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Use of the Ultra Low Temperature RC1e Reaction Calorimeter

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Abstract:

Experiments using the Ultra Low Temperature RC1e Reaction Calorimeter were carried out using acetone as the reaction medium. These experiments enabled the capabilities of the calorimeter to be determined. These included minimum operating temperature, temperature stability, baseline stability, cool down rates, and controllability of additions. Experiments were carried out with the standard SV01 reactor and glass head, both with and without specially designed lagging for the reactor and head. The experiments were then repeated with an MT01 head fitted. The MT01 head was cooled to −65 °C via the use of an external oil chiller. Additions of ambient temperature acetone were carried out over 30 min at reactor temperatures of −70, −50, and −30 °C. An actual chemical process was also evaluated using the RC1. This enabled the calorimeter to be tested in a real life situation. A suitable operating procedure has been developed which overcomes a number of problems, which were highlighted with respect to the RC1's built-in safety system. The temperature and baseline stability along with the minimum achievable temperature of the jacket and reactor were established when the RC1 was connected to a Huber 390W chiller. The degree of temperature control was determined for the additions at each temperature. This was established for the different reactor configurations.

1. Introduction

Reaction calorimetry is used to determine thermodynamic and kinetic data, which can be used in process design and optimisation, for any given chemical process. The Mettler RC1 Reaction Calorimeter is a computer controlled, electronically safeguarded laboratory reactor for the performance of isothermal and adiabatic reactions. It can be used to determine thermal data, which can be manipulated to ascertain the values of thermodynamic and kinetic parameters, such as heat of reaction, adiabatic temperature rise, rate constants, and Arrhenius parameters.

Rhodia ChiRex has pilot plant and large scale cryogenic capabilities at its UK and US sites. We have found that an increasing number of processes at cryogenic temperatures are being developed both in house and by customers, which require scale-up. There are however safety issues in operating reactions at these temperatures. Sensible heat output from an addition is much larger than that of normal reactions due to the effect of the heat of dosing. This may mask the true heat of reaction. It is not possible to carry out conventional thermal stability tests at these temperatures using normal methods, such as ARC.

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Figure 1. **Picture of standard RC1 setup.**

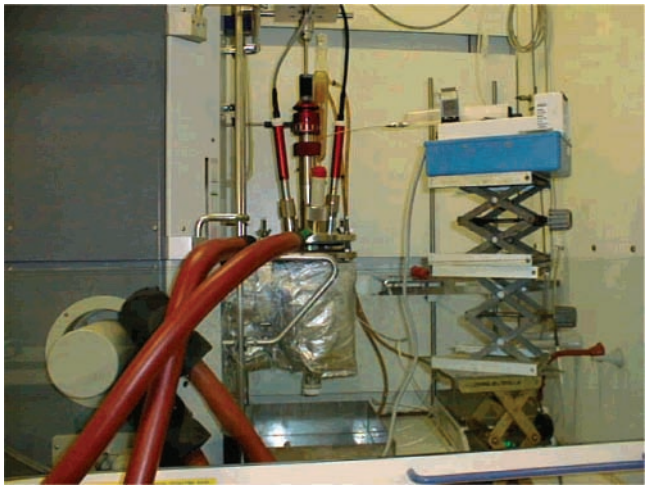

Figure 2. **Picture of RC1 with MT01 head fitted and the vessel lagged.**

2. Equipment

These experiments were carried out in a Slim-line RC1e Ultra Low Temperature Reaction Calorimeter, which was purchased early in 2000. A picture of the standard setup can be seen in Figure 1. Simple lagging was wrapped around the vessel and head in an attempt to reduce thermal contact with the surroundings; see Figure 2. The MT01 PTFE head was also fitted and cooled to −65 °C, to help reduce the thermal contact; a picture of this can be seen in Figure 3. A picture of the Huber chiller and the hoses connecting it to the RC1 can be seen in Figure 4. In all experiments, the Huber chiller was set at −90 °C.

Due to the arrangement of the RC1, fume cupboard, and chiller, the hose length is ∼4 m. If the hoses were shorter,

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Figure 3. **Picture of RC1 with MT01 head fitted.**

Figure 4. **Picture of Huber 390 W chiller and hoses.**

we assume that the amount of heat loss between the chiller and RC1 would be less and therefore the minimum jacket temperature may be lower.

