Use of ARC in screening for explosive properties

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Available online 31 July 2004

Abstract

The use of a modified version of the accelerating rate calorimeter (ARC) as a screening method for the explosive properties of chemicals has been investigated. Definitive tests for classifying energetic chemicals for transportation are provided by UN Recommendations [United Nations, Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, third revised ed., 1999]. Recently, decomposition energy screening criteria were added to the recommendations, however, maximum rate of pressure rise in a closed vessel may provide a less conservative, more accurate screen. Pressure rate data for organic chemicals are compared to the UN test results. Preliminary screens are suggested to minimize the need for the larger scale, more expensive, and time-consuming UN-recommended testing. Results from this method are compared to those from published mini-autoclave data [M.W. Whitmore, G.P. Baker, J. Loss Prev. Process Ind. 12 (1999) 207–216]. Further work is planned to expand the range of chemical classes tested and to specify acceptable, conservative screening criteria.
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Keywords: ARC; Explosives screening; Transport classification; Koenen; UN Gap; Time/Pressure

1. Introduction

Domestic and international requirements mandate classification of hazardous chemicals as a prerequisite for their transport. Class 1 Explosives, Division 4.1 Self-Reactives, and Division 5.2 Organic Peroxides cover chemicals with explosive hazards. The UN Recommendations test methods [2] specified for classification of energetic materials can be expensive and time consuming, and require quantities of chemicals that may not be available early in development. Readily applied, conservative filtering methodologies would minimize the need for this testing. Recently, Appendix 6 "Screening Procedures" was added to the UN Recommendations [3], providing examples of chemical groups indicating explosive properties and decomposition energy thresholds triggering the need for definitive testing. The energy breakpoints chosen are necessarily quite conservative because explosive properties as a function of decomposition energy vary widely by energetic functional group. Other considerations such as expected gas generation, knowledge of hazardous

energy levels by functional group, empirical information including UN method test results for analogs, DSC and accelerating rate calorimeter (ARC) data, etc. can be employed to reduce the number of candidates. Yoshida et al. [4] provided a useful relationship between DSC decomposition energy and extrapolated onset temperature to predict explosion propagation. More recently, Whitmore and Baker [1] and others have done promising work using the lab-scale Kuhner mini-autoclave indicating that the rate of pressure rise during decomposition in a closed pressure vessel may produce a more precise winnowing approach covering the gamut of Class 1 properties: detonation, deflagration, and heating under confinement.

This paper describes a new method utilizing ARC equipment for Class 1 screening and relates the resulting data to the three recommended Class 1 tests. This method may also be useful for screening for Division 4.1 Self-Reactives and Division 5.2 Organic Peroxides; however, since three additional tests are also specified for this task in Test Series C and E, its use for that purpose is premature. Understanding the potential of a material to detonate, or deflagrate, or to generate pressure rapidly under confinement is not only important for transport but also for other operations, including manufacture, storage, and waste destruction.

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2. Experimental

DSC experiments were conducted using the TA Instruments Model 2920 calorimeter. A sample of about 1 mg was sealed under nitrogen in a glass capillary [5], placed in a silver cradle, and heated in scanning mode at 10 °C/min from 25 °C to 420 °C. The instrument was calibrated using a dedicated 1 mg indium standard in a glass capillary at 10 °C/min. The TA2920 DSC computer automatically updates the cell constant, onset slope, and temperature correction factors.

The ARC experiments were conducted using a first-generation ARC with several modifications. The thermocouple attached to the outside of the sample bomb was used only to record the sample temperature. A second thermocouple was used to control the temperature ramp rate. It was attached directly to the side of a reference bomb placed below the sample bomb on the calorimeter floor. The bombs used were Hastelloy C 1 in. i.d., 0.035 in. walled sphere with 1/4 in. o.d. × 0.035 in. wall × 1 in. stem without clip. The bottom radiant heater was inactivated. A constant ramp rate of 5 °C/min, measured and controlled by the thermocouple attached to the reference bomb, was accomplished using custom software. The pressure system consisted of the bomb, 18 in. of 0.066 in. i.d. 316SS tubing, and a Sensotec Model TJE 0–10,000 psi pressure transducer, accuracy ±0.1% FS. A shunt calibration of the transducer was performed prior to each run. The thermocouples were N type (metal-sheathed, 0.032¨ in. o.d.). Temperature and pressure data was acquired using a customized LabVIEW program that recorded up to 10,000 points/s for each of four channels. The bomb void volume when loaded with a 1 g sample was approximately 8 mL; the tubing added about 1 mL. Experiments were conducted starting at room temperature and ending after the exotherm was completed. Sample size was generally nominally 1.0 g, except 0.5 g for more energetic materials. The parameters of interest were the peak temperature (T_p) and maximum rate of pressure rise (dP/dt_{max}). T_p was defined as the temperature measured by the reference bomb thermocouple at the point of maximum-recorded sample temperature. The dP/dt_{max} was determined using a nine-point moving regression of the seven-point moving median pressure data. The DSC and ARC experiments were run using aliquots of the same sample for each of 17 substances.

