BESTMANN-OHIRA REAGENT CASE STUDY: ENSURING STORAGE AND TRANSPORTATION SAFETY FOR DIAZO CONTAINING MATERIALS

JEFFREY SPERRY

MAY 2024

QUICK FACTS

Founded:
1989

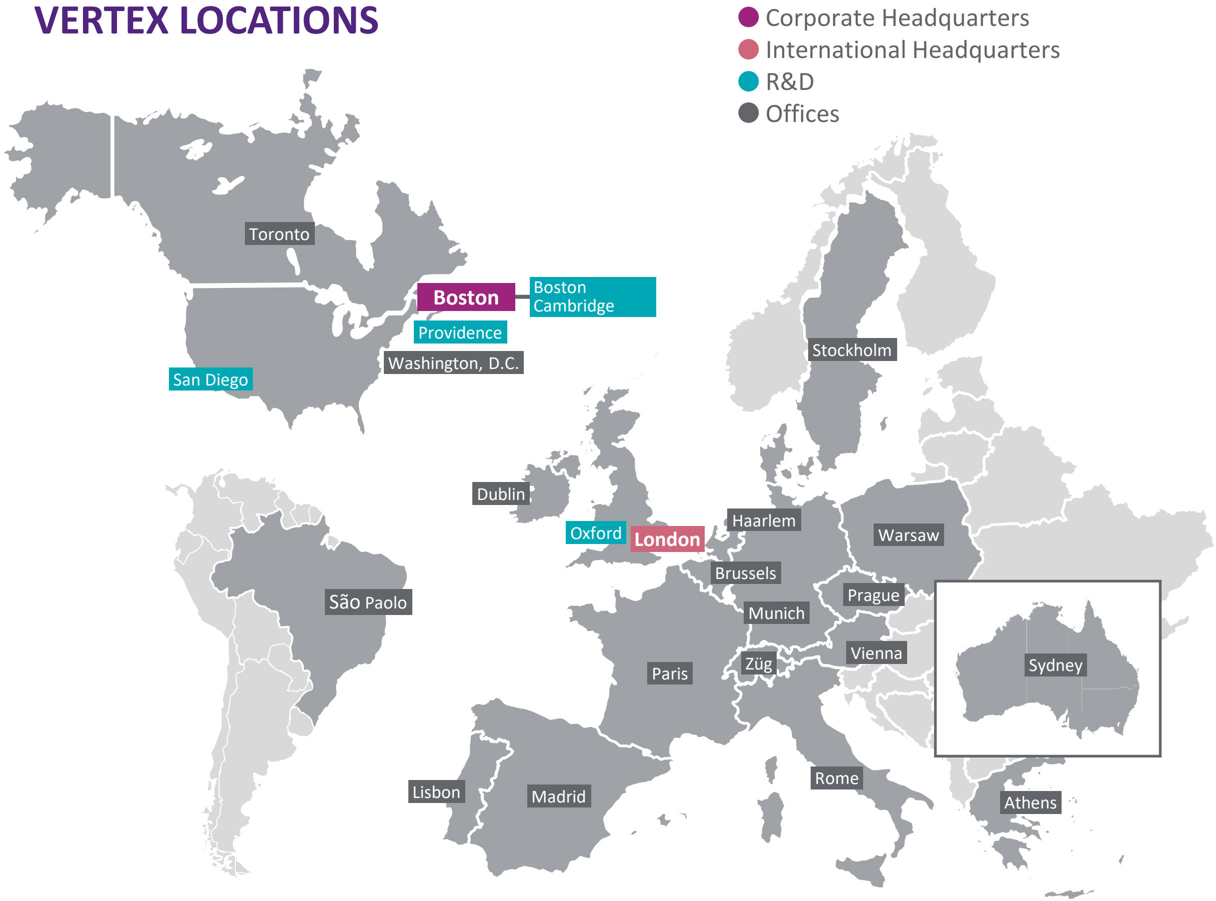
Headquarters:
Boston

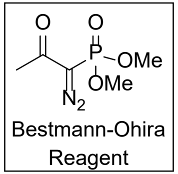
~4,700
Employees worldwide
(~3,800 in the U.S.)

$79B
Market Cap
(as of Feb. 2023)

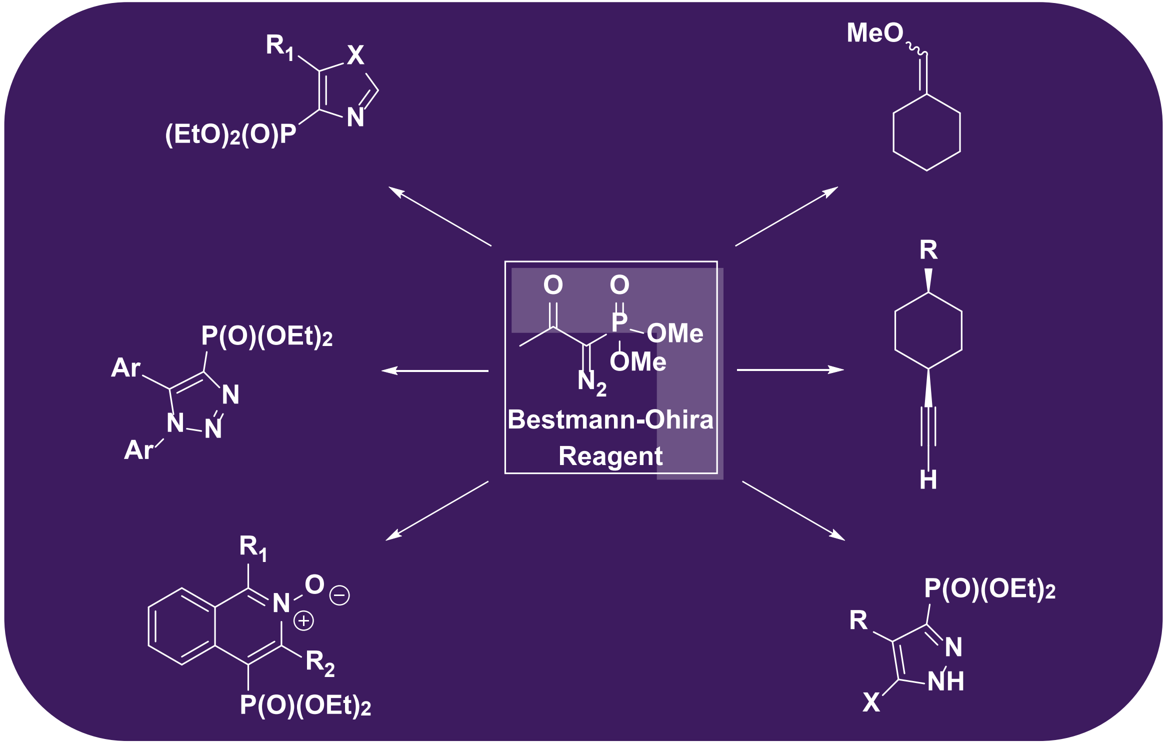
$8.9B
2022
Revenue

VERTEX LOCATIONS



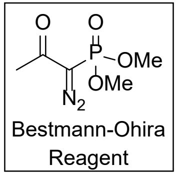


THE BESTMANN-OHIRA REAGENT



Ohira, S. *Synth. Commun.*, **1986**, *19*, 561

S. Müller, B. Liepold, G. J. Roth, H. J. Bestmann, *Synlett*, **1996**, 521-522



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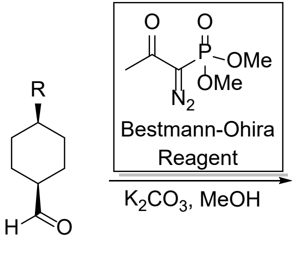

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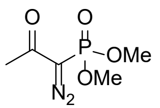
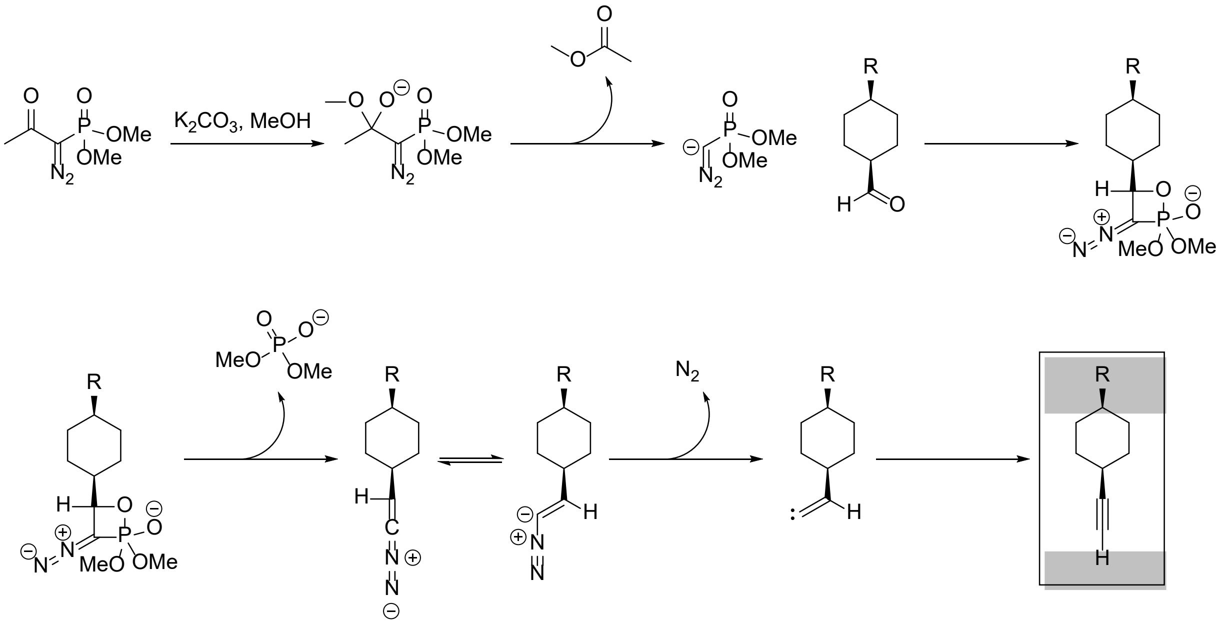
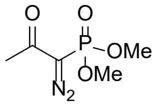
THE BESTMANN-OHIRA REAGENT - MECHANISM





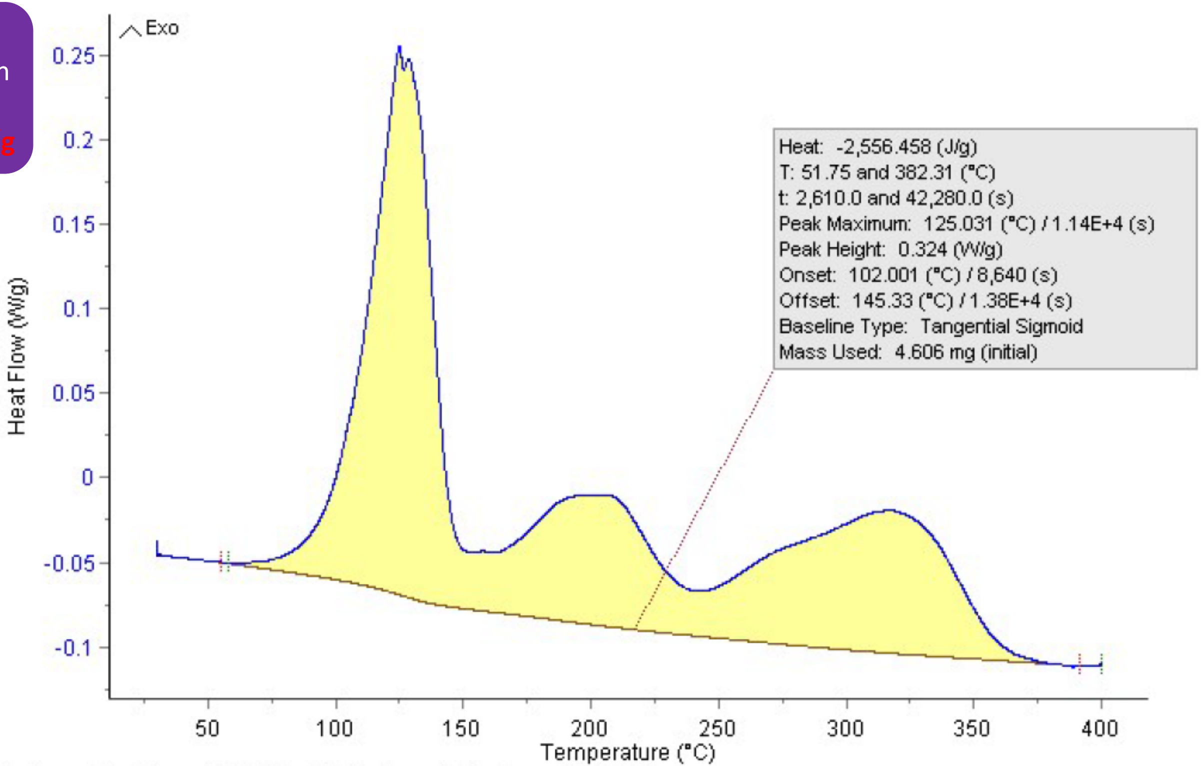
DIFFERENTIAL SCANNING CALORIMETRY (DSC) DATA



Bestmann-Ohira Reagent

BESTMANN-OHIRA REAGENT – DSC

DSC in air
Heating Rate = 0.5 °C/min
Left Limit = 51 °C
Heat Released = -2,556 J/g



Bestmann-Ohira Reagent (DSCs in air) / Bestmann-Ohira Reagent DSC 0.5cpm

YOSHIDA CORRELATIONS

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The Yoshida Correlation

A mathematical equation that correlates a materials onset temperature and energy from a DSC experiment to its ability to propagate an explosion and/or be shock sensitive

For explosive propagation (EP):

$$EP = \log(Q_{DSC}) - 0.38 \times \log(T_{DSC} - 25) - 1.67$$

Q_{DSC} is the energy of the exotherm in cal/g

T_{DSC} is the onset temperature of the exotherm in ˚C

If EP $\geq$ 0 material is predicted to demonstrate the ability to propagate and explosion