When the chiller operates at such low temperature, there is a large amount of condensation on the hoses. This condensation results in a pool of water on the floor, which may cause a slip hazard; therefore, absorbent mats were used to reduce this. The Huber chiller is very noisy when operating. To reduce the noise, the chiller was boxed in. As the chiller compressor is water-cooled and airflow is available via the back of the box, the chiller operates normally.

3. Trial Experiments

A number of experiments were carried out in an attempt to determine the capabilities of the calorimeter.

3.1. Experimental Section. All these experiments were carried out using acetone. An initial volume of 300 mL was used with additions of 50 mL being carried out.

3.1.1. Cool Down Rates. First, the rate at which the RC1 was able to cool was established for each setup, that is, with and without lagging and with the MT01 head. This involved using 300 mL of acetone and setting the RC1 in Tr mode at 0 °C and allowing a set amount of time for the chillers to reach an equilibrium temperature. The Tr set point was then changed to −70 °C, and the time for the reactor to reach temperature measured.

The minimum achievable temperature was also determined during these tests.

3.1.2. Calibrations. Calibrations were carried out at −30, −50, and −70 °C in each reactor setup. This was to establish if the temperature control was adequate enough to produce reliable UA values.

3.1.3. Additions. The acetone additions were carried out to determine how accurate the temperature control was at different temperature set points and with the different reactor configurations. In each case, the addition time used was 30 min and the acetone was added via a syringe pump. As no reaction is taking place, all the measured heat will be from the dosing.

3.2. Results. *3.2.1 Operation of Calorimeter*. Several operational issues were highlighted when using the calorimeter at these low temperatures.

1. The RC1 safety system in particular the "Tj − Tc > 5 °C" warning. This normally occurs at the start of the experiment when the RC1 injects oil into the vessel jacket directly from the chiller. When this happens, the jacket then becomes colder than the Tc reservoir and flashes the warning and then emergency. The only way around this is to set the RC1 to stir at ambient temperature for ∼30 min, by which time the RC1's Tc reservoir will have cooled to a temperature similar to that of the chiller.

2. There can also be significant oscillation in dTr/dt and Qr curves if the chiller is not set at a low enough temperature. Mettler recommended that when operating at temperatures around ambient to have the chiller set at −40 °C.

3. A large amount of extra oil is required when operating at temperatures around −70 °C as the oil contracts, to avoid "Low Oil Level" alarms.

4. Condensation on the hoses is a factor that must be addressed from a safety point of view.

5. Problems can arise with the indirect heat exchanger. If there is any moisture in the coil and the calorimeter is heated and then cooled normally, this trapped water may freeze and expand, causing the coil to crack. Therefore, the heat exchanger coils must be dry. A suitable method to ensure that this does not a happen is to flush the coil with acetone and then blow dry with nitrogen and to leave a nitrogen purge through the coil at all times.

3.2.2. Cool Down Rates. A plot of the cool down profiles can be seen in Figure 5. It can be seen that the time to −30 °C is the same in each system, 3 min, and the time to −50 °C is slightly faster with the lagging fitted, 7.5 min compared to 8 min. A significant improvement was seen in reaching −70 °C; with the lagging fitted, it was only 36.5 min compared to 46 min without the lagging.

The minimum achievable jacket temperature was found to be −74.5 °C, and the minimum reactor temperature, −73.5 °C when both the lagging and MT01 head were fitted. The corresponding values with the standard head were found to be −73 and −72 °C when only the lagging was fitted and −72.5 and −71.5 °C when there was no lagging.