The test results from the three recommended UN Class 1 methods [2] were acquired for the 17 substances from a number of sources and, therefore, were generally run on different samples than those used for the DSC and ARC experiments, and they were conducted over a substantial period of time. The methods were the UN Gap Series 1(a) for detonation, Koenen for heating under confinement, and Time/Pressure for deflagration. BAM 50/60 Steel Tube and TNO 50/70 Steel Tube results were used as surrogates for the UN Gap when UN Gap results were not available. The BAM and TNO tests were recommended Class 1 detonation tests in the past [6] and are considered to be reliable.

3. Results and discussion

Table 1 provides an explosivity-ranking scheme based on the three recommended UN tests. It is identical to that used by Whitmore and Baker [1], except this scheme gives precedence to the UN Gap result over the BAM 50/60. Ranks A and B identify potential Class 1 substances: A indicates substances that detonated, and B indicates those that did not detonate but were strongly positive in the Koenen and/or Time/Pressure. Rank C substances, those with milder results in the Koenen and Time/Pressure tests, will not be Class 1 but are candidates for classification as Self-Reactives or Organic Peroxides, if they are sufficiently thermally unstable. Rank D substances exhibited no positive results but may still be Self-Reactives or Organic Peroxides, based on the results of the other recommended tests. Also shown in Table 1 are the ARC-based dP/dt_{max} and T_p breakpoints for predicting explosivity rank. These criteria were derived empirically and were chosen to maximize the percent of predicted ranks equal to the actual rank while minimizing those predictions that are

Table 1
Explosivity rank and predictive ARC breakpoints

Explosivity rank	Severest Class 1 property	Correspondence to UN classification	Preliminary breakpoints based on ARC dP/dt_{max} (Mpsi/min), T_p (°C)
A	Detonates (positive result in UN Gap, or BAM 50/60 or TNO 50/70 if UN Gap unavailable)	Potentially Class 1	$dP/dt_{max} \geq 2.25$
B	Heating under confinement: violent (Koenen limiting diameter ≥ 2 mm), and/or Deflagration: rapidly (pressure in Time/Pressure ≥ 2070 kPa in <30 ms)	Potentially Class 1 but not detonable	$0.25 \leq dP/dt_{max} < 2.25$ and $dP/dt_{max} \geq 0.04T_p - 5$
C	Heating under confinement: medium or low (Koenen limiting diameter ≤ 1.5 mm), and/or Deflagration: slowly (pressure in Time/Pressure ≥ 2070 kPa in ≥ 30 ms)	Not Class 1	$0.25 \leq dP/dt_{max} < 2.25$ and $dP/dt_{max} < 0.04T_p - 5$
D	No effect of heating under confinement, and does not deflagrate (pressure rise in Time/Pressure < 2070 kPa)	No explosive properties with respect to transport classification	$dP/dt_{max} < 0.25$