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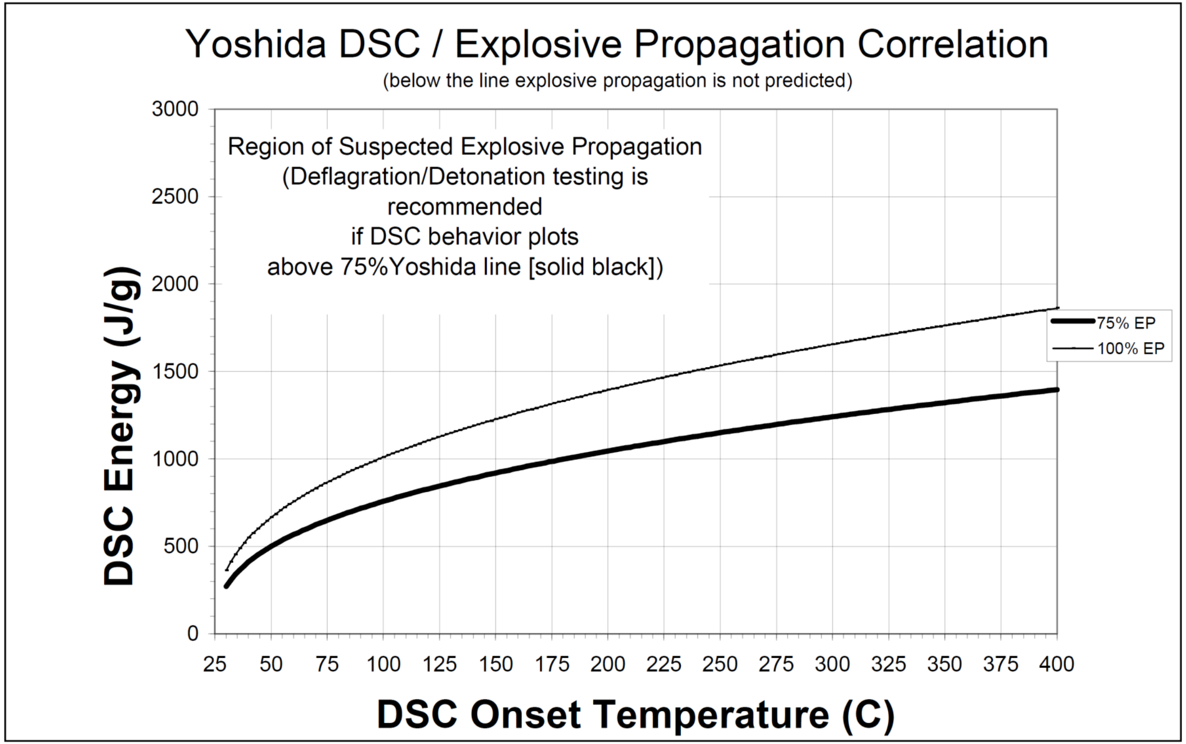


DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The Yoshida Correlation

A mathematical equation that correlates a materials onset temperature and energy from a DSC experiment to its ability to propagate an explosion and/or be shock sensitive

For shock sensitivity (SS):

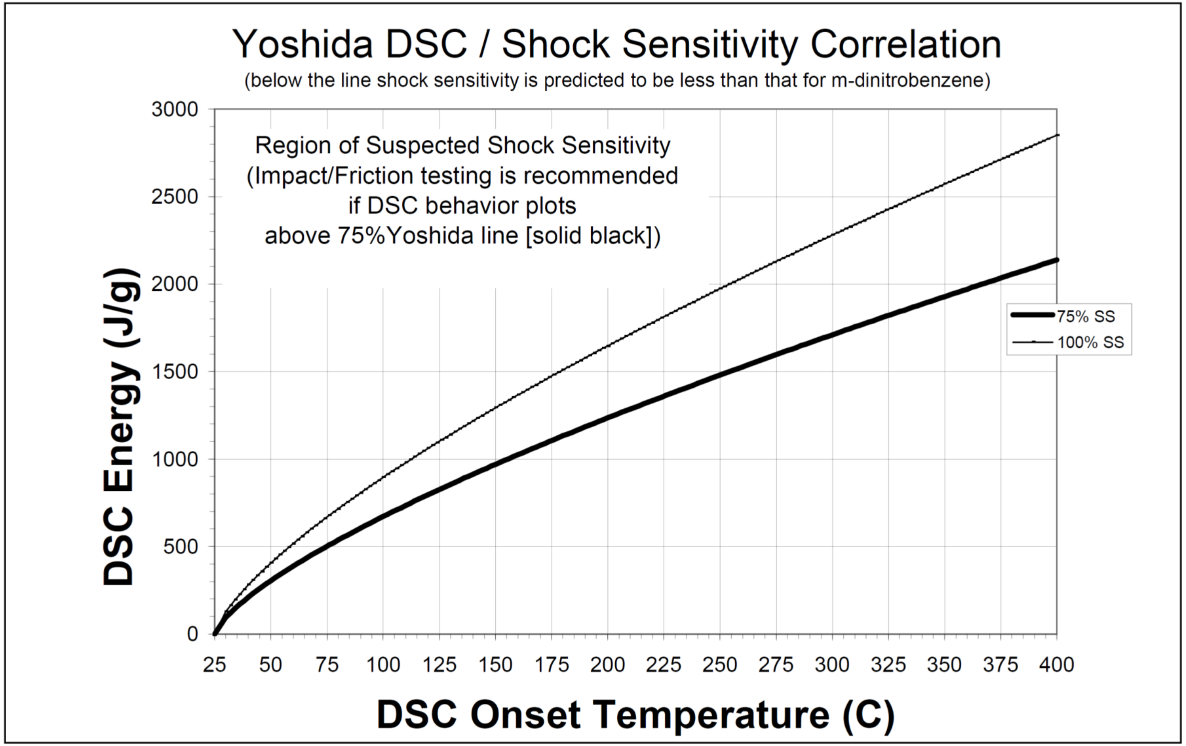
$$SS = \log(Q_{DSC}) - 0.72 \times \log(T_{DSC} - 25) - 0.98$$

Q_{DSC} is the energy of the exotherm in cal/g

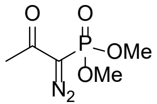
T_{DSC} is the onset temperature of the exotherm in ˚C

If $SS \geq 0$ material is predicted to demonstrate the ability to propagate and explosion

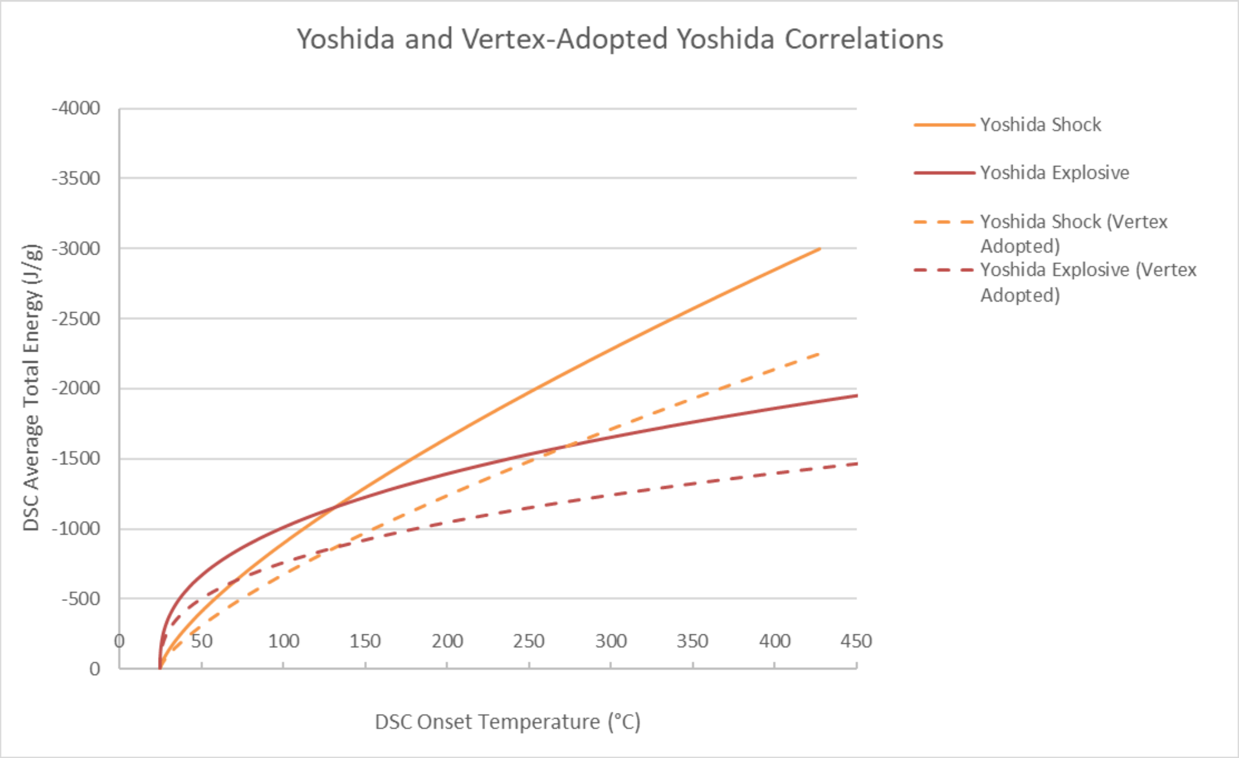
DIFFERENTIAL SCANNING CALORIMETRY (DSC)

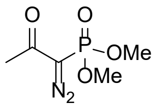


BESTMANN-OHIRA REAGENT – YOSHIDA CORRELATIONS



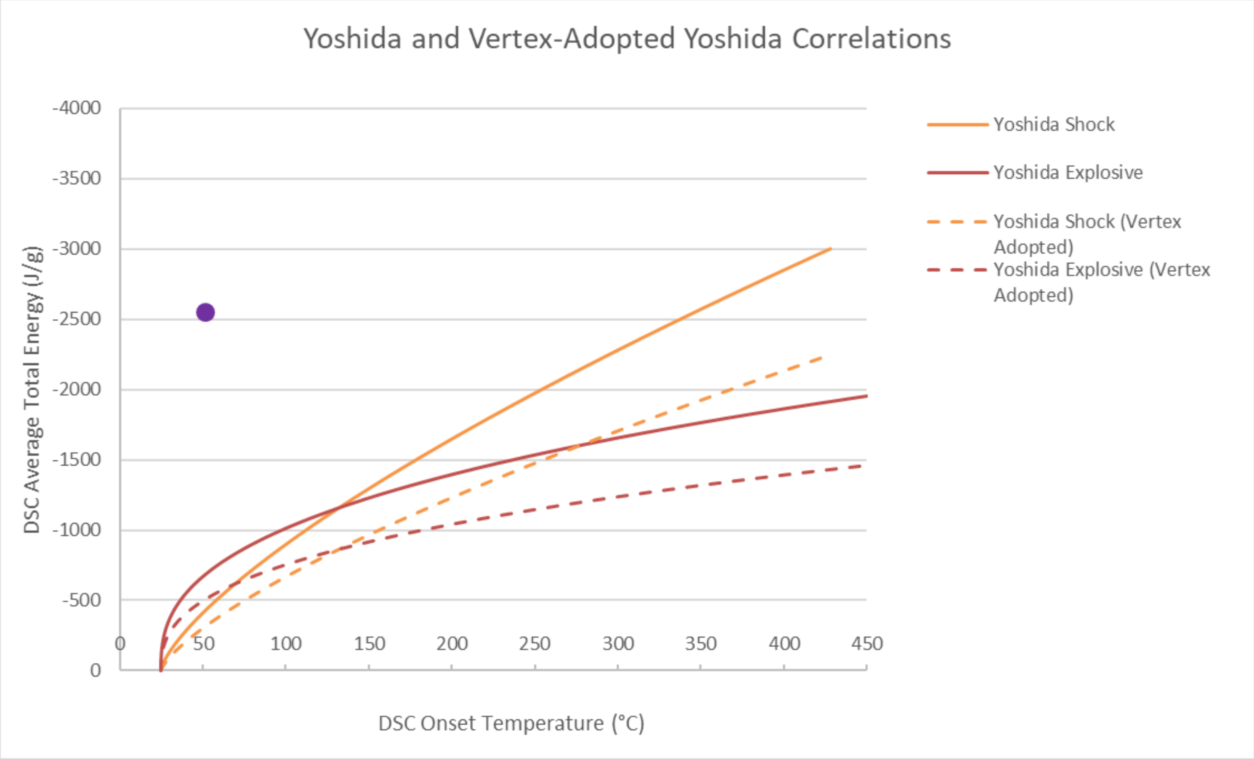
Bestmann-Ohira Reagent





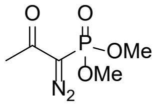
Bestmann-Ohira Reagent

BESTMANN-OHIRA REAGENT – YOSHIDA CORRELATIONS



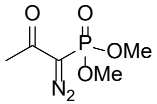
IMPACT TESTING

BESTMANN-OHIRA REAGENT – IMPACT TESTING



Bestmann-Ohira Reagent

- Sample is placed into cell
- Cell is secured on top on anvil
- 10 kg weight dropped from a measured height
- Possible experimental outcomes
  - Flame or visible light
  - Smoke
  - Audible noise above impact noise
  - Discoloration of sample



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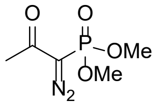
Drop Weight (kg)	Drop Height (cm)	Approximate Impact Energy (J)	Trial Results						Comments
			1	2	3	4	5	6	
10	100	100	NR	NR	NR	NR	NR	NR	No reaction

FRICTION TESTING



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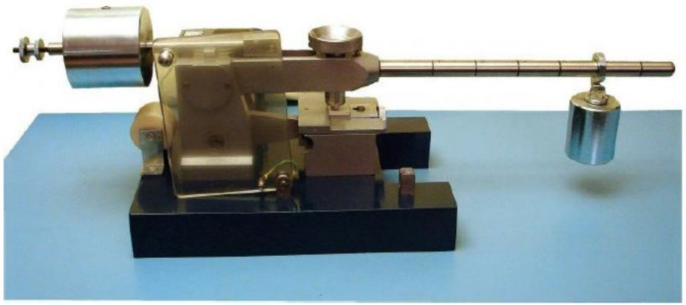
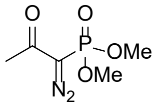


