ C– $331^{\circ}$ C, where permanganate alone would decompose (Fig. 23).

# 3.2.11 Dichromate

Little heat release was seen from the dichromate mixtures with sucrose, fructose, erythritol, or charcoal [20]. With the sugars the only exotherm observed was that correlated with the decomposition of the sugar itself, around 240°C (Fig. 24). With fructose or erythritol there was a small exotherm at  $\sim$ 398°C, the melt of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Fig. 25).

# 4. SUMMARY

Thermograms of the oxidizers alone were complex, including phase change(s), decomposition, and melts of the decomposition products. Use of the open pans in the SDT

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**FIG. 23:** KMnO<sub>4</sub> + 50% sulfur (mix 86).





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further complicated thermal scans, with vaporization of some components competing with decomposition.

Interestingly, neat oxidizers appeared to undergo decomposition roughly in line with standard reduction potentials (Table 2) [21]. Most of the oxidizers produced some heat when decomposed without fuel, but it is a few hundreds of joules per gram compared to 1500 to 3000 J/g when decomposed with fuel. The exceptions, of course, are the ammonium salts, which produce 1000–1500 J/g without fuel and double that with fuel.

The oxides of chlorine released the most heat, which is in line with the general trend that the larger the electronegative difference between oxygen and the central element, the more stable the oxyhalide. This order of stability was attributed to the degree of pi-bonding in each species:  $ClO_4^- > ClO_3^-$  and  $NO_3^- > NO_2^-$  [22, 23]. Among the oxochlorine or oxo-nitrogen species, perchlorate and nitrate are more stable than the less highly oxidized chlorate and nitrite. Chlorates are generally more sensitive than perchlorates. If oxygen is not allowed to escape, the pairs nitrate/nitrite, perchlorate/chlorate, and periodate/iodate can establish a psuedoequilibrium, Eqs. (1)–(3) [22].

$$\mathrm{KClO}_4 \leftrightarrows \mathrm{KClO}_3 + 0.5\mathrm{O}_2 \tag{1}$$

$$\mathrm{KClO}_3 \leftrightarrows \mathrm{KCl} + 1.5\mathrm{O}_2 \tag{2}$$

For the oxyhalides the final product, as temperature was ramped to above 700°C, was the potassium halide, and appropriate endotherms were observed in the SDT thermogram. Details of the chlorine oxides are complicated. In a combination of controlling reactions, simplified as Eqs. (1) and (2), perchlorate decomposes to form chlorate and chloride, melting, and further decomposing until decomposition produces a resolidification and complete decomposition occurs [4, 24]. For the nitrate/nitrite pair in an enclosed environment, this occurs in the temperature regime 550°C–750°C [24]:

$$\text{KNO}_3 \leftrightarrows \text{KNO}_2 + 0.5\text{O}_2$$
 (3)

KNO<sub>3</sub> undergoes an orthorhombic to rhombohedral transformation at ~130°C and melts (333°C-334°C) to a liquid stable to 550°C. Above that the quasiequilibrium [Eq. (3)] sets in depending on the experimental conditions [25]. The decomposition of potassium nitrate and nitrite can produce NO<sub>2</sub>, NO, N<sub>2</sub>, and, finally, K<sub>2</sub>O. KNO<sub>2</sub> is reported to evolve NO<sub>2</sub> at 410°C, which is below its melting point (440°C). This continues as the temperature is raised and KNO<sub>3</sub> can be formed. Since the nitrate is more stable than the nitrite, it takes a higher temperature to result in complete decomposition [24].

In this study, DSC heat release values had standard deviation plural of over 25%. Some of the variation in heat release may have been poor mixing, despite the use of an acoustic mixer. However, in the past we have found that even scanning ammonium nitrate alone resulted in a 15% variation. We suspect that with energetic materials it may be difficult for the thermocouples to accurately track the fast release of heat. Nevertheless, the poorest oxidizer in terms of heat release was clearly potassium dichromate, with

roughly 100–200 J/g heat release with the chosen fuels. The rest of the oxidizers released heat ranging from 1100 to 2200 J/g with an average of 1500 J/g, regardless of the fuel. Of those oxidizers, nitrite released the least heat  $\sim$ 1000 J/g, while the two ammonium salts and chlorate release the most heat.

