DIERS ROUND-ROBIN INVITATION

Date: October 14, 2022

To: All DIERS members

From: Marc Levin / DIERS Round-Robin Testing Committee

Reaction: DTBP (di-tert-Butyl Peroxide) in Toluene

*** Please see below for specific instructions ***

For questions and data submittal, please contact:

- Marc Levin: marc.levin@gmail.com (data submission and general questions)
- Kevin Kunkel: kunkel@fauske.com (VSP2 and ARSST questions)
- S.K. Singh: singh@belmontscientific.com (DSC, ARC, and APTAC questions)

Please submit data no later than March 6, 2023. *Submitted data will be "sanitized" to obscure its origin before sharing with DIERS membership.*

Results will be discussed at the Spring 2023 DIERS meeting.

Thank you all in advance for your participation!!!

DIERS Round-Robin Test

20 wt% DTBP/Toluene

As part of the re-launch of DIERS Round-Robin Testing Committee's activities, the next round-robin testing system revisits DTBP (20 wt%) in toluene. This is a common, standard system for testing calorimeters that is relatively easy to perform.

This recipe uses two chemical species:

(1) **di-tert-Butyl Peroxide (DTBP)** (MW = 146.23, CAS#110-05-4). The molecular formula is $(CH_3)_3COOC(CH_3)_3$ and the species is also known as Luperox®. Sigma-Aldrich / Millipore-Sigma offers 98% purity in 5 ml (SKU 168521-5ML), 250 ml (SKU 168521-250ML), and 1 liter (SKU 168521-1L) quantities. The recommended storage temperature is 2-8°C. It is also helpful to avoid repeated exposure of the peroxide to air (for example, do not open & close the bottle many times unless in a purged dry box).

(2) **Toluene** (MW = 92.14, CAS#108-88-3). The molecular formula is $C_6H_5CH_3$. Sigma-Aldrich / Millipore-Sigma offers ≥99.5% purity in 500 ml (SKU 179418-500ML) and 1 liter (SKU 179418-1L) quantities.

Obtaining the chemicals from Sigma-Aldrich / Millipore-Sigma is strongly preferred.

The proposed recipe is a DTBP concentration of 20 wt% with toluene at 80 wt%, or:

DTBP – 20 units (mass)
Toluene – 80 unit (mass)

ARC/VSP2/APTAC/ARSST/DSC Test Conditions

	ARC (Netzsch or CSI)	VSP2	APTAC	ARSST	DSC
Test cell material	SS	304 SS	Titanium	Pyrex Glass	SS or other
Volume of test cell [ml]	~10	110	130	10	20-40 μL
DTBP [g]	0.86	9.0	12.0	1.76	([4])
Toluene [g]	3.40	36.0	48.0	7.04	([4])
Total sample charge [g]	4.26	45.0	60.0	8.80	([4])
Stirring rate [rpm]	300[1]	300	500	([2])	N/A
Test start temperature [°C]	80	80	80	ambient	ambient
Test end temperature [°C]	250	250	250	270	300
Temperature step size [°C]	5	5	5	([3])	([3])
Exotherm threshold [°C/min]	0.02	0.20	0.04	N/A	N/A
Pad gas	Air	Air[5]	Air	Nitrogen	Air

[1]where stirring is available
[2]Setting of 7 or 8 (see procedure)
[3]ARSST heating rate nominally at 2°C/min; DSC heating rate at 10°C/min
[4]20 wt% DTBP / 80 wt% toluene with a sample mass-to-crucible volume ratio of 1:4 – 1:3 mg:μL
[5]Can be evacuated initially to measure vapor pressure

ARC Test Procedure (additional run guidance available)

It is recommended that one should use a 1/8” stainless steel pressure transfer tube connected to the pressure transducer through 1/16” tubing. The pressure transducer fitting should be filled with silicone oil. It is also recommended to use a Netzsch-supplied plug inside the fitting over the pressure transducer to reduce the void volume inside the fitting. In any case, a photograph or drawing/sketch of the pressure tube configuration is requested to be documented and shared along with data submission. Your instrument should be calibrated and drift tested before starting the test. It is recommended that the pressure transducer be calibrated by (1) heating water and comparing the observed pressure at particular temperatures with the literature vapor pressure for those temperatures or (2) against a more accurate pressure sensor/gauge connected to the same pressure supply.