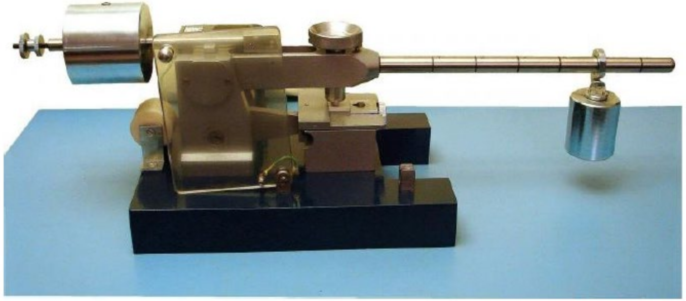
BAM Friction Load (N)						
Weight # and Mass* (kg)	**Notch No.**					
	1	**2**	**3**	**4**	**5**	**6**
B1 (0.28)	5	6	7	8	9	10
B2 (0.56)	10	12	14	16	18	20
B3 (1.12)	20	24	28	32	36	40
B4 (1.68)	30	36	42	48	54	60
B5 (2.24)	40	48	56	64	72	80
B6 (3.36)	60	72	84	96	108	120
B7 (4.48)	80	96	112	128	144	160
B8 (6.72)	120	144	168	192	216	240
B9 (10.08)	180	216	252	288	324	360

**The mass of the weight includes the mass of the hook*

BESTMANN-OHIRA REAGENT – FRICTION TESTING



Bestmann-Ohira Reagent



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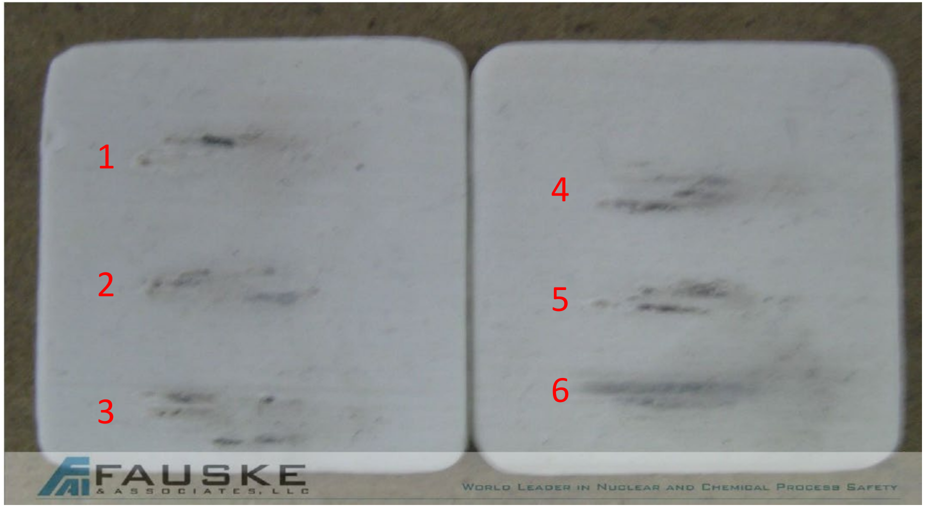
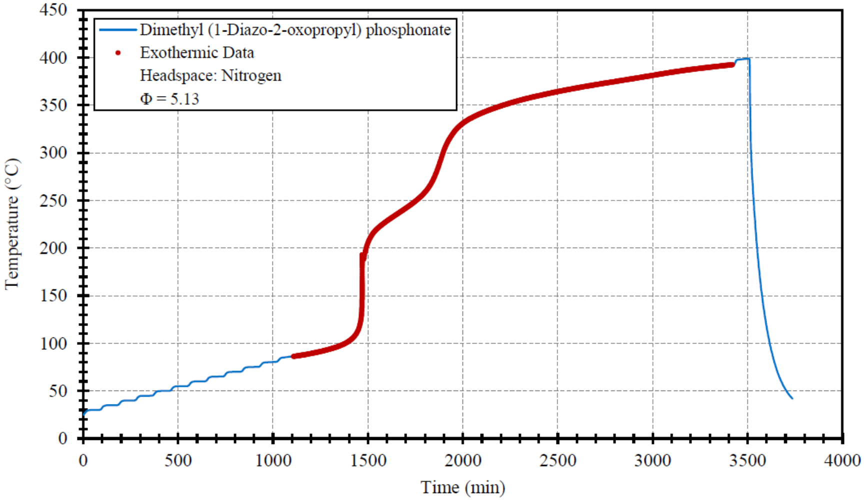
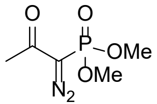


Weight (kg)	Notch #	Resulting Load on the Sample (N)	Trial Results						Comments	Test Result (+/-)
			1	2	3	4	5	6		
10.08	6	360	D	D	D	D	D	D		-

ACCELERATING RATE CALORIMETRY (ARC)

BESTMANN-OHIRA REAGENT – ARC





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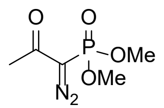
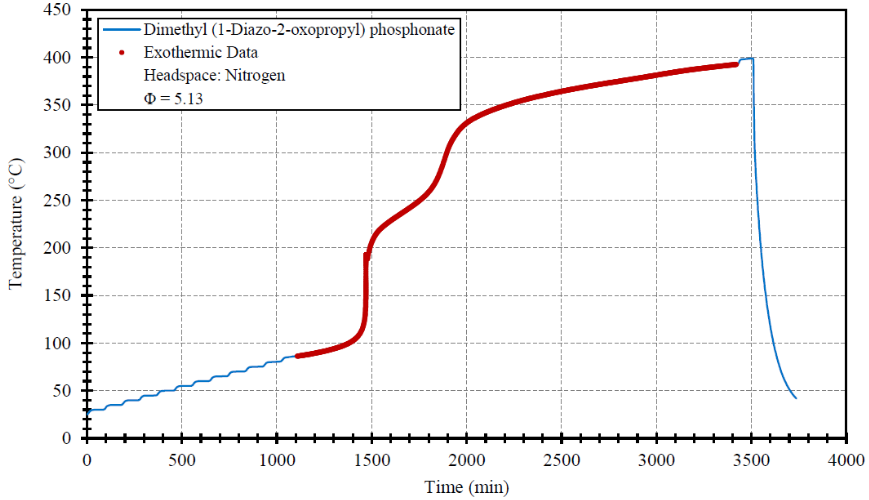
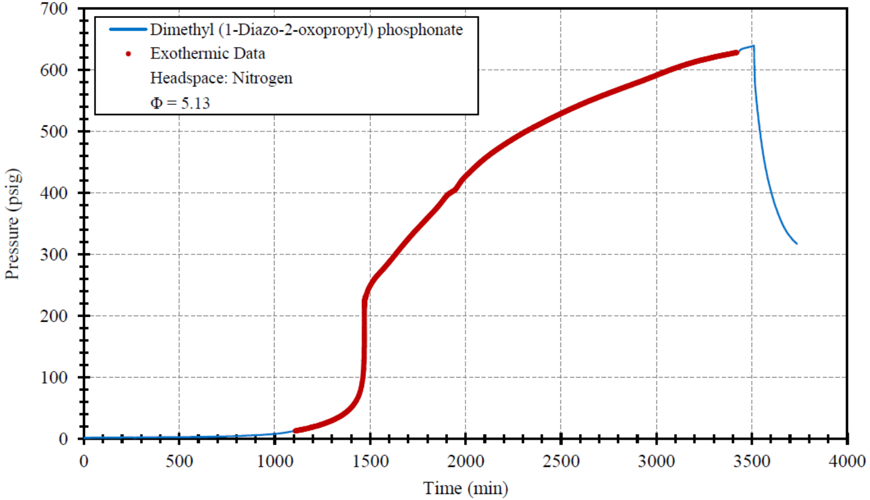
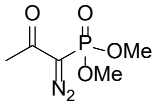


BESTMANN-OHIRA REAGENT – ARC







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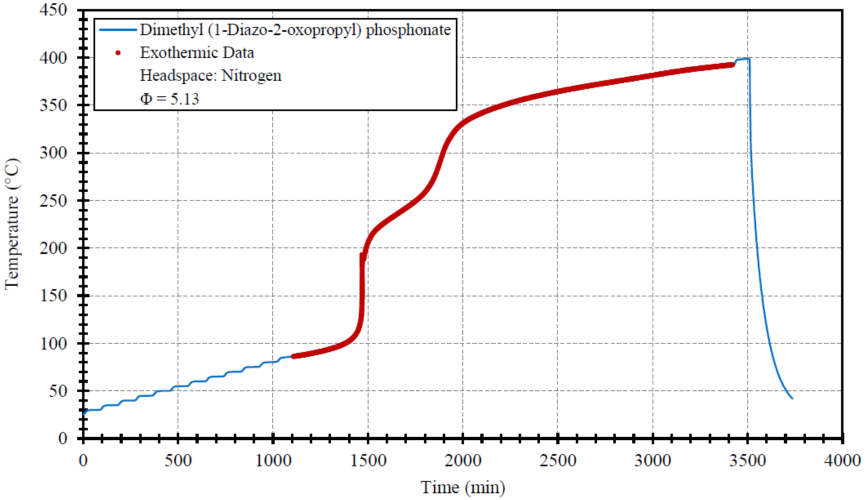
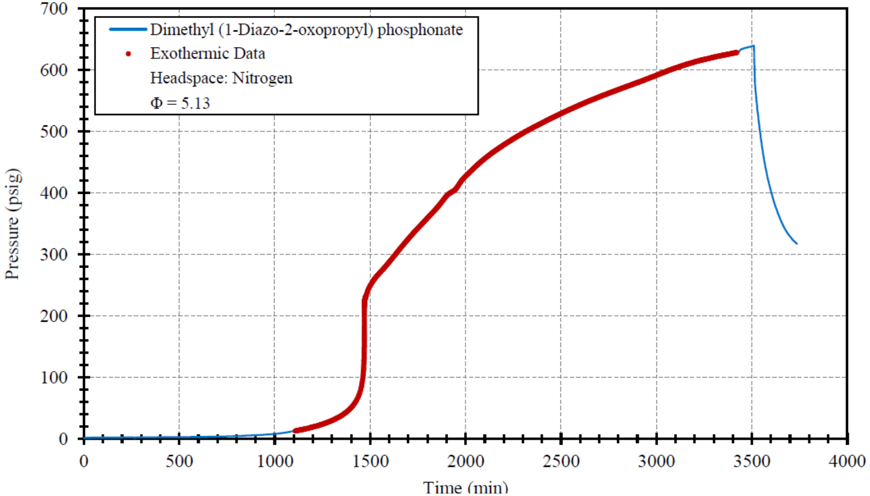
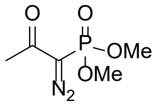




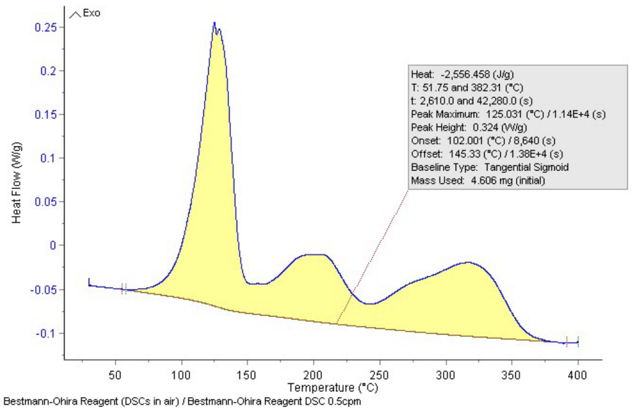
Sample Name	Thermal Inertia, Φ (-)	Onset Temperature, T_o (°C)	Final Reaction Temperature, T_f (°C)	Observed Temperature Rise, ΔT_{obs} (°C)	Adiabatic Temperature Rise, ΔT_{ad} (°C)	Specific Heat of Reaction, $-\Delta H_R$[1] (J/g)
Dimethyl (1-Diazo-2-Oxopropyl) Phosphonate	5.13[1]	85.19	>392.76	>307.57	>1578	>2383

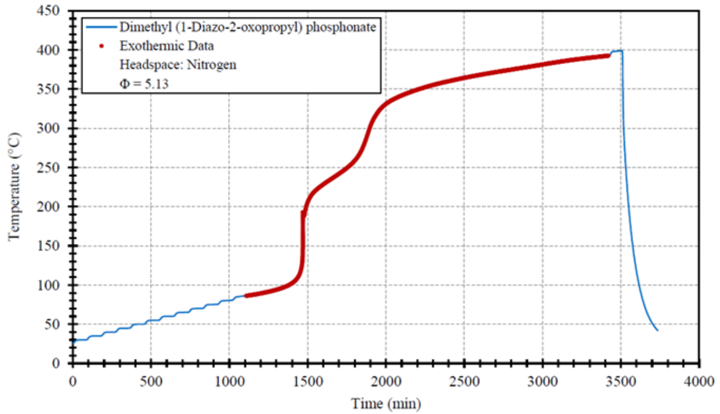
1: A specific heat capacity of 1.51 J/g/K was estimated using DIPPR [1]



Bestmann-Ohira Reagent

BESTMANN-OHIRA REAGENT – DSC VERSUS ARC COMPARISON





DSC in air

Left Limit = 51 °C
Heat Released = **-2,556 J/g**

ARC under nitrogen

Onset T = 85 °C
Heat Released = >**-2,383 J/g**

TMR AND SADT DETERMINATION

TMR AND SADT DEFINITION

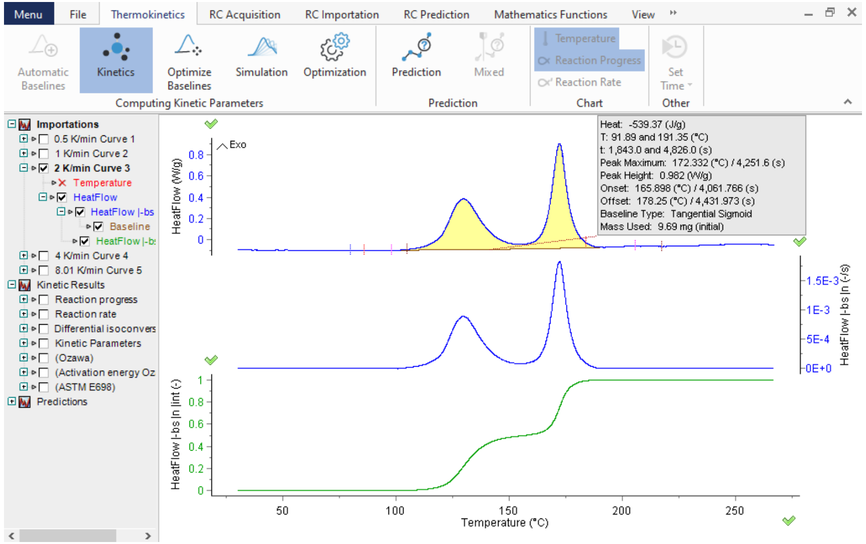
Time to Maximum Rate (TMR): The time between the start of a thermal runaway reaction and the maximum reaction rate (maximum self-heating rate).