Experimentally it was found that differences in DSC and SDT traces appeared to be related to the ability of reactants/products to vaporize in the SDT open containers. Evidence for this interpretation was threefold. First, occasionally exotherms in the DSC where containers were sealed appeared as endotherms in SDT where they were not sealed. Second, certain prominent well-behaved exotherms by DSC were sometimes split into two exotherms by an overlapping endotherm. Third, total heat released was usually lower in the open crucibles compared to the closed capillary tubes.

When fuels were added to the oxidizer, the thermograms became more complicated. Lack of mixture homogeneity played a role, as did heating rate. It has been shown that ignition temperatures are affected by sample weight and heating rates [26]. Particle size has been mentioned as important. We and others [27, 28] have shown that particle size can affect the temperature at which the exotherm is observed (Fig. 26). Large particles are harder to mix homogeneously throughout the mixture; they are harder to ignite on purpose, and it is easier to accidently "excite" them. These issues make smaller particles preferable, but handling them can be a major problem.

With the exception of charcoal, all the fuels chosen for this study melted below  $200^{\circ}$ C. With the sugars, the first exotherms often occurred after the melt. In DSC scans this often appears as one large, broad exotherm having an energy content of 1000-2000 J/g. To ensure this observation was not a result of excess fuel, each oxidizer was heated



# KNO3/Charcoal 1:1 mix Particle Size vs Decomposition Temperature

FIG. 26: Effect of particle size on DSC exothermic temperature.

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with 20 wt % sucrose (i.e., below stoichiometric proportions). Three different behaviors were observed and are cataloged in Table 4.

In mixtures where DSC traces indicate appearances of exotherms during the fuel melt, SDT also demonstrated exotherms at similar positions but one or more exotherms appeared later in the scan. There was often an exotherm at around  $300-350^{\circ}$ C, where KIO<sub>4</sub> and KMnO<sub>4</sub> decompose and KNO<sub>3</sub>, KNO<sub>2</sub>, KClO<sub>3</sub>, and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> experience phase changes or melts. For KIO<sub>4</sub> the 350°C exotherm signals its decomposition. For the neat oxidizer this decomposition was conversion into KIO<sub>3</sub>; the rest of the thermal scan (up to 1000°C) was identical to that observed for KIO<sub>3</sub>. Decomposition of the 50/50 chlorate/lactose mixture has been examined in detail [14]. As in this study, per-chlorate formation was not observed. Interconversion of oxidizers becomes unimportant compared to the reaction with the fuel [Eq. (4)]. It is speculated that the decomposition of the chlorate was initiated when molten lactose partially solubilizes KClO<sub>3</sub>. Solvents with OH groups readily dissolved chlorate. We now extend that observation to a number of oxidizers.

$$8KClO_3 + C_{12}H_{12}O_{11} \cdot H_2O \to 8KCl + 12CO_2 + 12H_2O$$
(4)

With the exception of charcoal all fuels used in the study melted below 200°C. It was found that decomposition of the mixture was usually initiated by a thermal "event" in the oxidizer or the fuel. This behavior was so general that we have classified the decomposition of the fuel-oxidizer mixtures as fuel or oxidizer controlled. Oxidizer-controlled mixtures, such as those made with KClO<sub>4</sub>, NH<sub>4</sub>ClO<sub>4</sub>, or KNO<sub>3</sub>, did not exhibit substantial exotherms until the oxidizer underwent a phase change or decomposition (Table 5). Fuel-controlled mixtures underwent decomposition immediately after the fuel melt; this was the case when KIO<sub>4</sub>, KIO<sub>3</sub>, KBrO<sub>3</sub>, KNO<sub>2</sub>, KMnO<sub>4</sub>, and KClO<sub>3</sub> were mixed with the sugars. Fuel-controlled mixtures exhibited lower decomposition temperatures than oxidizer-controlled mixtures. With AN/sugar mixtures the melting point of the sugars and that of the AN were very close,  $\sim 170^{\circ}$ C; thus it was difficult to assign these mixtures as oxidizer or fuel controlled. However, when AN was mixed with pentaerythritol or erythritol, the exothermic maximum was essentially the same in both cases,  $\sim 270^{\circ}$ C, which is above the melt of the erythritols and AN, but near the normal decomposition temperature of AN.