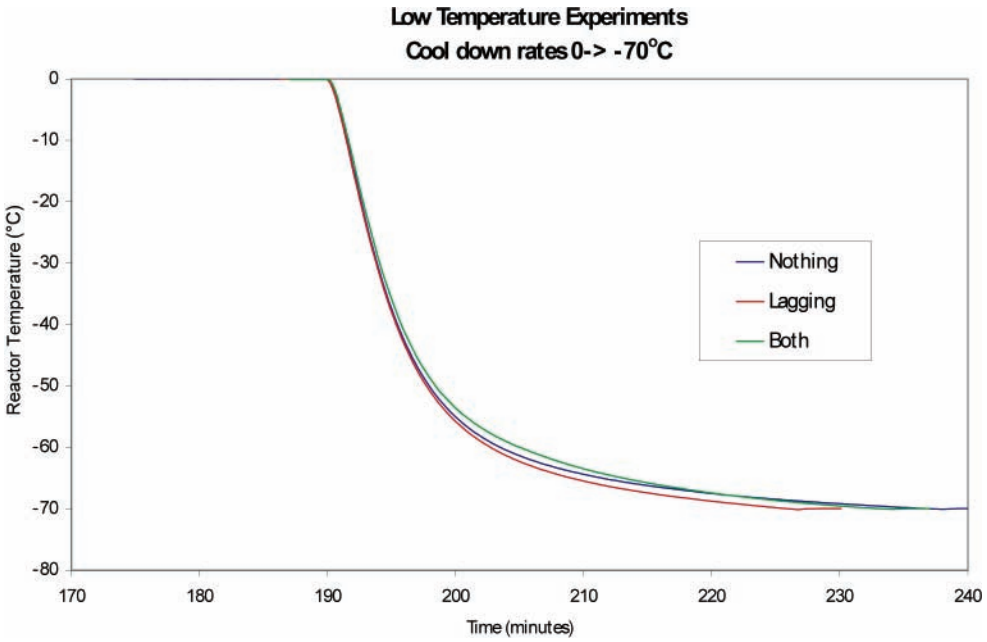

Figure 5. **Cool down rates.**

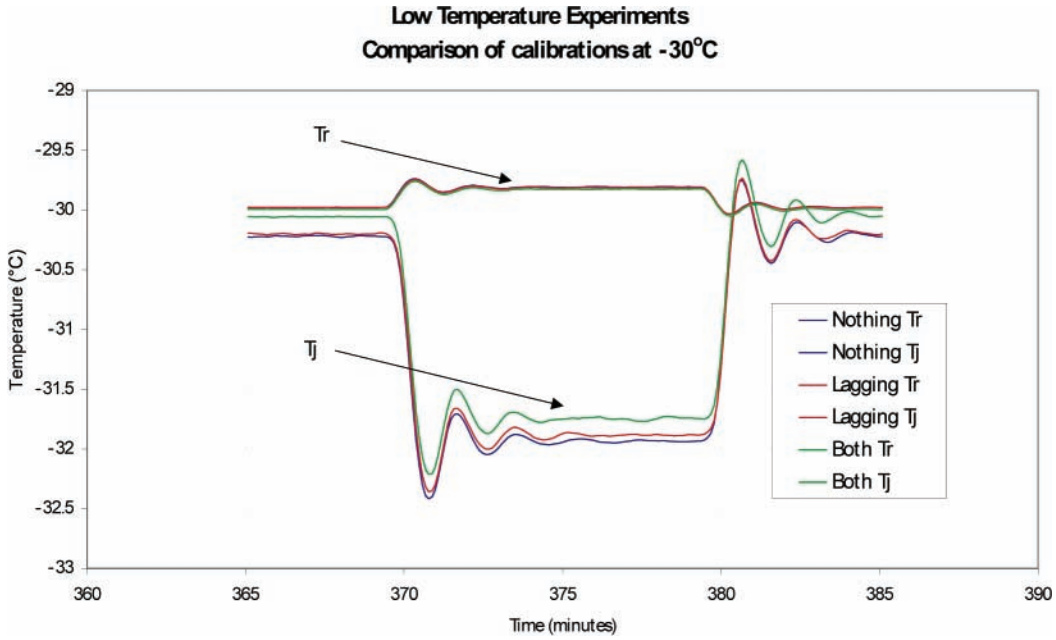

Figure 6. **Comparison of calibrations at −30 °C.**

3.2.3. Calibrations. A comparison of calibrations at −30 °C can be seen in Figure 6.

The calibrations at −30 °C all appear to be fine with the reactor temperature traces virtually identical for all configurations. However, it can be seen from the jacket temperature plots that when the vessel has neither lagging on nor the MT01 head fitted, the temperature the jacket is required to attain, to control the reactor, is much lower. This is due to lower thermal effects from the vessel surroundings because of the lagging and the MT01 head.