Self-Accelerating Decomposition Temperature (SADT): The lowest temperature that a mass of material, capable of an exothermic decomposition reaction, must be held such that the heat of decomposition exceeds the amount of energy lost to the surroundings. This will result in an increase in the mass temperature and acceleration of the decomposition reaction rate. SADT is package dependent.

AKTS TK AND TS SOFTWARE

Advanced Kinetics and Technology Solutions (AKTS) Thermokinetics (TK) and Thermal Safety (TS) software:

- Determination of the reaction rate dα/dt and reaction extent α evaluated from heat-flow signals
- Differential isoconversional analysis based on heat-flow signals
- Prediction of the influence of the atmospheric temperature profiles on the reaction course
- Prediction of the reaction course at customized temperatures
- Evaluation of Safety Parameters TMR and Safety Diagrams
- Simulation of ARC and Runaway Reactions, Determination of SADT

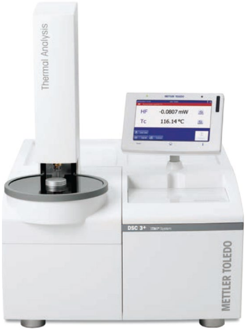


https://www.akts.com/tk/thermokinetics-software-thermal-analysis-isoconversional-model-fitting-DSC-TG-short-description/

https://engineering.purdue.edu/P2SAC/research/documents/TemperatureMaximumRate.pdf

TMR AND SADT ESTIMATION

TMR and SADT can be predicted by extracting kinetic parameters from DSC, ARC, and TAM (thermal activity monitor) experiments (Reaction rate, activation energy, preexponential factor)



DSC

ARC

TAM

J. Loss Prev. Process Ind. 1997, *1,* 31-41

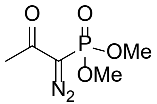
https://akts.com/newsletter/docs/November-2009-Safety-Kinetics-Paper.pdf

TMR AND SADT ESTIMATION

DSC – collect at 3 different heating rates (0.5 °C/min, 1 °C /min, and 2 °C /min) under nitrogen and air

ARC – under nitrogen

TAM – under nitrogen



Bestmann-Ohira Reagent

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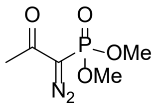
Headspace	Ramp Rate (°C/min)	Left-Limit Onset Temp (°C)	Extrapolated Onset Temp (°C)	Peak Temp (°C)	Specific Heat of Reaction ($-\Delta H_R$)
Nitrogen	0.5	73.4	109.9	131.9	2,248
Nitrogen	1.0	79.2	115.8	138.7	2,144
Nitrogen	2.0	85.2	122.0	145.8	2,190
Air	0.5	51.8	102.0	125.0	2,556
Air	1.0	55.2	117.0	136.9	2,407
Air	2.0	58.3	121.0	144.1	2,447



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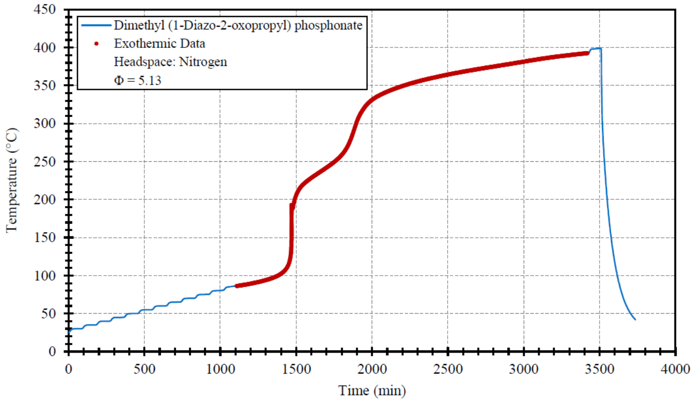

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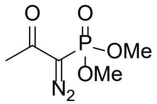

Bestmann-Ohira Reagent

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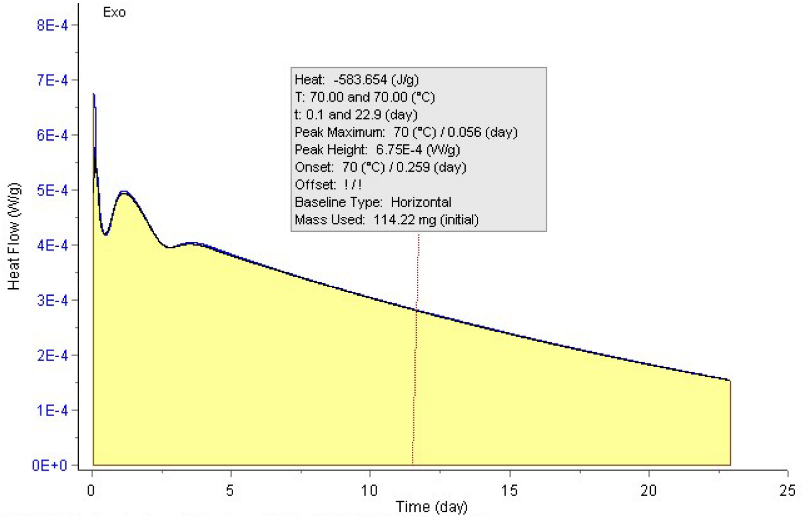
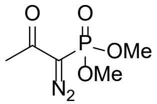


TAM Experiment:

- Isothermal hold at 70 °C for 23 days
- Peak Heat Flow = 6.75E-4 W/g
- Measured ΔH_R = -584 J/g (~27% of total energy)

KINETIC PARAMETERS EXTRACTED FROM DSC IN AIR



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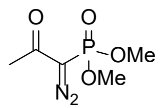

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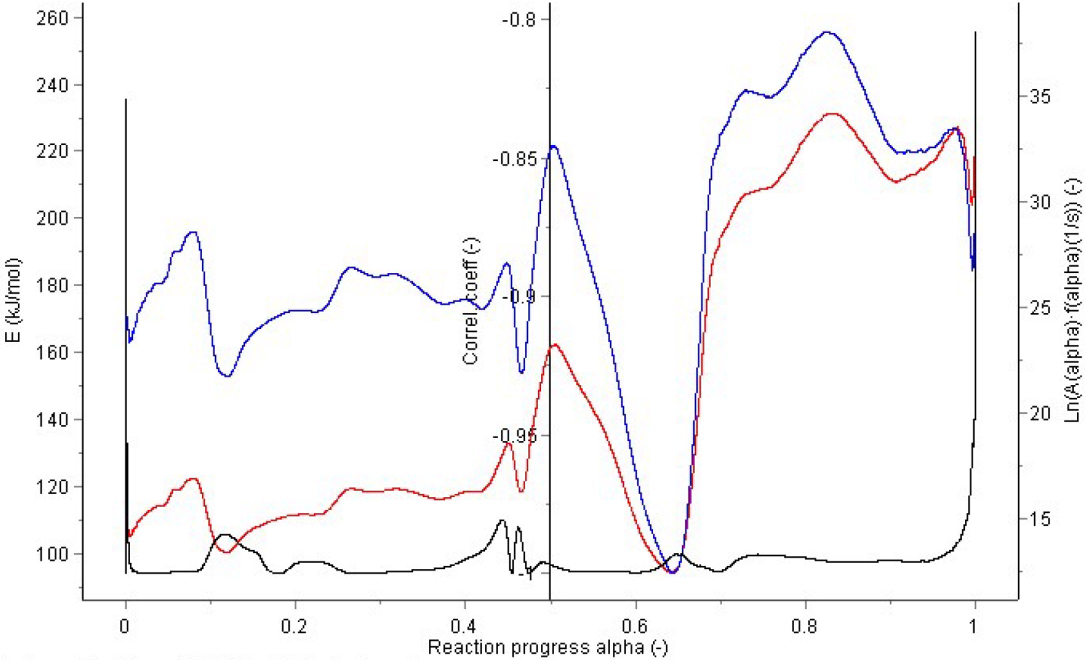
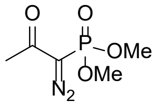


Bestmann-Ohira Reagent (DSCs in air) / Kinetic Parameters



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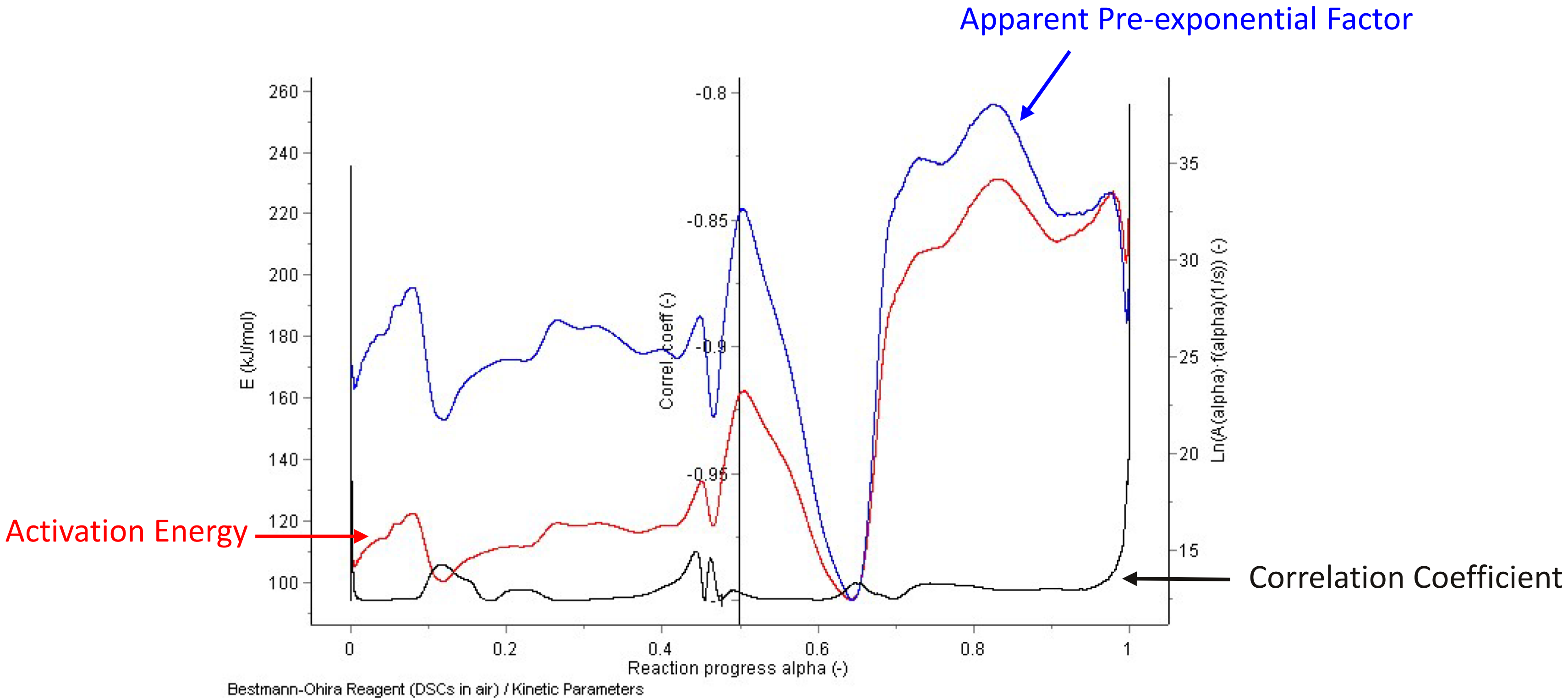

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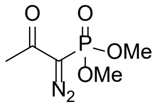
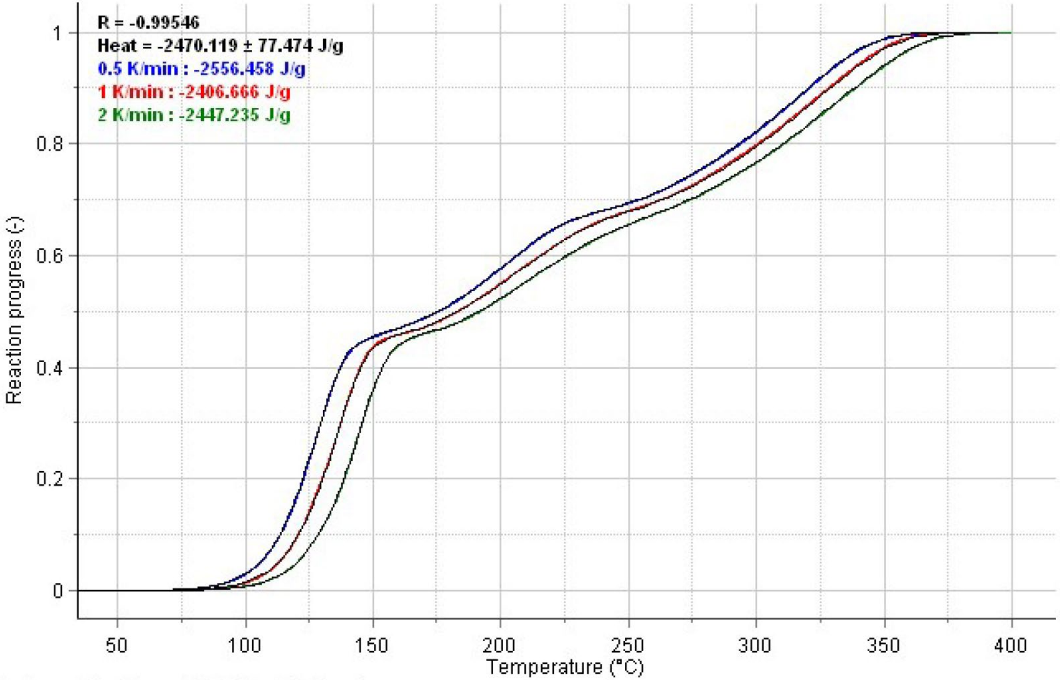
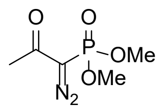