1. Record weight of test cell (stainless steel cell, ~13 g), nut, ferule.
    a. A titanium nut is recommended
    b. 316 SS ferrules are okay for reducing thermal inertia
2. Prepare the mixture according to the formulation in the above table.
3. Weigh the mixture in the test cell (stainless steel cell, ~13g).
4. Attach the test cell to the calorimeter at ambient pressure and temperature
5. Enter the test parameters below:
    a. Head space = air
    b. Start temperature = 80°C
    c. Heat step = 5°C
    d. Heating rate between steps = 2°C/min
    e. Exotherm detection threshold = 0.02°C/min
    f. End Temperature = 250°C
    g. Cool down temperature = 35°C (preferably without compressed air cooling)
    h. Shut down if temperature rise rate is >100°C/min
    i. Shut down if Pressure is more than 3000 psia
    j. Wait time = 25 min
    k. Heat mode = heat wait search
    l. Turn on the radiant heater (if present)
    m. Enable collection of cool down data
6. Record cool down pressure, temperature, ending weight of test cell with remaining sample

VSP2 Test Procedure (additional run guidance available)

Follow recommended pre-test campaign checks (see complete VSP document)

1. Obtain required materials and equipment.
2. Document materials and equipment.
3. Perform systems checks (see complete VSP document).
4. Program Experimental Parameters (see complete VSP document).
5. Set-up test cell and heater and insulation assembly and install into VSP2 containment vessel.
6. Configure Balancing Gas Supply (see complete VSP document).
7. Evacuate containment vessel and test cell headspace.
8. Isolate the vacuum source from the pressure control cabinet.
9. Load chemicals to test cell through fill line:
    a. Pre-mix solution.
    b. Inject solution to test cell.
    c. Document mass of sample injected to test cell.
10. Allow air to enter the test cell headspace through the fill port until the test cell headspace reaches atmospheric pressure, then isolate the fill port.
    a. Alternatively, if it is desired to obtain temperature-pressure data without an air pad, then instead of allowing air through the fill port, briefly turn the three-way ball valve to the bypass line to the containment vessel to remove any residual air in the test cell headspace (refer to footnote 5 in the table above).
11. Initiate experiment:
    a. Enable Stirring: 300 rpm (Super Magnetic Stirrer)
    b. Enable Automatic Pressure Balancing
    c. Enable Guard Heater (Auto Hi/Lo)
    d. Enable Auxiliary Heater (Lo)
    e. Vent throttle valve: full open
    f. Nitrogen throttle valve: ¼ to 1 full turn open (initially)
12. Monitor systems as necessary:
    a. Adjust Nitrogen throttle valve accordingly during runaway.
13. Once reaction has completed, disable heaters and allow the sample to cool down.
14. After the sample has cooled down to below 30°C, stop the experiment and exit the control software.
15. Depressurize the test cell, as described below
    a. Open a new instance of the VSP2 control software.
    b. Enter the appropriate psi/volt for the pressure sensors.
    c. Continue to experiment window and begin experiment.
    d. Enable automatic pressure balancing and disable the stirring.
    e. Depressurize test cell and containment vessel pressure.
    f. Highly recommended to install a metering valve on the test cell fill line port and depressurize slowly using the metering valve as a throttle.
16. Remove test cell from containment vessel and heater assembly.

17. Record final mass of test cell and sample.

APTAC Test Procedure

Your instrument should be calibrated and drift tested before starting the test.

1. Use a 2-½ inch diameter titanium or stainless steel APTAC test cell (APTAC test cells can be purchased from https://store.fauske.com/shop-all/arc/test-cells/aptac/)
2. Record the weight of the test cell, stir-bar (1” Teflon coated stir bar, curved end), nut, ferrule.
3. Drop the stir bar into the test cell.
4. Add the prescribed amounts of DTBP and toluene into the test cell.
5. Place the nut and ferrule onto the test cell.
6. Attach the test cell to the APTAC.
7. Evacuate the test cell to 2-3 psia or when pressure stops dropping using vacuum pump.
8. Enter the test parameters below:
    a. Head space = air
    b. Start temperature =50°C
    c. Heat step = 5°C
    d. Heating rate between steps = 5°C/min
    e. Exotherm detection threshold = 0.04°C/min
    f. End Temperature = 300°C
    g. Cool down temperature = 35°C
    h. End temperature in case of exotherm = 350°C.
    i. Stirrer speed = 500 rpm
    j. Wait time = 25 min
    k. Search time = 25 min
    l. Exotherm exit time = 10 min
    m. Heat mode = heat wait search
9. Shut down criteria:
    a. Temperature >400°C
    b. Self-heat rate > 400°C/min
    c. Pressure rise rate > 5000 psi/min
    d. Pressure > 1500 psi
10. Record cool down pressure, temperature, weight of cell with products