Table 2
DSC, ARC, explosivity test results, and actual vs. predicted rank

Material	DSC H_d (J/g)	DSC R_{max} (W/g)	ARC sample mass (g)	ARC T_p (°C)	ARC pressure (psi)	ARC dP/dt_{max} (Mpsi/min)	Koenen	Time/Pressure	UN Gap	Actual rank	Predicted rank
Benzoyl peroxide 100%	1211	10.0	1.01[a]	111[a]	1368[a]	49.56[a]	Violent	Rapid	Yes[c]	A	A
Benzoyl peroxide 70% with H_2O	908	6.0	1.01	112	1073	17.96	Violent	Rapid	Yes (no[c])	A	A
2-Bromo-2-nitropropane-1,3-diol	2154	24.6	1.01	216	4255	11.49	Low	No	Yes[c]	A	A
2,2′-Dithiobis(4-methyl-5-nitrothiazole)	2221	13.8	1.02[a]	214[a]	3732[a]	8.95[a]	Medium	Slow	Yes	A	A
3,5-Dinitrobenzoic acid	2909	38.6	**0.50**	**364**	**3355**	**6.80**	Low	NA	Yes	A	A
4-Nitrophenylhydrazine 100%	2377	7.7	**0.50**	**190**	**2828**	**5.30**	Violent	Rapid	Yes	A	A
2-Chloro-5-nitrobenzoic acid	1722	14.4	1.01[b]	349[b]	4021[b]	2.49[b]	Medium	No	Yes	A	A
2-Diazo-1-napthol-5-sulphochloride	859	5.3	1.01	131	1964	1.52	Violent	NA	No[c]	B	B
t-Butyl peroxybenzoate	1333	5.7	0.98	123	1494	2.03	Violent	Slow	No[c]	B	B
4-Nitrophenylhydrazine 76% with H_2O	2224	6.2	**0.50**	**194**	**3071**	**6.83**	Medium	No	No	C	**A**
2-Amino-4-chloro-5-nitrophenol	1685	35.4	1.01	237	3888	3.06	Low	Slow	No	C	**A**
3-Nitrobenzenesulfonic acid sodium salt	1099	50.4	1.01	349	2235	0.72	No	Slow	No	C	C
1-Phenyl-5-mercapto tetrazole	1235	32.9	1.01	158	1278	0.72	Low	Slow	No[d]	C	C
Di-t-butyl peroxide	1253	6.8	0.96	161	1310	0.36	No	Slow	No[c]	C	C
Benzenediazonium, 2-methoxy-4-(phenylamino)-, sulfate (1:1)	832	12.1	1.01	189	660	0.11	Low	No	No	C	**D**
3-Thiosemicarbazide	908	6.1	1.01	194	904	0.11	No	No	No	D	D
Dilauroyl peroxide	721	3.9	1.01	101	410	0.11	No	No	No[c]	D	D

0.5 g ARC results in bold.

[a] Mean of three runs.

[b] Mean of two runs.
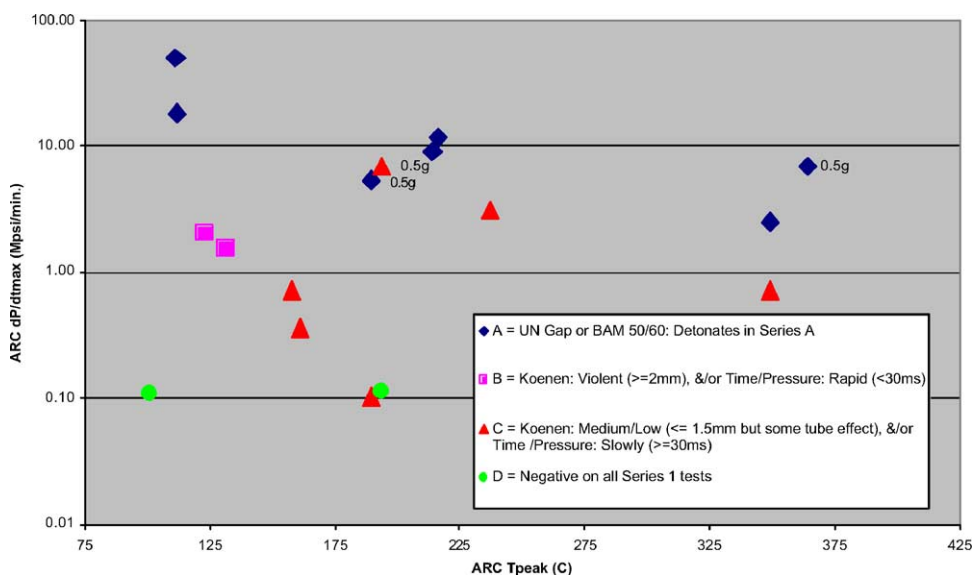
[c] BAM 50/60.

[d] TNO 50/70 instead of UN Gap.

Fig. 1. Actual explosivity rank related to ARC dP/dt_{max} and T_p.

nonconservative. The proposed cutoffs in Table 1 are best understood with reference to Fig. 1.