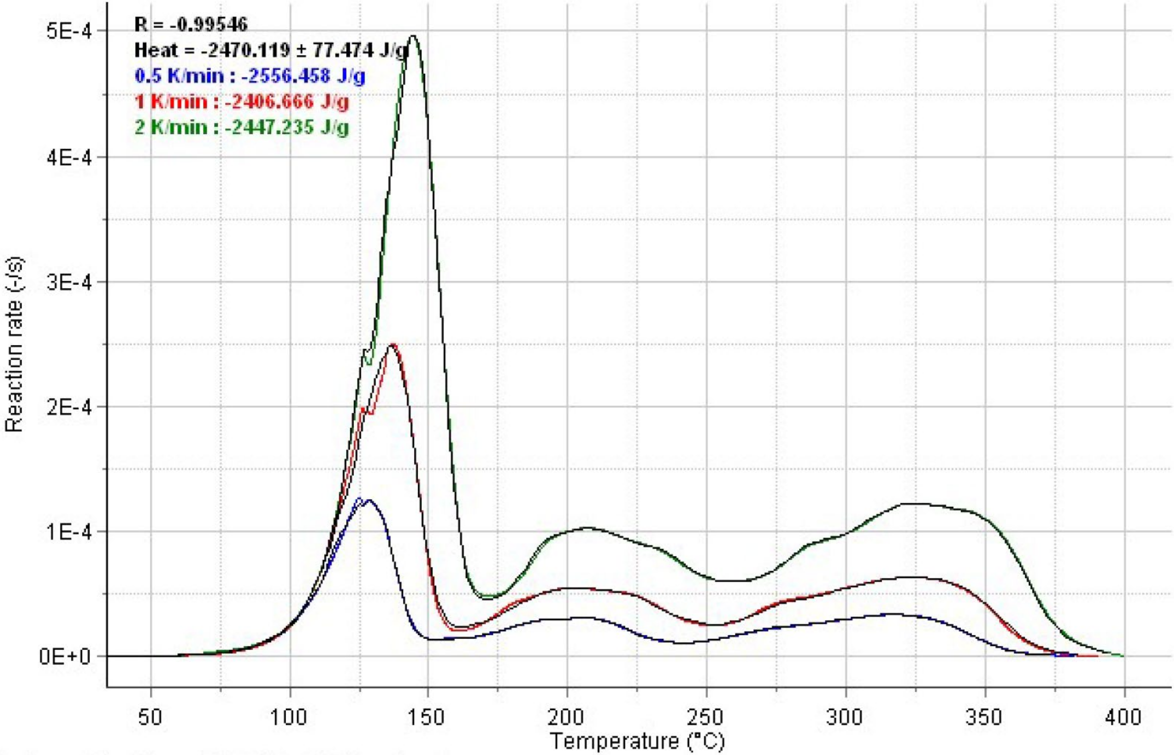
Bestmann-Ohira Reagent



Bestmann-Ohira Reagent (DSCs in air) / Reaction progress

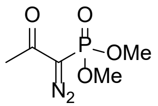
KINETIC PARAMETERS EXTRACTED FROM DSC IN AIR



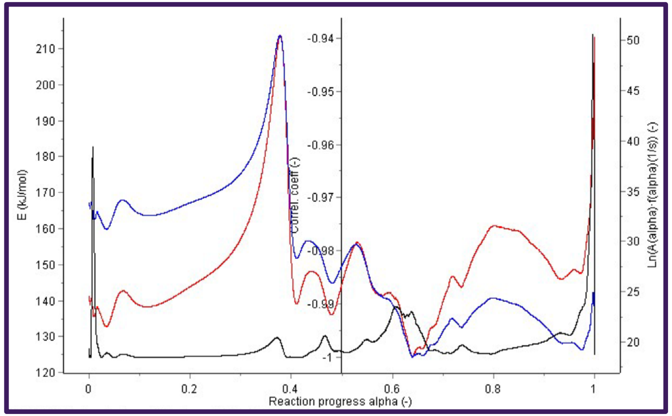


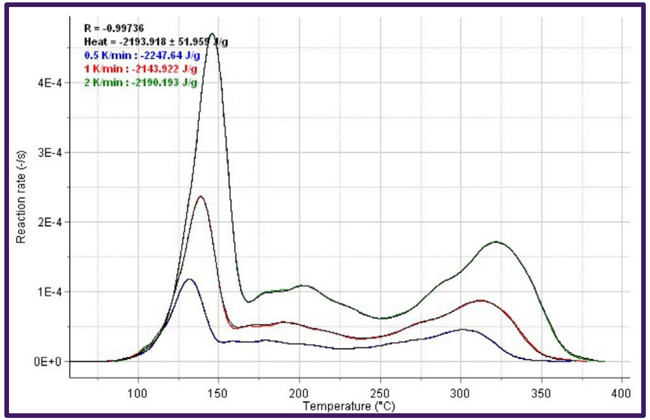
Bestmann-Ohira Reagent (DSCs in air) / Reaction rate

