DIERS ROUND-ROBIN INVITATION

Date: October 25, 2024

To: All DIERS members

From: Garrett Dupre / DIERS Round-Robin Testing Committee

Reaction: Allyl Phenyl Ether

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

For questions and data submittal, please contact:

- Garrett Dupre: Garrett.Dupre@grace.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 7, 2025. *Submitted data will be "sanitized" to obscure its origin before sharing with DIERS membership.*

Results will be discussed at the Spring 2025 DIERS meeting.

Thank you all in advance for your participation!!!

DIERS Round-Robin Test

Allyl Phenyl Ether

This round-robin testing system is allyl phenyl ether. This material is very friendly in terms of reaction (a rearrangement), phase (liquid), and composition (CHO). This material undergoes a known thermal isomerization that produces a clear liquid followed by a pressure-generating thermal decomposition that produces a dark brown/black liquid.

It is recommended to obtain material from the listed supplier for greater likelihood of consistency, but material may be used from an alternate supplier. Please note source, purity, and lot number on the Round-Robin Test Data Sheet at the end of this invitation.

Allyl phenyl ether, 99%, Thermo Scientific Chemicals, Catalog number L03359.14 (25g) or L03359.22 (100g)
https://www.thermofisher.com/order/catalog/product/L03359.14

ARC/VSP2/APTAC/ARSST/DSC Test Conditions, for other instruments contact Garrett.Dupre@grace.com

	ARC	VSP2	APTAC	ARSST	DSC
Test cell material	316 SS	304 SS	Titanium	Pyrex Glass	AuSS
Volume of test cell [ml]	~10	110	130	10	20-40 µL
Allyl phenyl ether [g]	5.0	50.0	60.0	8.9	([4])
Stirring rate [rpm]	300[1]	300	500	500([2])	N/A
Test start temperature [°C]	140	150	140	ambient	ambient
Test end temperature [°C]	400	450	450	500	400
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	Nitrogen	Nitrogen[5]	Nitrogen	Nitrogen	Nitrogen

[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]Sample mass-to-crucible volume ratio of 1:4 – 1:3 mg:µL; for example, 5.0 to 6.7 mg of sample in a 20 µL volume crucible.
[5]Can be evacuated initially to measure vapor pressure

While running tests in alignment with the above test conditions is highly encouraged, tests will still be accepted if they do not meet all the above conditions. On the Round-Robin Test Data Sheet at the end of this invitation, please record any deviations from the above conditions. For example, if a test is run in air instead of nitrogen, record this on the Round-Robin Test Data Sheet.

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 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 weights of test cell (stainless steel cell ~13 g), nut, ferrule.
2. Test sample 'as received.'
3. Weigh the sample in the test cell.
4. Attach the test cell to the calorimeter at ambient pressure and temperature
    a. Inert test cell headspace with nitrogen.
5. Enter the test parameters below:
    a. Head space = nitrogen
    b. Start temperature = 140°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 = 400°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 (or transducer/test cell limit)
    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. Isolate the test cell headspace from the containment vessel headspace.
10. Load sample to test cell through fill line.
11. Document mass of sample injected into test cell.
12. 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).
13. 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)
14. Monitor systems as necessary:
    a. Adjust Nitrogen throttle valve accordingly during runaway.
15. Once reaction has completed, disable heaters and allow the sample to cool down.
16. After the sample has cooled down to below 30°C, stop the experiment and exit the control software.
17. 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.
18. Remove test cell from containment vessel and heater assembly.
19. 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
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 amount of sample 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 = nitrogen
    b. Start temperature =140°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 = 400°C
    g. Cool down temperature = 35°C
    h. End temperature in case of exotherm = 450°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 >450°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. Load the sample into an all-plastic syringe or all-glass syringe. (Reminder: Account for hold-up)
22. Slowly charge 8.75 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; +/- 0.25 grams
    b. Record the mass of sample charged to the test cell.
23. Ensure that the sample thermocouple is positioned appropriately and is secure.
24. Ensure that the gas space thermocouple is positioned appropriately and is secure.
25. Seal the containment vessel.

26. 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.
27. Enable stirring and set the speed control knob as appropriate.
28. In the ARSST Software: Start the data acquisition and enable the heater with a polynomial to heat the sample at ~2.0°C/min.
29. Allow the sample to heat-up and runaway reaction to complete.
30. Disable heater power
31. Allow sample to cooldown to ambient temperature.
32. Disable Stirring.
33. 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).
34. 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.
35. Remove the thermocouples from the test cell and headspace and disconnect the heater connections.
36. Remove the test cell assembly from the vessel.
37. Carefully remove the test cell from the heater and insulation assembly.
38. Record the final mass of the test cell and residual sample.
39. Optional: take a photograph of the test cell and post-test sample.
40. Clean-up.

DSC Test Procedure

1. Use high-pressure crucibles. Gold-plated stainless-steel or other high-pressure 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 400°C. The base-line test is expected to provide a constant heat flow.
5. Add the sample 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: 5.0 to 6.7 mg of sample 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 400°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.

Data Submission

Send via E-mail to Garrett Dupre at Garrett.Dupre@grace.com and copy Kevin Kunkel at kunkel@fauske.com

NO LATER THAN MARCH 7, 2025

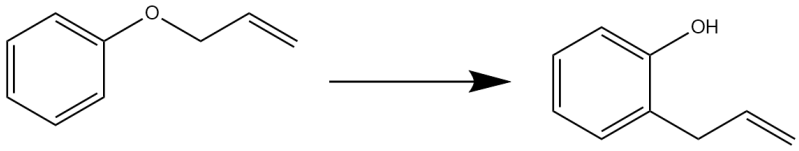
Submitted Data Should Include

- 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

- Allyl phenyl ether undergoes a well-known thermal isomerization referred to as a Claisen rearrangement. Claisen rearrangements are a well-known class of chemical reactions, see Martín Castro, Ana M. "Claisen rearrangement over the past nine decades." *Chemical Reviews* 104, no. 6 (2004): 2939-3002.



Round-Robin Test Data Sheet (*to be submitted with each test*)

Contact Information

Company Name: _____

Primary Contact Name: _____ Secondary Name: _____

Primary Contact Email: _____ Secondary Email: _____

Primary Telephone #: _____ Secondary Tel. #: _____

Test Identification

Test Type: _____ (i.e. DSC, ARC, ARSST, VSP2, APTAC)

Test Date: _____ (YYYY / MM / DD)

Test ID: _____

File Name(s): _____

_____

Sample Details

Sample Name: _____

Supplier / Source: _____ Product Number: _____

Date of Procurement: _____ Purity/Grade: _____

Mass of Initial Charge: _____ grams Lot Number: _____

Storage Remarks: _____

Calorimeter Equipment Details

Make & Model: _____

Configuration Details: _____

Guard Heater Type: _____ (i.e. Single Zone, Dual-Zone)

Test Cell Details

Test Cell Type: _____ Material: _____

Test Cell Make/Model: _____ Empty Volume: _____

Mass without fittings: _____ grams Mass with fittings: _____ grams

Additional Details: _____

Experimental Conditions

Headspace Composition: _____ (i.e. N_2, Evacuated, Air)

Initial Pressure: _____ psia

Stirring: _____ rpm

Cooldown Temp.: _____ °C Cooldown Pressure: _____ psia

Observations/Remarks: _____

_____

_____

Post-Test Observations

Post-test Mass: _____ grams (test cell + sample)

Post-test Observations: _____

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