ARSST Test Procedure (additional run guidance available)

Follow recommended pre-test campaign checks (see complete ARSST document)

1. In the ARSST Software: enter the test name.
2. Record the empty test cell mass.
3. Place the stir bar into test cell and record mass.
4. Record the resistance of the Digital Multimeter (DMM) test lead probes.
5. Record the resistance of the ARSST heater.
6. Subtract the resistance of the DMM test leads from the ARSST heater.
7. Enter the value calculated from previous step into the heater resistance input field on the ARSST control software. (Default value is 24 ohms).
8. In the ARSST Software: On the test set-up page ensure that the following parameters entered/programmed, as specified in the complete ARSST document.
9. Attach the ARSST heater to the test cell and secure with heater belt. It is permissible to cut off excess steel wire from the heater belt.
10. Apply aluminum foil wrap around the test cell and heater assembly. Smooth foil to outer surface of test cell and heater belt.
11. Place the test cell and heater assembly into the insulation contained inside of the insulation sheath.
12. Secure the top half of the insulation sheath to the bottom half using supplied tape or stainless steel wire.
13. Apply tape around the bottom perimeter of the insulation sheath assembly where the top and bottom halves meet.
14. *Optional: record the mass of the insulated test cell assembly.*
15. Install insulated test cell assembly into the ARSST containment vessel.
16. Connect TC 1 thermocouple gland to the thermocouple destined for the sample temperature measurement.
17. *Optional: Connect TC 2 thermocouple gland to the thermocouple destined for the gas space temperature measurement. Or connect TC 2 to monitor the room temperature.*
18. Make necessary signal and electrical connections.
19. Verify proper equipment electrical grounding.
20. Install the thermocouple and extension tube assembly to the neck of the test cell.
21. Prepare a 10-20 gram solution of 20 wt.% DTBP in toluene in a clean Erlenmeyer flask.
22. Load the 20 wt.% DTBP in toluene solution into an all-plastic syringe or all-glass syringe. (Reminder: Account for hold-up)
23. Slowly charge 8.8 grams of the sample directly through the 1⁄4” diameter test cell neck with a syringe. Do not use the fill tube on the vessel lid if one is present.
    a. Charge mass tolerance; +/- 0.2 grams
    b. Record the mass of 20 wt. % DTBP in toluene charge to the test cell.
24. Ensure that the sample thermocouple is positioned appropriately and is secure.
25. Ensure that the gas space thermocouple is positioned appropriately and is secure.
26. Seal the containment vessel.

27. Pressurize the test cell and containment vessel with 300 psig of nitrogen.
    a. Allow for gas space temperature to return to within the ambient temperature range (20°C to 27°C).
    b. Top off nitrogen backpressure as needed.
    c. Tolerance for initial backpressure of nitrogen: +10/-5 psig.
28. Enable stirring and set the speed control knob as appropriate.
29. In the ARSST Software: Start the data acquisition and enable the heater with a polynomial to heat the sample at ~2.0°C/min.
30. Allow the sample to heat-up and runaway reaction to complete.
31. Allow the heaters to continue heating the sample for an additional 10 to 20°C after the runaway.
32. Disable heater power
33. Allow sample to cooldown to ambient temperature.
34. Disable Stirring.
35. Slowly depressurize the containment vessel through the center lid port.
    a. A metering valve may be used for tighter manual control to achieve a slow depressurization rate of the containment vessel. (Depressurization time: ~10 to 20 minutes or ~1 to 2 psi/s).
36. Open the containment vessel and note any observations. (e.g. thermocouple positioned correctly, electrical connections undamaged and intact, condensate presence and location).
    a. Optional: take a photograph of the containment vessel contents and underside of vessel lid.
37. Remove the thermocouples from the test cell and headspace and disconnect the heater connections.
38. Remove the test cell assembly from the vessel.
39. Carefully remove the test cell from the heater and insulation assembly.
40. Record the final mass of the test cell and residual sample.
41. *Optional: take a photograph of the test cell and post-test sample.*
42. Clean-up.