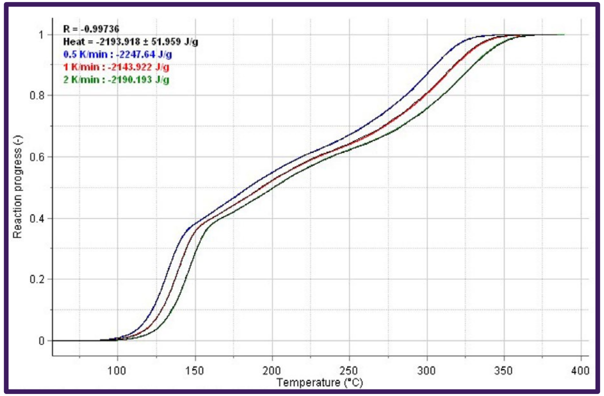
KINETIC PARAMETERS EXTRACTED FROM DSC IN NITROGEN



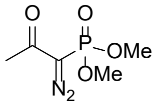
Bestmann-Ohira Reagent





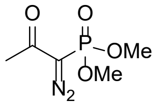


KINETIC PARAMETERS EXTRACTED FROM DSC AND TAM IN NITROGEN

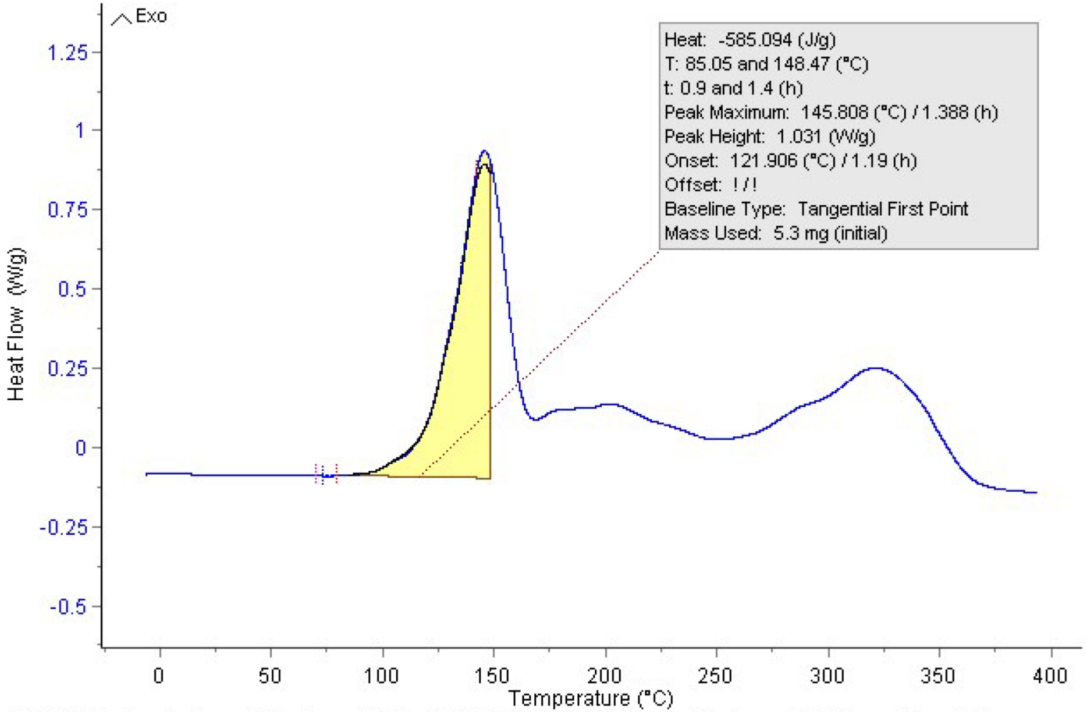


Bestmann-Ohira Reagent

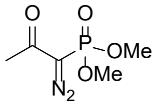
KINETIC PARAMETERS EXTRACTED FROM DSC AND TAM IN NITROGEN



Bestmann-Ohira Reagent

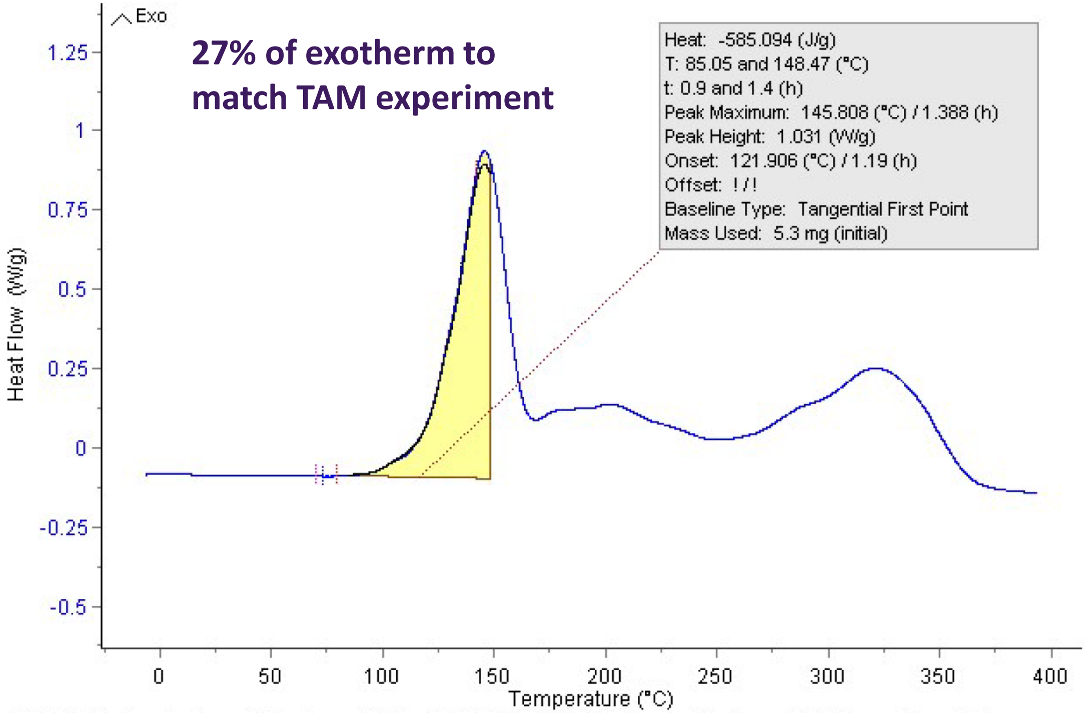


KINETIC PARAMETERS EXTRACTED FROM DSC AND TAM IN NITROGEN

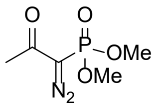


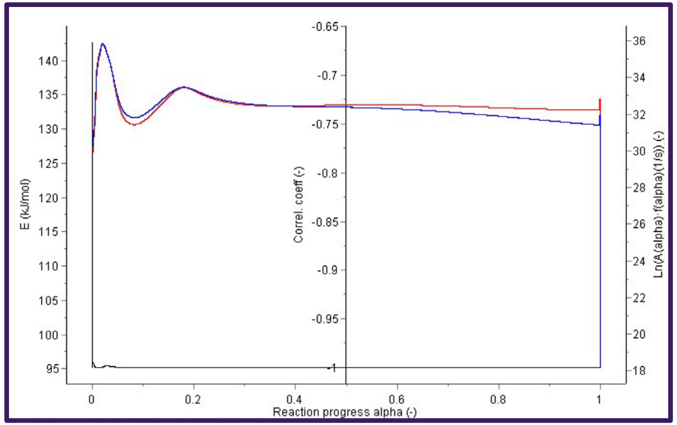
Bestmann-Ohira Reagent

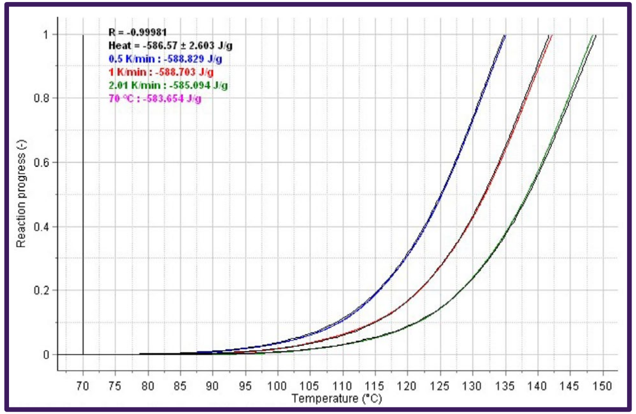
27% of exotherm to match TAM experiment

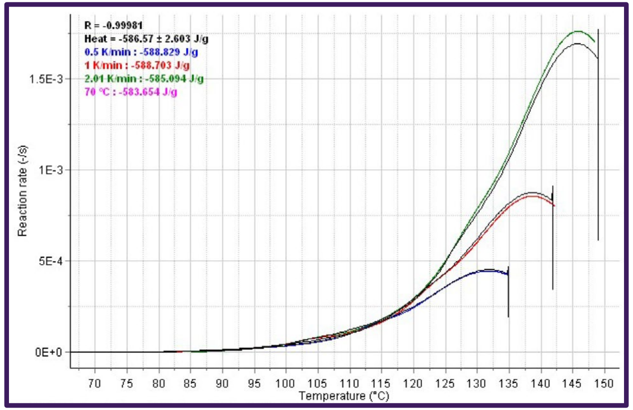


KINETIC PARAMETERS EXTRACTED FROM DSC AND TAM IN NITROGEN

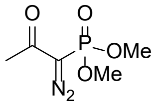




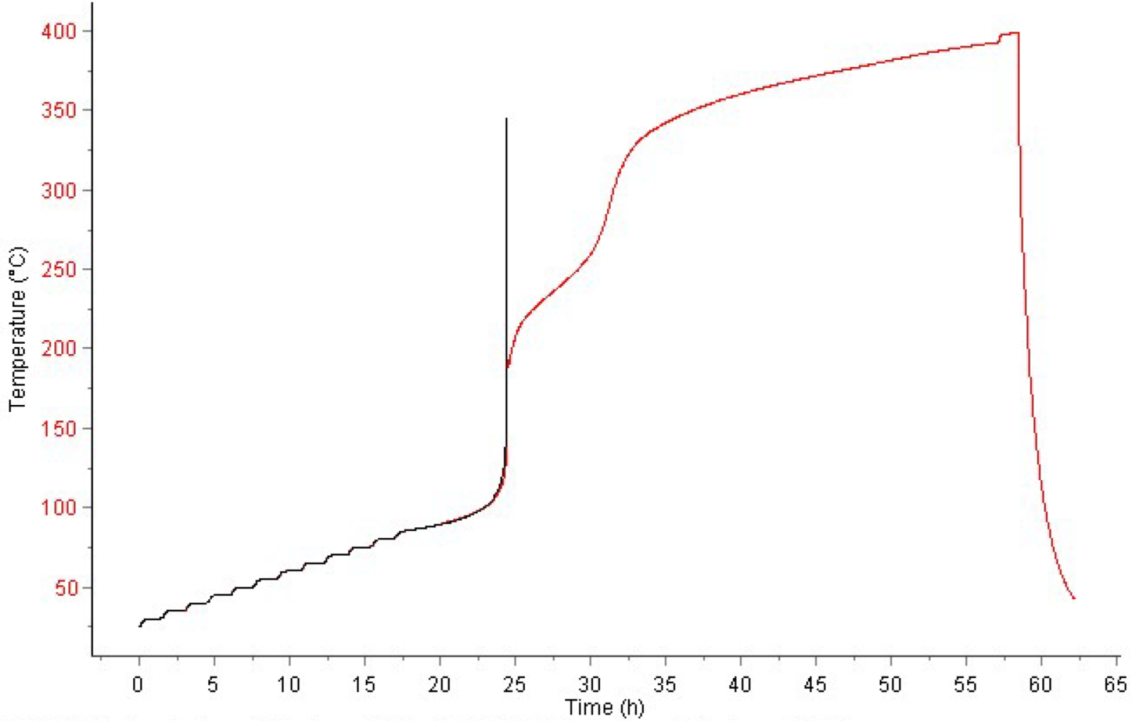


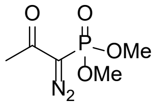


KINETIC PARAMETERS EXTRACTED FROM DSC AND ARC IN NITROGEN



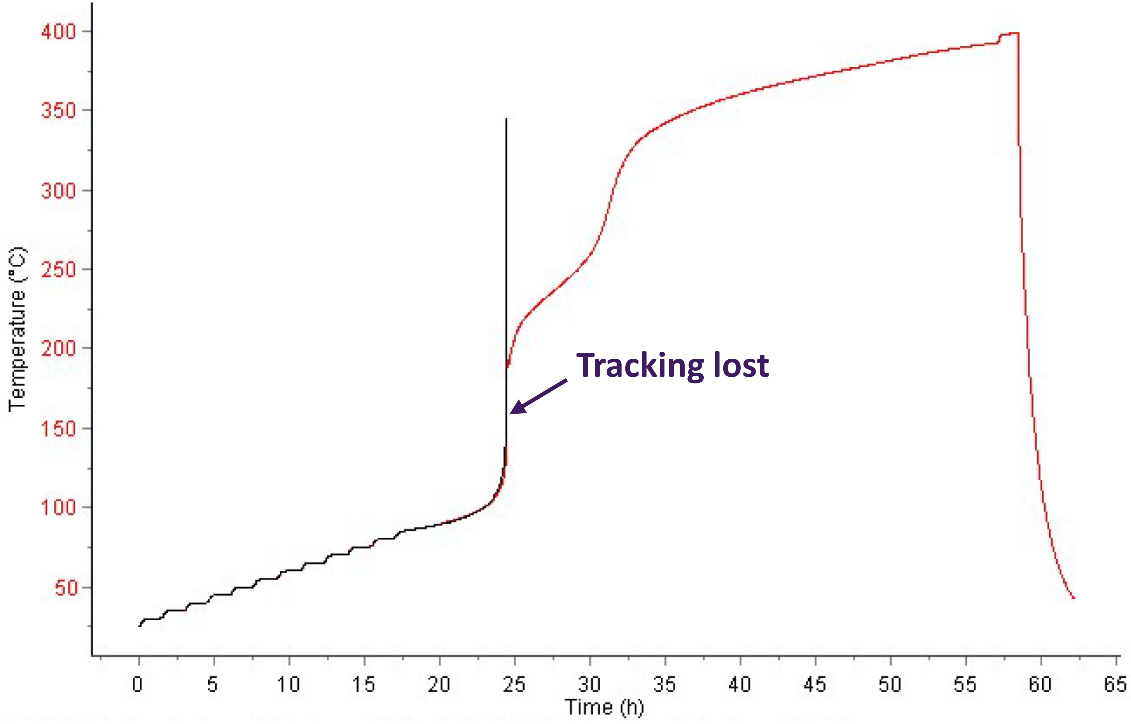
Bestmann-Ohira Reagent



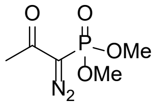


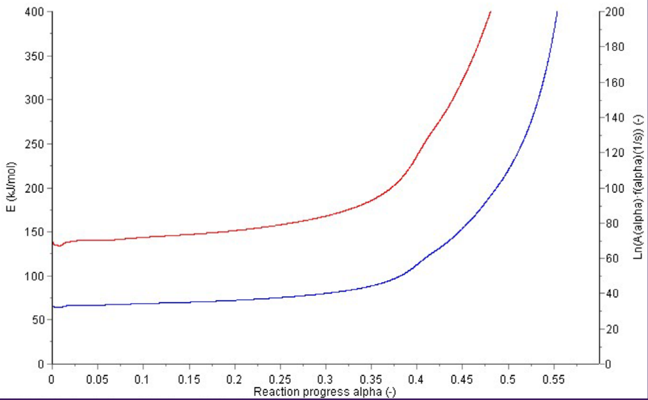
Bestmann-Ohira Reagent

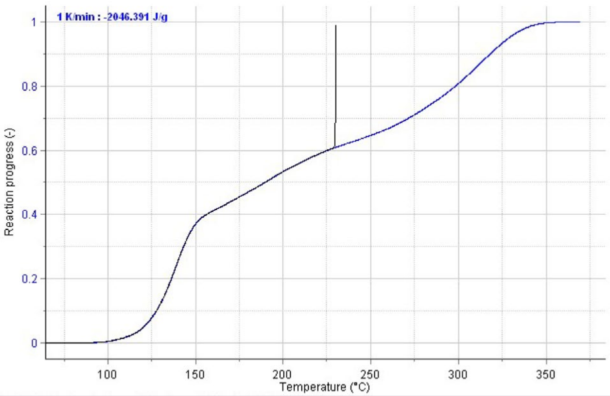
KINETIC PARAMETERS EXTRACTED FROM DSC AND ARC IN NITROGEN

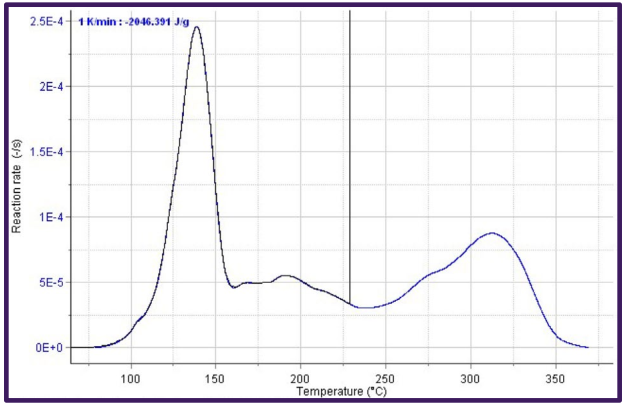


KINETIC PARAMETERS EXTRACTED FROM DSC AND ARC IN NITROGEN


Bestmann-Ohira Reagent

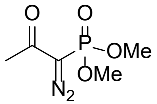




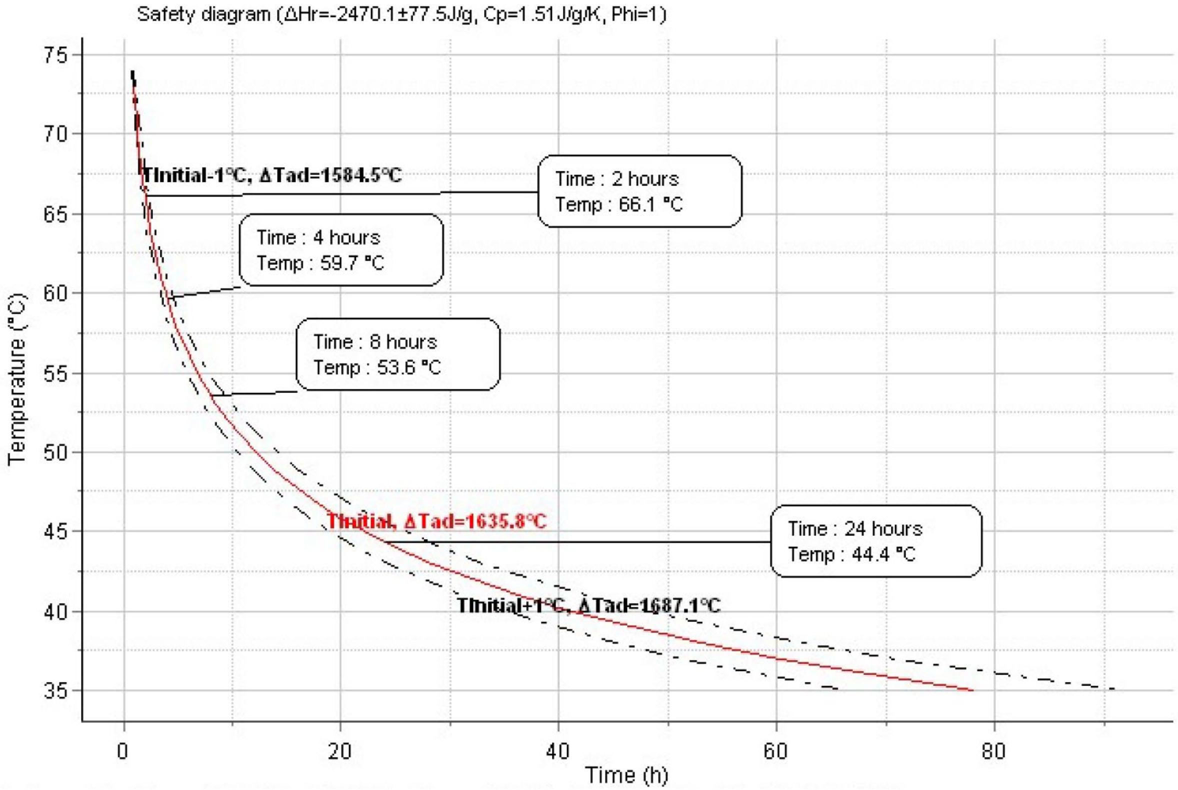


TMR RESULTS

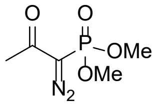
SAFETY DIAGRAMS – DSC IN AIR



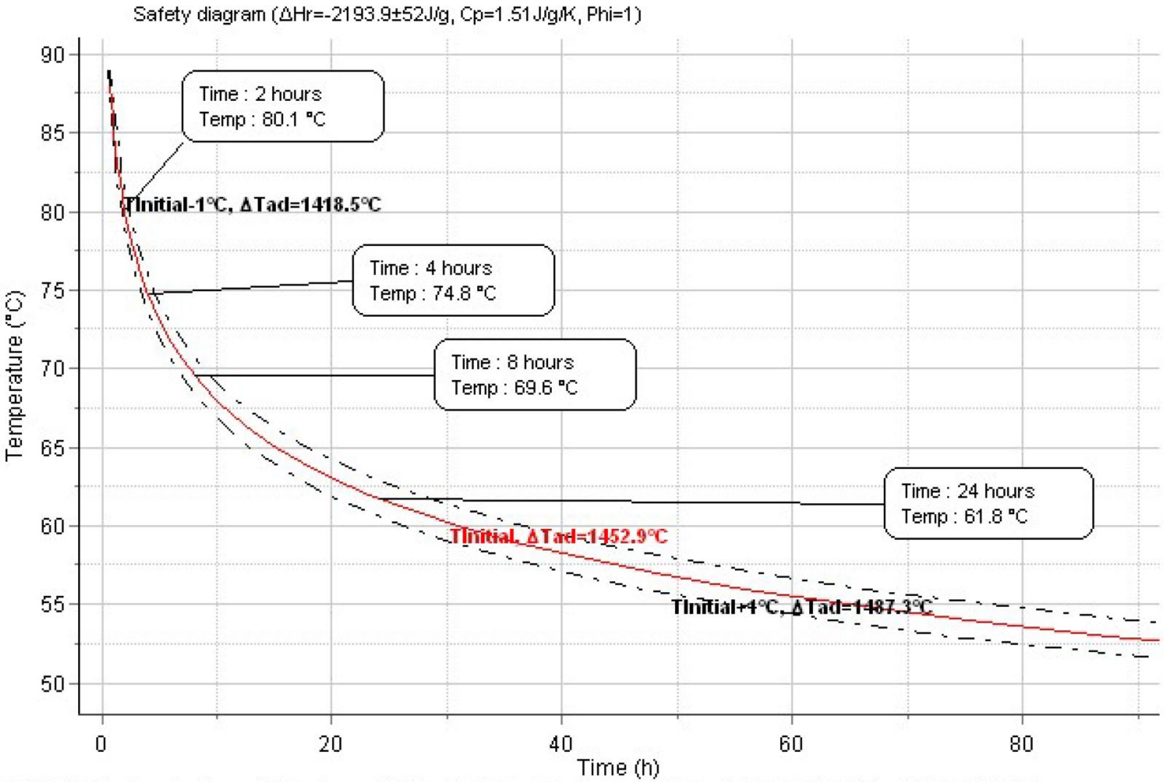
Bestmann-Ohira Reagent

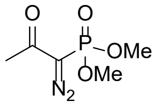


SAFETY DIAGRAMS – DSC IN NITROGEN



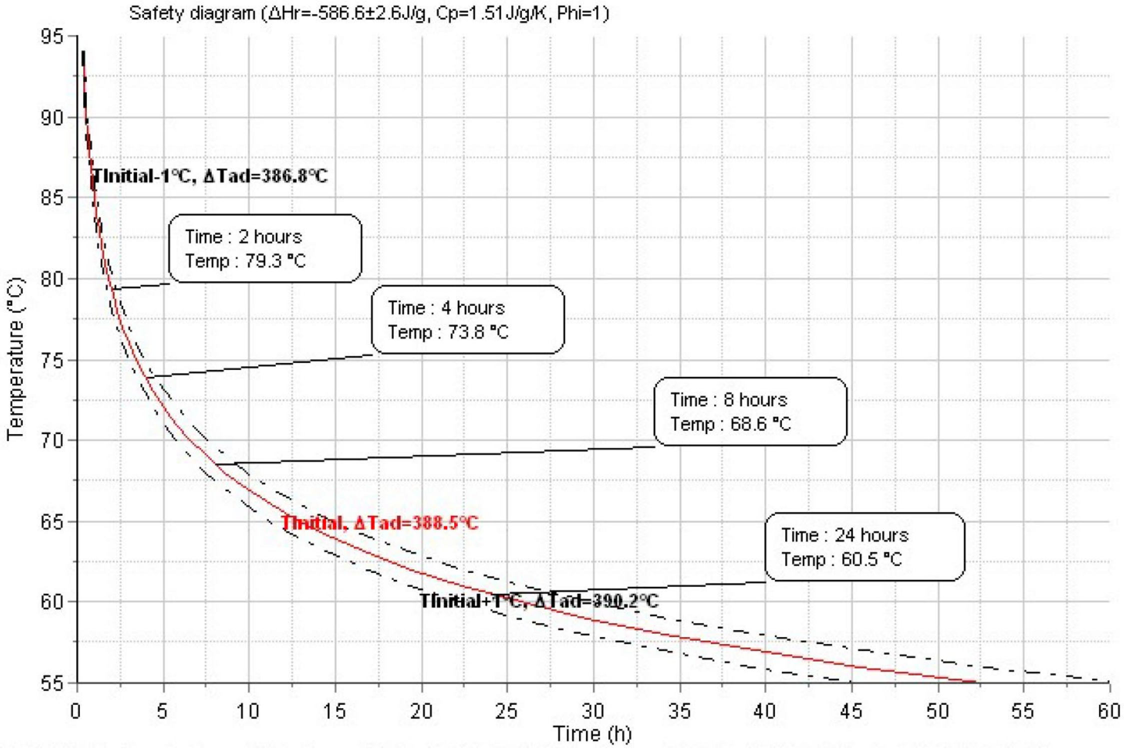
Bestmann-Ohira Reagent

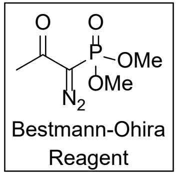




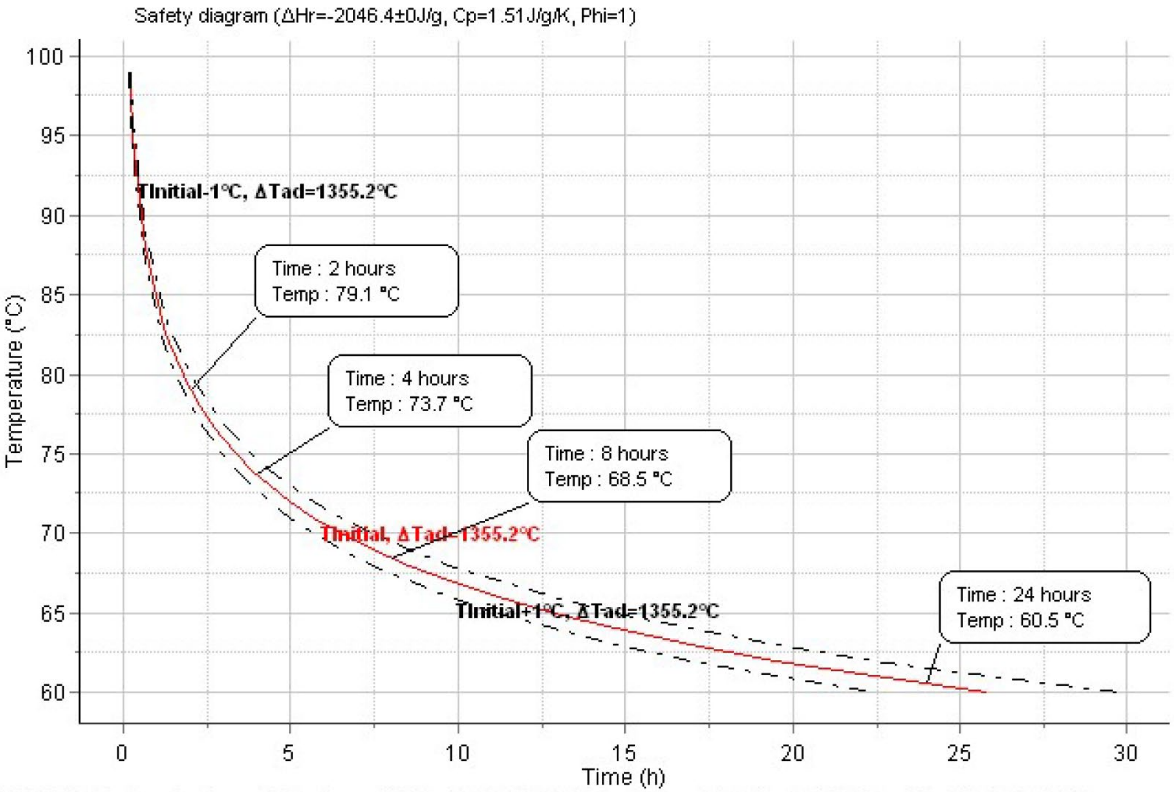
Bestmann-Ohira Reagent

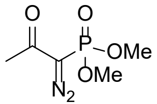
SAFETY DIAGRAMS – DSC AND TAM IN NITROGEN





SAFETY DIAGRAMS – DSC AND ARC IN NITROGEN