Table 2 provides the DSC, ARC, and UN explosivity test results for the chemicals, as well as their actual and predicted rank. It is clear that rate of pressure rise in ARC is a better predictor of explosivity rank than DSC enthalpy (H_d) or even DSC enthalpy and peak power per unit mass (R_{max}) taken together. For example, benzoyl peroxide has one of the lowest heats of decomposition and a modest R_{max}, but it resulted in the highest dP/dt_{max} and was positive in all three UN tests. A slightly more energetic substance with a much higher R_{max}, 1-phenyl-5-mercapto tetrazole, has a low dP/dt_{max} and was negative or low in all three UN tests. For B and C ranked substances, there is also an apparent trend for those ranked B to have a lower T_p, see Fig. 1. This is not surprising when one considers the hazard properties and the methods involved in the Time/Pressure and Koenen tests. For a positive result to occur in the Time/Pressure test, the

deflagration front must generate sufficient heat to raise the temperature of adjacent unreacted material to the point where decomposition will begin. The lower the T_p, the more readily this will occur. For the Koenen test, it seems probable that a lower T_p will result in a greater fraction of the material decomposing simultaneously, and that a lower T_p will tend to result in more decomposition prior to loss of unreacted material from the tube due to boiling. All of the "Rapidly" or "Violent" outcomes occur for substances with $T_p <$ 200 °C.

Comparing the actual and predicted ranks in Table 2, 14 coincide, 2 predicted ranks are conservative and 1 is non-conservative. The single nonconservative outcome is at the C versus D level, which is less critical because neither denotes a potential Class 1 material. These breakpoints are preliminary; testing of additional materials is needed.

The standard deviation and associated coefficient of variance for three ARC parameters are shown in Table 3 for three

Table 3
ARC repeatability

Material	T_p (°C)	P_{max} (psi)	dP/dt_{max} (Mpsi/min)
Benzoyl peroxide 100% (sample mass 1.01 ± 0.00 g)			
Mean	111	1370	50
Standard deviation	1	70	4
Coefficient of variance (%)	1	5	8
2,2′-Dithiobis(4-methyl-5-nitrothiazole) (sample mass 1.02 ± 0.01 g)			
Mean	214	3700	9.0
Standard deviation	6	100	0.7
Coefficient of variance (%)	3	3	8
Di-t-butyl peroxide (sample mass 1.95 ± 0.02 g)			
Mean	160	3800	1.77
Standard deviation	3	20	0.04
Coefficient of variance (%)	2	0.5	2
Coefficient of variance (nine tests) (%)	2	3	6

Table 4
ARC and mini-autoclave comparison data

Chemical	ARC			Mini autoclave			Actual rank
	T_p (°C)	P_{max} (psi)	dP/dt_{max} (Mpsi/min)	T_p (°C)	P_{max} (psi)	dP/dt_{max} (Mpsi/min)	
Benzoyl peroxide 100%	111[a]	1368[a]	49.56[a]	86	1286	2.95	A
Benzoyl peroxide 70% with water	112	1073	17.96	89	1250	2.56	A
2-Bromo-2-nitropropane-1,3-diol	216	4255	11.49	172	2573	3.62	A
t-Butylperoxybenzoate	123	1494	2.03	108	1213	0.49	B
Dilauroyl peroxide	101	410	0.11	68	184	0.02	D

Sample size: 1 g, all mini autoclave data is mean of two runs.

[a] Mean of three runs.

substances, indicating excellent repeatability for T_p and P_{max} and very good repeatability for dP/dt_{max}.

Table 4 provides all available comparison data between the ARC and Kuhner mini-autoclave [1]. Although the testing was performed on different samples, the results for all three parameters follow the same trends. Using their respective explosivity breakpoints, both methods predict the correct rank for all five substances. Similar relative results would be expected from the two methods because both are closed pressure vessel tests using similar temperature ramp rates (5 °C/min versus 2.5 °C/min) and sample mass-to-vessel volume ratios (0.1 g/mL versus 0.17 g/mL). Demonstrating that the ARC method has similar predictive capability for ranking is useful. The 2001/2002 biennium Programme of Work of the UN Committee of Experts on the Transport of Dangerous Goods includes a joint Japanese/Netherlands proposal [7] to develop a Modified Closed Pressure Vessel Test, anticipated to be the mini-autoclave, as a screening procedure in the UN Recommendations for potential Class 1 substances.

4. Conclusions

A modified ARC test method has been described which shows promise as a screen for identifying potential Class 1 materials. The rate of pressure rise data obtained are substantially more predictive of Class 1 properties and explosivity rank than the traditional energy screens such as those in UN Recommendations [3]. The method provides predicted explosivity ranks similar to those from the mini-autoclave method, which may eventually be adopted as a UN recommended screen. The method should be valuable as a supplement to current approaches for identifying and categorizing likely explosivity hazards in manufacture, storage, and waste destruction. Additional work is needed to demonstrate the validity of the method for a wider variety of substances and to better define appropriate pressure rate and temperature breakpoints for the explosivity ranks.

References

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