First exotherm after fuel melt	KIO <sub>4</sub>	*	KIO <sub>3</sub>	*	KBrO <sub>3</sub>	*	KNO <sub>2</sub>	*
	1603	2	838	5	2239	4	1689	2
Principle exotherm follows	KClO <sub>3</sub>		KMnO <sub>4</sub>		NH <sub>4</sub> NO <sub>3</sub>			
melt but also other exotherms	2413	4	1798	2	2809	3		
First exotherm oxidizer con-	KNO <sub>3</sub>		NH <sub>4</sub> ClO <sub>4</sub>		KClO <sub>4</sub>		$KCr_2O_7$	
trolled	967	2	1357	3	800+		102	

**TABLE 4:** Oxidizers with 20 wt % sucrose (DSC response and average J/g)

\* Number of scans averaged

	$KCr_2O_7$	398		>398		402	50		I				>398		390		129	I				>398			100	
	$0_4$	ŝ					ω								2		0				ω					
	KMn	260,	305	melt+		239	1169		I				melt+		325		1836	270		309	808	ı				olled
	$0_3$	ŝ					4					4					4				0				2	ontro
	NH <sub>4</sub> N	130,	167, 316	melt	AN & fuel	171	2136		269+	267		2087	270		269		1817	170		219	2103	223			1611	dizer co
	5	S					З								5		S				ω					oxi
	KNO	323,	430	melt		254	1231		I				270		316		1014	290		299	1006	1				fuel or
		ů					ω					4					ω				4				4	
s)	KNO	133,	330	262,	>330	386	926		>400	471		1669	>400		413		2471	${\sim}300$		333	916	>400	467		1403	
run	$0_4$	ů					6										З				ω				ε	
umber	NH4 CI	248,	400	melt+	>248	338	2341		I				>248+	>400	313		3616	>248		422	1747	>248	450		951	tolling
g n		ç				sdt	5														ω		sdt		4	con
rage J/	KCl0	305		>400		495	1320		1				>305+		181		881	>400		468	1612	>400	526		1482	xidizer
ave		U U					ю					ω	/ \				5				m				2	
onse &	<b>KCIO</b>	350, °	415	melt+		175	2033		<mark>melt+</mark>	270		1797	200		253		2314	150		194	1031	335			1470	
espo	<u>_</u>	ç					9										З				$\top$	$\square$		_		
DSCr	KBrO	417,	460	melt		206	1110		1				melt+		229		1160	I				1				olling
uel		ç					7										З				4	$\vdash$				ontro
)wt% f	KI0	553		melt		187	1643		I				melt		185		871	220		298	659	1				fuel co
n 50	4	ů					7								sdt		7				4					
ers witl	KIO	350		melt		167	2054		I				melt+		142		1327	250		303	1410	I				
TABLE 5: Oxidize		Thermal change	,	Sugars	(130–190°C)	Peak temperature °C	J/g for 50 wt%	sucrose	PE (190, 233, 305)	Peak temperature	°C	Heat released J/g	Erythritol	(124, 330)	Peak temperature	°C C	Heat released J/g	Sulfur	(116, 180, 315)	Peak temperature °C	Heat released J/g	Charcoal	Peak temperature	°C	Heat released J/g	