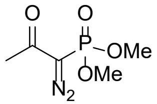


Bestmann-Ohira Reagent

TMR DATA

Time to Maximum Rate (hrs)	Temperature (°C) (DSC data in Air)	Temperature (°C) (DSC data in Nitrogen)	Temperature (°C) (DSC + TAM data in Nitrogen)	Temperature (°C) (DSC + ARC data in Nitrogen)
2	66.1	80.1	79.3	79.1
4	59.7	74.8	73.8	73.7
8	53.6	69.6	68.6	68.5
24	44.4	61.8	60.5	60.5

SADT DETERMINATION



Bestmann-Ohira Reagent

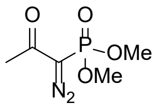
SADT CALCULATION

- The SADT, as defined by Test H.1 United States SADT test, is the lowest ambient temperature at which the center of the material within the package heats to a temperature 6°C greater than the environmental temperature after a lapse of a seven-day period or less
- This period is measured from the time when the temperature in the center of the packaging reaches 2°C below the ambient temperature
- The SADT is a measure of the combined effects of the ambient temperature, decomposition kinetics, package size, and the heat transfer properties of the substance and its packaging
- AKTS uses finite element analysis to solve heat balance equations and predict the temperature at any location within a package at any given time
- The sample is a liquid, and it is assumed to be well mixed
- Kinetic parameters from DSC and TAM experiments in nitrogen were used for this evaluation

Recommendations on the Transport of Dangerous Goods - Manual of Tests and Criteria, 6th revised edition, United Nations, ST/SG/AC.10/11/Rev.7, New York and Geneva, 2019.

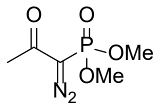
Recommendations on the Transport of Dangerous Goods – Model Regulations, 21st revised edition, United Nations, ST/SG/AC.10/1/Rev.21, New York and Geneva, 2019.

SADT CALCULATION PARAMETERS



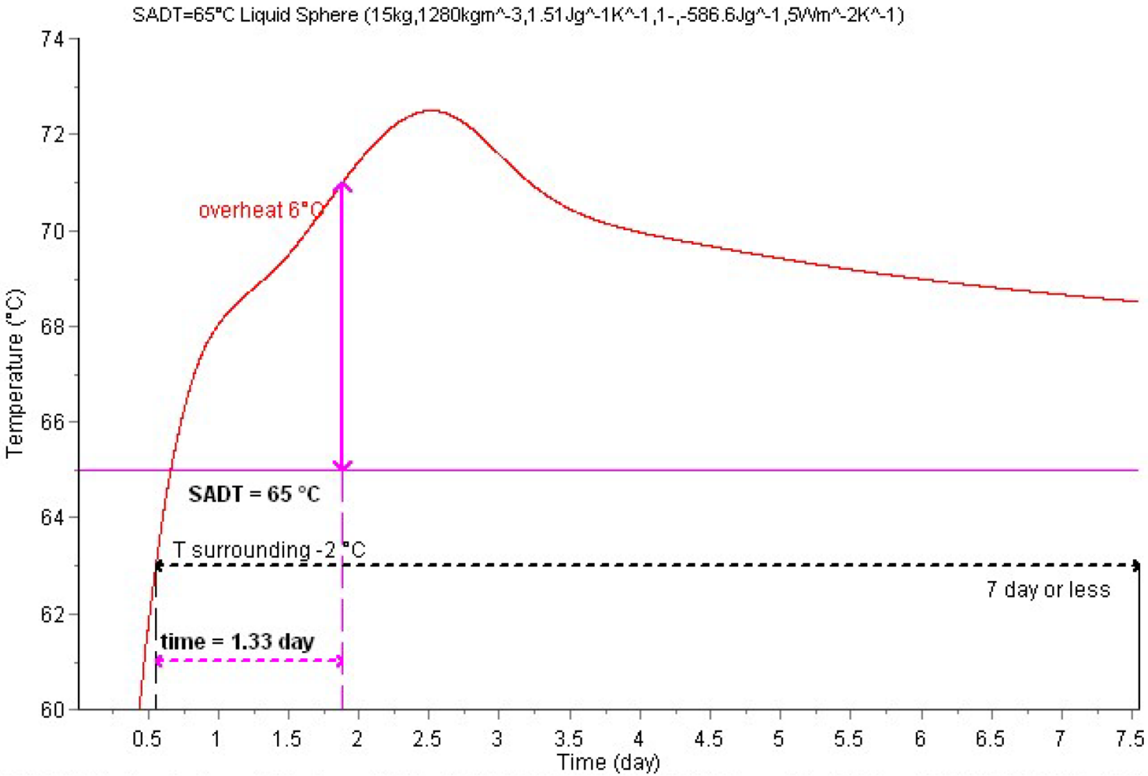
Bestmann-Ohira Reagent

Parameter	15 kg Package	50 kg Package	1000 kg Package
Package Material of Construction	Plastic	Plastic	Metal
Mass of Reactant, kg	15	50	1000
Density of Reactant, kg/m^3	1280		
Specific Heat of Reactant, J/kg/K	1510		
Heat Transfer Coefficient from Container, $W/m^2/K$	5	5	10