DSC Test Procedure

1. Use high-pressure crucibles capable of at least 110 barg at 300°C. Stainless steel crucibles are recommended; aluminum crucibles should not be used.
2. Wash the crucibles with an acetone (or high purity toluene) and dry.
3. Record the empty weight of all components of the sample and reference crucibles.
4. Run a base-line test with two similar weight crucibles (one as reference and other as a sample) at a 10°C/min heating rate between room temperature (RT) to above 300°C. The base-line test is expected to provide a constant heat flow.
5. Add the 20 wt% DTBP mixture to the above sample crucible and close/seal it. The sample mass-to-crucible volume ratio should be between 1:4 to 1:3 g:μL. For example: 6 mg of 20 wt% DTBP in a 20 μL volume crucible.
6. Record the weight of the crucible with sample.
7. Place the sample crucible inside the DSC
8. Start the DSC program with the same heating rate (10°C/min) from RT to 300°C.
9. Record purge gas type and flow rate.
10. Record the ending weight of the sample crucible with sample. There should be minimal weight loss. If the *sample* weight loss exceeds 1%, a leak is indicated and the test should therefore be repeated.

Procedures for Other Instruments

Participation by operators of other laboratory instruments, such as the Dewar calorimeter, PhiTec 2, Mettler-Toledo RC-1e, is welcomed. Please contact Marc Levin (marc.levin2@gmail.com), Kevin Kunkel (kunkel@fauske.com), or S.K. Singh (singh@belmontscientific.com) for further information and testing guidance.

Data Submission
Send via E-mail to Marc Levin at marc.levin2@gmail.com and copy Kevin Kunkel at kunkel@fauske.com

NO LATER THAN MARCH 6, 2023

Submitted Data Should Include

- Summary sheet filled in (see attached sheet)
- Tabulated data with columns (label and units clearly identified)
- Any relevant plots
- (Optional) Compositional analysis of the final liquid and gas product

Note that your data will be "sanitized" to obscure its origin and archived for future use by DIERS; thus we urge that you submit all necessary data.

Background Information

- Free-radical polymerization is often practiced in the chemical industry to build polymer compounds from monomeric units. Di-tert-butyl peroxide (DTBP) is a common free-radical initiator for this reaction and its behavior has been widely studied (e.g., J. Murawski, J.S. Roberts, and M. Szwarc, J. Chem. Phys., **19**, 698 (1951); D.H. Shaw and H.O. Pritchard, Can. J. Chem., **46**, 2721 (1968); D.I. Townsend and J.C. Tou, Thermochimica Acta, **37**, 1-30 (1980)).
- The peroxide is relatively easy to handle. Its decomposition behavior is well-behaved and quite repeatable. The usual products include t-butanol, acetone, and methane. Though the behavior in an adiabatic calorimeter has the appearance of a simple reaction, its reactivity is more complex. There are multiple reaction steps and the solvent can participate in reaction through hydrogen abstraction. The decomposition of DTBP in various solvents has been studied (E.S. Huyser, R.M. VanScoy, J. Org. Chem., **33** (9), 3524 (1968); G.G. Midyana, R.G. Makitra, and E.Y. Pal'chikova, Russian J. Org. Chem., **40** (10), 1407-1411, 2004) and dimers of certain solvent molecules are observed (N.O. Gonzales and M.E. Levin, DIERS Users Group presentation D38-840-1 (2006)).
- Because of its ease in handling and reliable behavior, DTBP in toluene frequently serves as a standard for gauging the performance of adiabatic calorimeters. The system was one of the early subjects of a round-robin in the DIERS Users Group (J.C. Leung, M.J. Creed, and H.G. Fisher, *International Symposium on Runaway Reactions*, 1989). A round-robin exercise among European chemical companies was also performed in 2005 (R.J.A. Kersten, M.N. Boers, M.M. Stork, C. Visser, J. Loss Prevention, **18**, 145-151 (2005)).

<u>Round-Robin Test Data Sheet</u> (to be submitted with each test)

Contact Person: ______________________________ Date: ________________________

Company: ____________________________________

E-mail: _______________________________________ Tel. No.: ________________________

Test ID: ______________________________________ Test Date: ______________________

File name: ___________________________________

Calorimeter with model number: ____

Test Cell Description (including internals and stirrer): ____________________________________

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Pad gas: _________________________ Initial pad gas pressure: _______________ bara/kPa/psia

	Source	Lot Number	*Actual* Mass [g]	*Actual* Fraction	Target Fraction
DTBP					20 wt%
Toluene					80 wt%
Total Sample					

	Source	Lot Number	Mass [g]	Material
Empty cell/pan (without nut & ferrules)				
Nut				
Ferrules				
Cell (with nut & ferrules)				
Cell+Sample (at end of test)				

End of test: Temperature ____________________ °C Pressure: _______________ bara/kPa/psia

Agitation comments - (stirrer speed during test)

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Other Remarks - ____

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