All the UA values are similar, but the value for the configuration with the MT01 head is slightly greater; see Table 1. This reflects the fact that the jacket does not have to cool so much to control the reactor temperature.

Table 1. **UA values for calibrations at −30 °C**

configuration	UA value
standard	2.93
lagging	2.97
lagging and MT01 head	3.20

Here also, the calibrations at −50 °C appear to be satisfactory but again the jacket has to work harder to maintain the reactor temperature; see Figure 7.

Again, the same trend is seen in the UA values with the lagged configuration having a slightly larger value; see Table 2.

The calibrations at −70 °C do not look the same as a normal calibration; see Figure 8. This is due to the jacket being unable to cool quickly enough to control the reactor

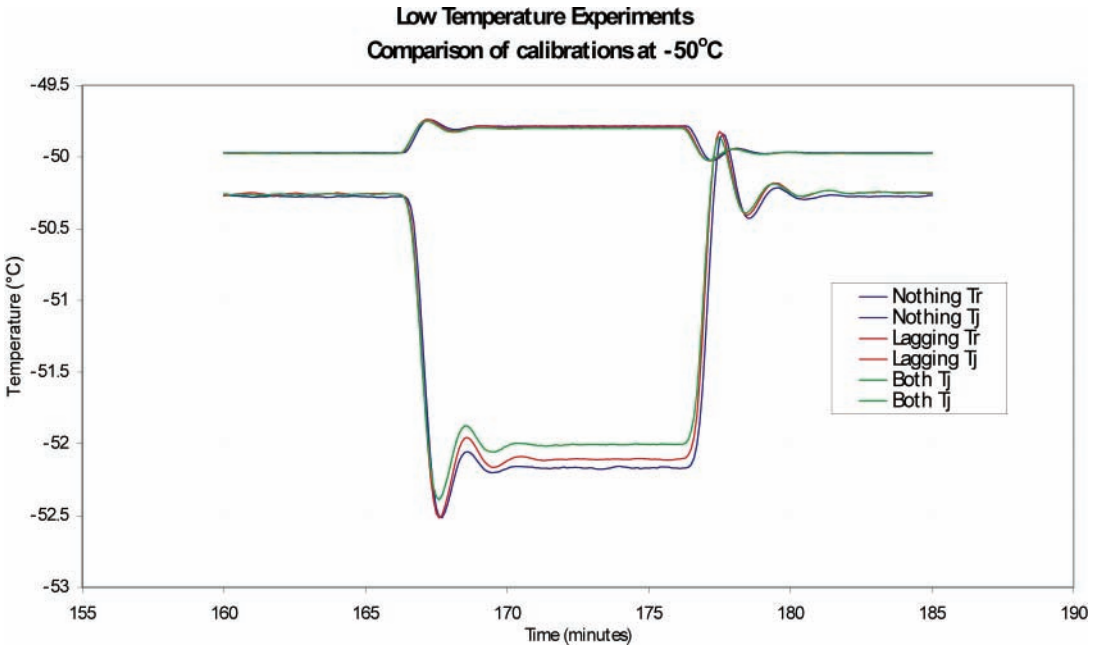

Figure 7. **Comparison of calibrations at −50 °C.**

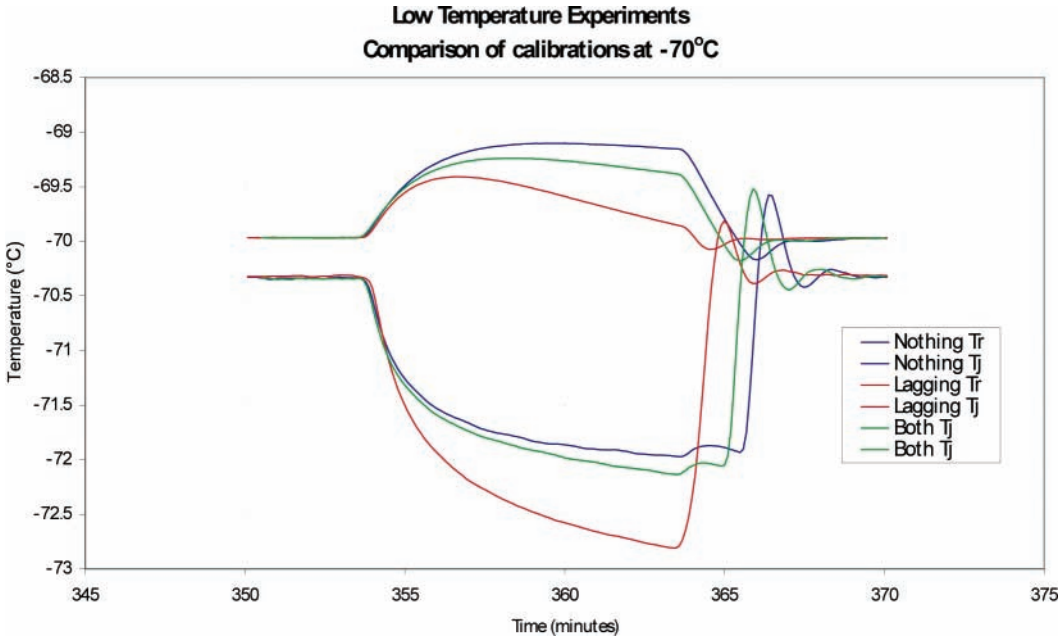

Figure 8. **Comparison of calibrations at −70 °C.**