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PE and erythritol (ET), both polyalcohols, were included in this study for comparison with the sugars. Since with a number of oxidizer mixtures the melt of the fuel initiated decomposition, it was thought that an alcohol with a higher melting point would impart greater thermal stability. PE (m.p. 191°C) and ET (115°C) were chosen to bracket the melting points of the sugars used in this study. It was expected that PE would impart slightly greater thermal stability to the fuel-oxidizer mixtures. For the three oxidizers (KClO<sub>3</sub>, KNO<sub>3</sub>, AN) which were examined with both erythritol and pentaerythritol, the decomposition temperature with PE was raised only slightly or not at all. The chlorate/PE mix had an exotherm which initiated immediately after the PE melt (191°C), peak maximum ~270°C. The chlorate/ET mixture had an exotherm around 253°C, but this is 50 to 60° above its melt. KNO<sub>3</sub> mixtures with any of the fuels did not experience exotherm until near its melt at 330°C; for PE and ET this resulted in peak maxima around 470°C and 413°C, respectively.

An illustration of one component control was observed in the four oxidizer mixtures containing charcoal. In three cases, the melt of the oxidizer controlled the temperature at which the exotherm of the mixture appeared: KClO<sub>3</sub> 336°C (m.p.), KClO<sub>4</sub>  $520^{\circ}$ C (m.p.), K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> 400°C (m.p.). In the fourth case, the oxidizer, AP, did not melt, and the exothermic reaction between it and charcoal occurred above the highest AP exotherm.

Sulfur is a low-melting inorganic fuel often used as part of pyrotechnic formulations. It is this low-melting property which is generally believed to make the addition of sulfur to pyrotechnic mixtures hazardous. However, only with chlorate and AN did the combination with sulfur result in exotherms around 200°C or lower. With periodate and iodate the exotherm occurs around 220°C to 250°C, which could have been connected to the polymerization of sulfur.

While heat release values had standard deviations on the order of 25%, the poorest oxidizer was clearly potassium dichromate, which yielded barely 100 J/g. The rest of the oxidizers released heat ranging from 1100 to 2200 J/g, with an average of about 1500 J/g, regardless of the fuel employed. Of those oxidizers, nitrite was the poorest, and the best were ammonium perchlorate, ammonium nitrate, and potassium chlorate. No fuel stood out as clearly the "best" in terms of releasing the most heat; they averaged 1500 J/g by DSC analysis. Response to hot-wire ignition was assessed by the length of the burn and the light output. Table 2 orders the oxidizers left to right as highest oxidizing power to lowest in terms of electromotive potential. This trend is roughly followed by burn time, either measured visually or by light-sensitive detector. The fastest burn time oxidizers are on the left (highest oxidizing power) and those with longest burn times are on the right. Light output, when the fuel was sucrose, did not show a clear trend. However, when the fuel was aluminum, those on the furthest to the right of the table, i.e., those with the lowest oxidation potential, failed to light the aluminum. Seemingly out of place in this series is AN, which is high in heat output, and dichromate, which is extremely low in heat output.