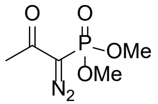


Bestmann-Ohira Reagent

SADT CALCULATION – 15 KILOGRAM LIQUID SPHERE

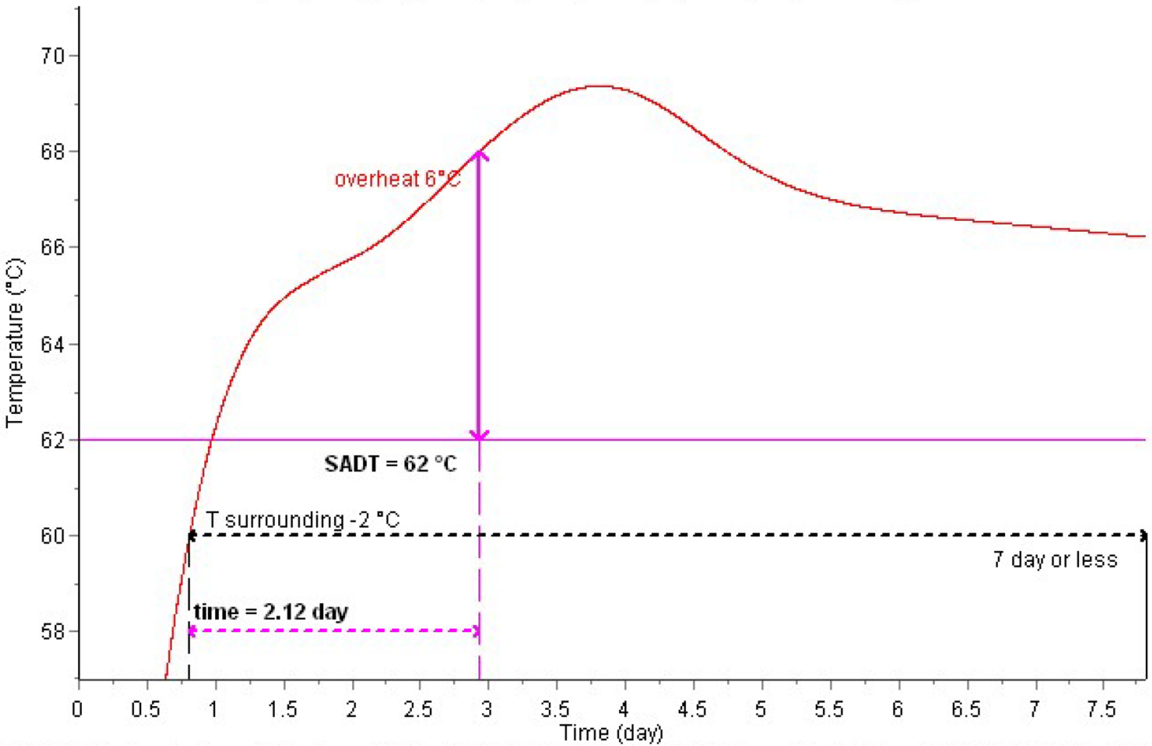


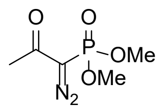
SADT CALCULATION – 50 KILOGRAM LIQUID SPHERE



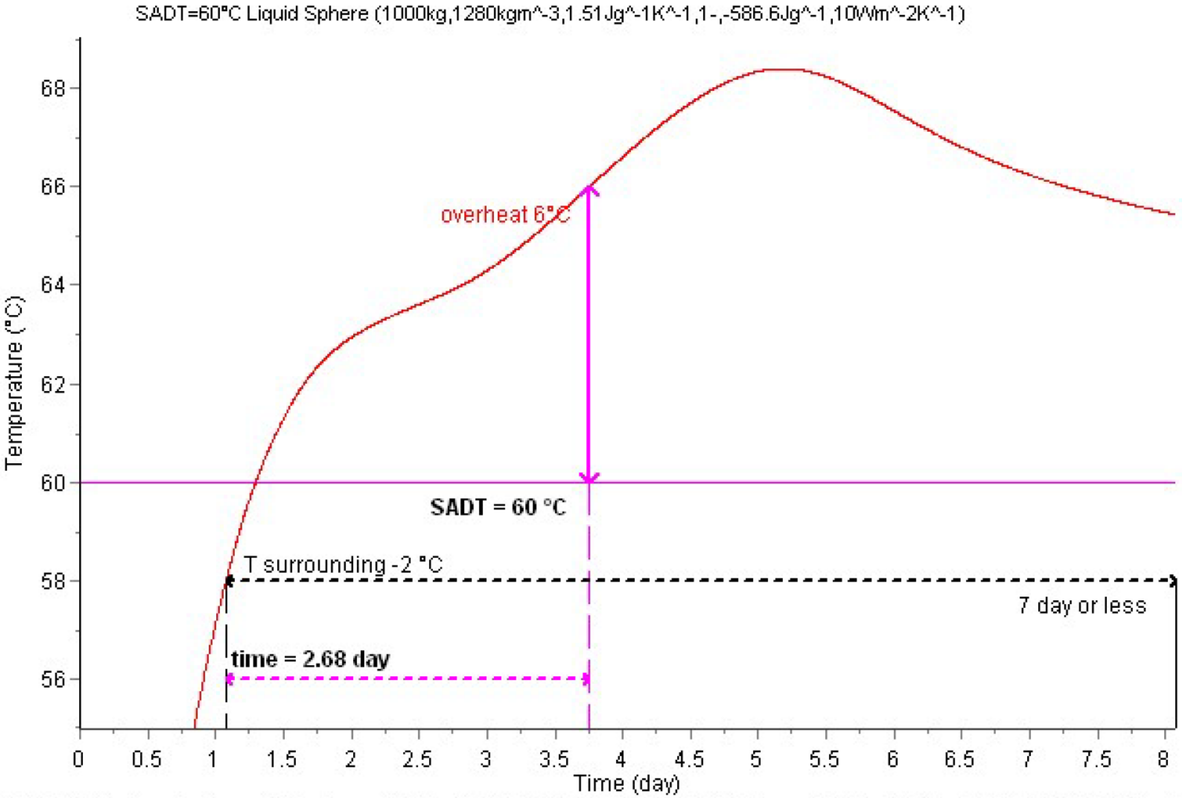
Bestmann-Ohira Reagent

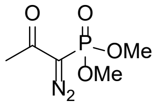
SADT=62°C Liquid Sphere (50kg,1280kgm^-3,1.51Jg^-1K^-1,1-,-586.6Jg^-1,5Wm^-2K^-1)





SADT CALCULATION – 1000 KILOGRAM LIQUID SPHERE



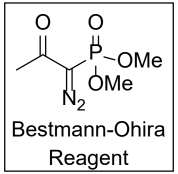


Bestmann-Ohira Reagent

SADT CALCULATION – RESULTS FOR BESTMANN-OHIRA REAGENT

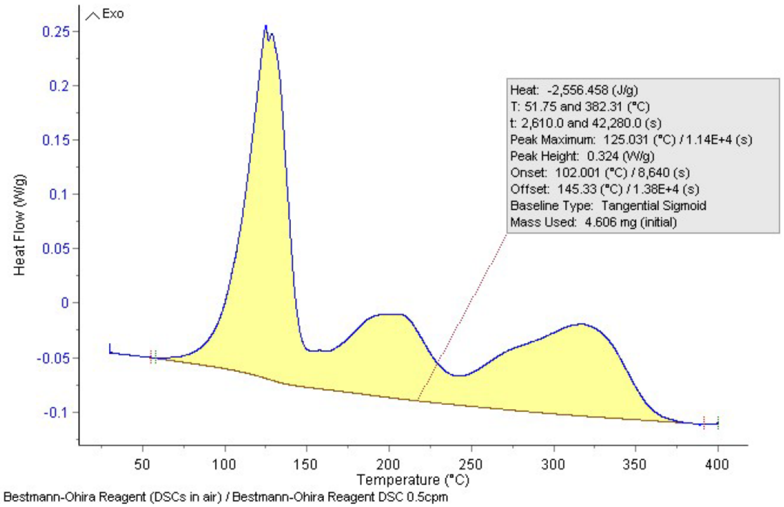
Container Size (kg)	Self-Accelerating Decomposition Temperature (°C)
15	65
50	62
1000	60

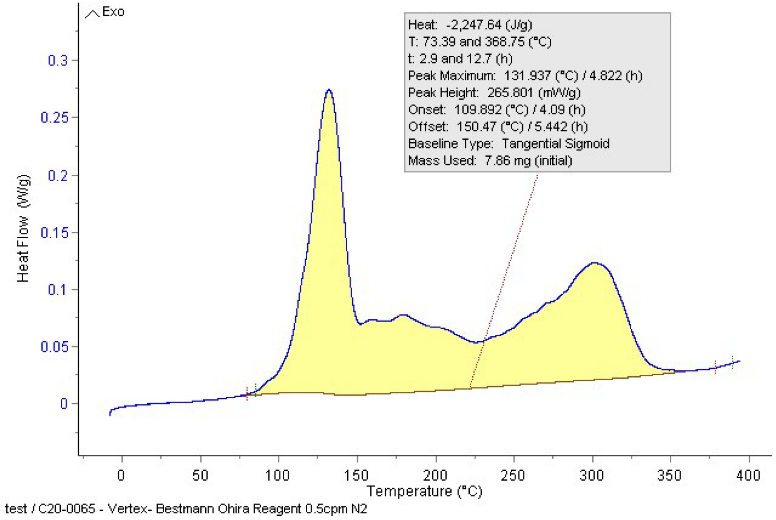
CONCLUSIONS

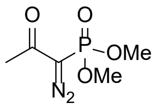


CONCLUSIONS

- Bestmann-Ohira Reagent undergoes exothermic decomposition starting at 51 °C by DSC in air and 73 °C when the DSC is performed under a nitrogen headspace



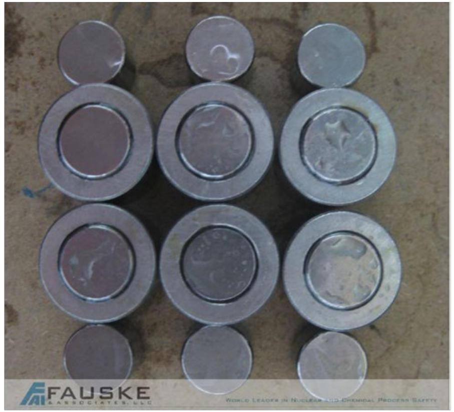




Bestmann-Ohira Reagent

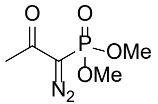
CONCLUSIONS

- Bestmann-Ohira Reagent undergoes exothermic decomposition starting at 51 °C by DSC in air and 73 °C when the DSC is performed under a nitrogen headspace
- Although the reagent flagged as potentially shock sensitive and capable of explosive propagation by the Yoshida Correlations, the material is neither impact sensitive nor friction sensitive
  - U.N. Test Series 2 testing was not performed



Drop Weight (kg)	Drop Height (cm)	Approximate Impact Energy (J)	Trial Results						Comments
			1	2	3	4	5	6	
10	100	100	NR	NR	NR	NR	NR	NR	No reaction

Weight (kg)	Notch #	Resulting Load on the Sample (N)	Trial Results						Comments	Test Result (+/-)
			1	2	3	4	5	6		
10.08	6	360	D	D	D	D	D	D		-



Bestmann-Ohira Reagent

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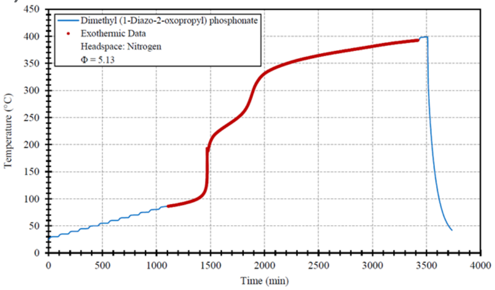
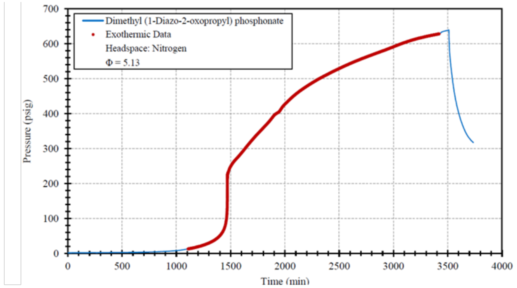
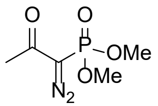
- Although the reagent flagged as potentially shock sensitive and capable of explosive propagation by the Yoshida Correlations, the material is neither impact sensitive nor friction sensitive
  - U.N. Test Series 2 testing was not performed
- ARC testing revealed a thermal onset temperature of 85 °C (under nitrogen) and an accompanying adiabatic temperature rise of > 1,578 °C





Sample Name	Thermal Inertia, Φ (-)	Onset Temperature, T_o (°C)	Final Reaction Temperature, T_f (°C)	Observed Temperature Rise, ΔT_{obs} (°C)	Adiabatic Temperature Rise, ΔT_{ad} (°C)	Specific Heat of Reaction, $-\Delta H_R$[1] (J/g)
Dimethyl (1-Diazo-2-Oxopropyl) Phosphonate	5.13[1]	85.19	>392.76	>307.57	>1578	>2383

1: A specific heat capacity of 1.51 J/g/K was estimated using DIPPR [1]



Bestmann-Ohira Reagent

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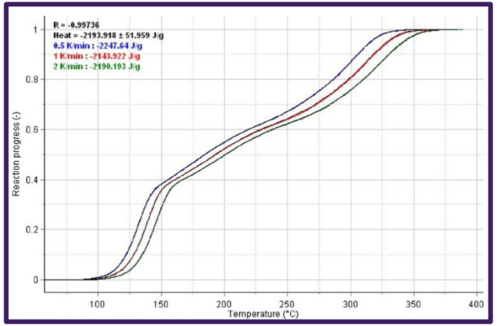
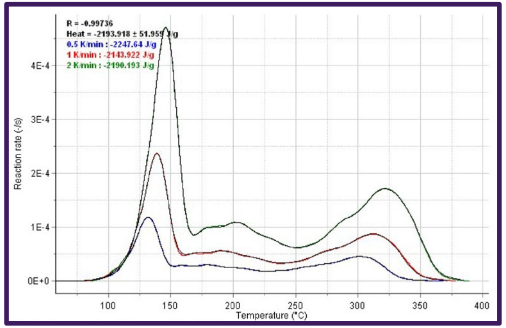
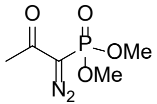
- DSC, ARC and TAM tests were used to construct kinetic models for the decomposition







Bestmann-Ohira Reagent

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- TMR and SADT values were calculated from these models

Time to Maximum Rate (hrs)	Temperature (°C) (DSC data in Air)	Temperature (°C) (DSC data in Nitrogen)	Temperature (°C) (DSC + TAM data in Nitrogen)	Temperature (°C) (DSC + ARC data in Nitrogen)
2	66.1	80.1	79.3	79.1
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24	44.4	61.8	60.5	60.5

Container Size (kg)	Self-Accelerating Decomposition Temperature (°C)
15	65
50	62
1000	60

ACKNOWLEDGEMENTS

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Shane Stone and Michael Azuma

Elizabeth Meenan, Marie-Christin Holt, and William Spreadbury