# REFERENCES

- Johns, C., Shellie, R. A., Potter, O. G., O'Reilly, J. W., Hutchinson, J. P., Gu ijt, R. M., Breadmore, M. C., Hilder, E. F., Dicinoski, G. W., and Haddad, P. R., Identification of homemade inorganic explosives by ion chromatographic analysis of post-blast residues, *J. Chromatogr. A*, 1182:205–214, 2008; Kuila, D. K., Chakrabortty, A., Sharma, S. P., and Lahiri, S. C., Composition profile of low explosives from cases in India, *Forensic Sci. Int.*, 159:127–131, 2006.
- U.N. Manual of Tests and Criteria, Section 34, 5th revised ed., United Nations Economic Commission for Europe, 2010.
- Markowitz, M. M., Boryta, D. A., and Stewart, H., Jr., The differential thermal analysis of perchlorates, VI. Transient perchlorate formation during the pyrolysis of the alkali metal chlorates, *J. Phys. Chem.*, 68(8):2282–2289, 1964.
- Harvey, A. E., Wassink, C. J., Rodgers, T. A., and Stern, K. H., Isothermal and isopiestic decomposition of potassium perchlorate and potassium chlorate, *Ann. N.Y. Acad. Sci.*, 79:971–987, 1960.
- Rudloff, W. K. and Freeman, E. S., The catalytic effect of metal oxides on thermal decomposition reactions, I. The mechanism of the molten-phase thermal decomposition of potassium chlorate and of potassium chlorate in mixtures with potassium chloride and potassium perchlorate, *J. Phys. Chem.*, 78(5):1209–1215, 1969.
- Muraleedharan, K., Abdul Mujeeb, V. M., Aneesh, M. H., Gangadevi, T., and Kannan, M. P., Effect of pre-treatments on isothermal decomposition kinetics of potassium metaperiodate, *Thermochim. Acta*, 510:160–167, 2010.
- Phillips, B. R. and Taylor, D., Thermal decomposition of potassium metaperiodate, J. Chem. Soc. (Resumed), pp. 5583–5590, 1963; Takriti, S. and Duplâtre, G., Decomposition of KIO<sub>4</sub> and NaIO<sub>4</sub> in relation to solid-state isotopic exchange reactions, J. Chem. Soc., Faraday Trans., 84(8):2831–2841, 1988; Hector, A. L., Henderson, S. J., Levason, W., and Webster, M., Hydrothermal synthesis of rare earth iodates from the corresponding periodates: Structures of Sc(IO<sub>3</sub>)<sub>3</sub>, Y(IO<sub>3</sub>)<sub>3</sub> · H<sub>2</sub>O, La(IO<sub>3</sub>)<sub>3</sub> · 1/2H<sub>2</sub>O, and Lu(IO<sub>3</sub>)<sub>3</sub> · 2H<sub>2</sub>O, Z. Anorg. Allg. Chem., 628:198–202, 2002.
- 8. Fairbrother, F., The spontaneous decomposition of ammonium chlorate, *J. Am. Chem. Soc.*, 44(11):2419–2422, 1922.
- Kraeutle, K. J., The response of ammonium perchlorate to thermal stimulus, Report to Ammonium Perchlorate Technical Consortium, Naval Weapons Center, China Lake, CA, 1989.
- Hughes, G. and Nevell, T. P., The mechanism of the oxidation of glucose by periodate, *Trans. Faraday Soc.*, 44:941–948, 1948; Honeyman, J. and Shaw, C. J. G., Periodate oxidation, Part III. The mechanism of oxidation of cyclic glycols, *J. Chem. Soc.*, 492:2451– 2454, 1959.
- Muraleedharan, K. and Kannan, M. P., Thermal decomposition kinetics of sodium metaperio- date, *React. Kinet. Catal. Lett.*, 39(2):339–344, 1989; Muraleedharan, K., Kannan, M. P., and Ganga Devi, T., Thermal decomposition kinetics of potassium iodate, *J. Therm. Anal. Calorim.*, 103:943–955, 2011.

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- Diefallah, E.-H. M., Basahl, S. N., Obaid, A. Y., and Abu-Eittah, R. H., Kinetic analysis of thermal decomposition reactions: I. Thermal decomposition of potassium bromate, *Thermochim. Acta*, 111:49–56, 1987.
- Natarajan, R. and Venkatasubramanian, N., Kinetics and mechanism of oxidation of secondary alcohols by potassium bromate, *Tetrahedron*, 30(16):2785–2789, 1974.
- Scanes, F. S. and Martin, R. A. M., Heats of reaction of pyrotechnic compositions containing potassium chlorate, *Combust. Flame*, 23:357–362, 1974; Scanes, F. S., Thermal analysis of pyrotechnic compositions containing potassium chlorate and lactose, *Combust. Flame*, 23:363–371, 1974.
- Hosseini, S. G., Pourmortazavi, S. M., and Hajimirsadeghi, S. S., Thermal decomposition of pyrotechnic mixtures containing sucrose with either potassium chlorate or potassium perchlorate, *Combust. Flame*, 141:322–326, 2005.
- Pakkirisamy, S. V., Mahadevan, S., Paramashivan, S. S., and Mandal, A. B., Adiabatic thermokinetics and process safety of pyrotechnic mixtures, *J. Therm. Anal. Calorim.*, 109:1387–1395, 2012; Tanner, H. G., Instability of sulfur-potassium chlorate, *J. Chem. Educ.*, 36(2):58–59, 1959.
- 17. Inami, S. H., Rosser, W. A., Jr., and Wise, H., Heat-release kinetics of ammonium perchlorate in the presence of catalysts and fuel, *Combust. Flame*, 17:41–44, 1968.
- Herbstein, F. H., Kapon, M., and Weissman, A., Old and new studies of the thermal decomposition of potassium permanganate, *J. Therm. Anal.*, 41:303–322, 1991.
- Odebunmi, E. O. and Owalude, S. O., Kinetics and mechanism of oxidation of some simple reducing sugars by permanganate ion in alkaline medium, *J. Iran. Chem. Soc.*, 5(4):623– 630, 2008; Odebunmi, E. O., Iwarere, S. A., and Owalude, S. O., Kinetics of oxidation of fructose, sucrose, and maltose by potassium permanganate in NaHCO<sub>3</sub>/NaOH buffer and iridium (IV) complex in sodium acetate/acetic acid buffer, *Int. J. Chem.*, 16(3):167–176, 2006.
- Charsley, E. L. and Chen, C.-H., Differential thermal analysis and temperature profile analysis of pyrotechnic delay systems: Ternary mixtures of silicon, boron and potassium dichromate, *Thermochim. Acta*, 35(2):141–152, 1980.
- Ayres, G. H., *Quantitative Chemical Analysis*, 2nd ed., Appendix V, Harper and Row Publishers, New York, 1968; *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983–1984.
- Chantry, G. W. and Plane, R. A., Raman intensities of the A1 lines of oxyanions, *J. Chem. Phys.*, 32(2):319–321, 1960; Chantry, G. W. and Plane, R. A., Raman intensities and the structure of some oxyanions of group VII, *J. Chem. Phys.*, 34:1268–1271, 1961.
- 23. Wagner, E. L., Bond character in XY<sub>M</sub>-type molecules: Chlorine-oxygen compounds, J. *Chem. Phys.*, 37(4):751–759, 1962.
- 24. Stern, K., High temperature properties and decomposition of inorganic salts, J. Phys. Chem. Ref. Data, 1(3):747–772, 1972.
- 25. Olivares, R. I., The thermal stability of molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres, *Solar Energy*, 86:2576–2583, 2012.
- 26. Barton, T. J., Williams, N., Charsley, E. L., Ramsey, J., and Ottaway, M. R., Factors af-

fecting the ignition temperature of pyrotechnics, *The 8th Intl. Pyrotechnics Symposium*, Steamboat Springs, CO, pp. 99–111, 12–18 July 1982.

- Pourmortazavi, S. M., Hajimirsadeghi, S. S., Kohsari, I., Fathollahi, M., and Hosseini, S. G., Thermal decomposition of pyrotechnic mixtures containing either aluminum or magnesium powder as fuel, *Fuel*, 87:244–251, 2008; Pourmortazavi, S. M., Hajimirsadeghi, S. S., and Hosseini, S. G., Characterization of the aluminum/potassium chlorate mixtures by simultaneous TG-DTA, *J. Therm. Anal. Calorim.*, 84(3):557–561, 2006.
- Shafirovich, E., Mukasyan, A. S., Varmak, A., Kshirsagar, G., Zhang, Y., and Cannon, J. C., Mechanism of combustion in low-exothermic mixtures of sodium chlorate and metal fuel, *Combust. Flame*, 128:133–144, 2002.