Table 2. **UA values for calibrations at −50 °C**

configuration	UA value
standard	2.66
lagging	2.72
lagging & MT01 head	2.79

Table 3. **UA values for calibrations at −70 °C**

configuration	UA value
standard	2.34
lagging	2.12
lagging and MT01 head	2.38

temperature properly. The UA values calculated from calibrations at this low temperature must be regarded as suspect; see Table 3.

The unreliability of such calibrations at this temperature is illustrated here with the value with the lagging being *less* than that without the lagging. This is contrary to what was found in the previous experiments and is due to the lack of temperature control at this low temperature.

3.2.4. Additions. The calorimeter is able to maintain the batch temperature within 0.1 °C of the set point; see Figure 9. The temperature control is slightly better when the MT01 head is fitted. But as with the calibrations, the required jacket

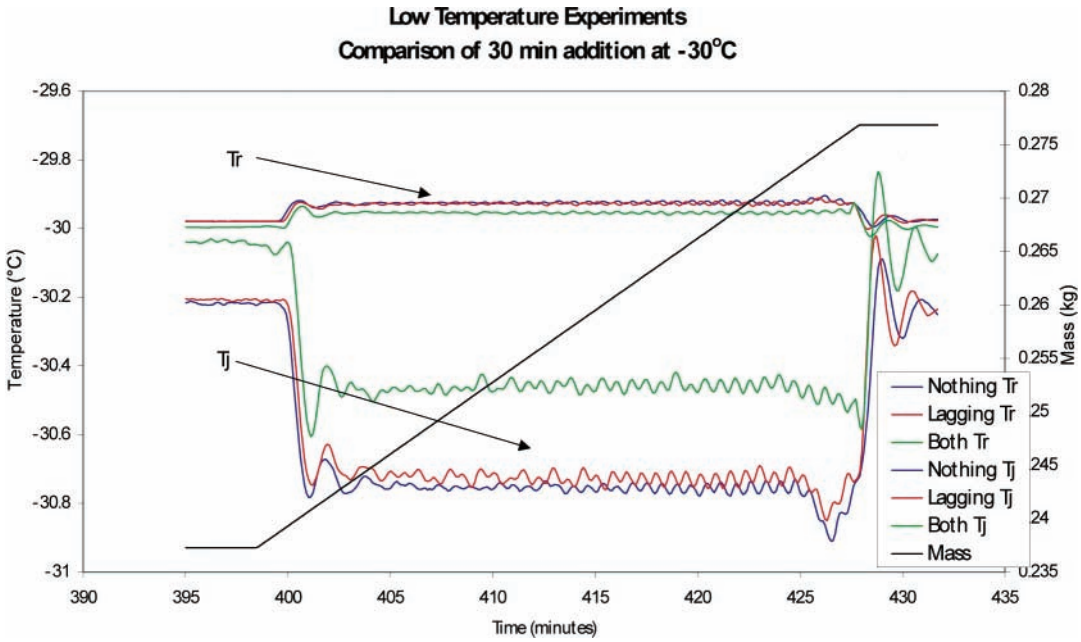

Figure 9. **30 min addition at −30 °C.**

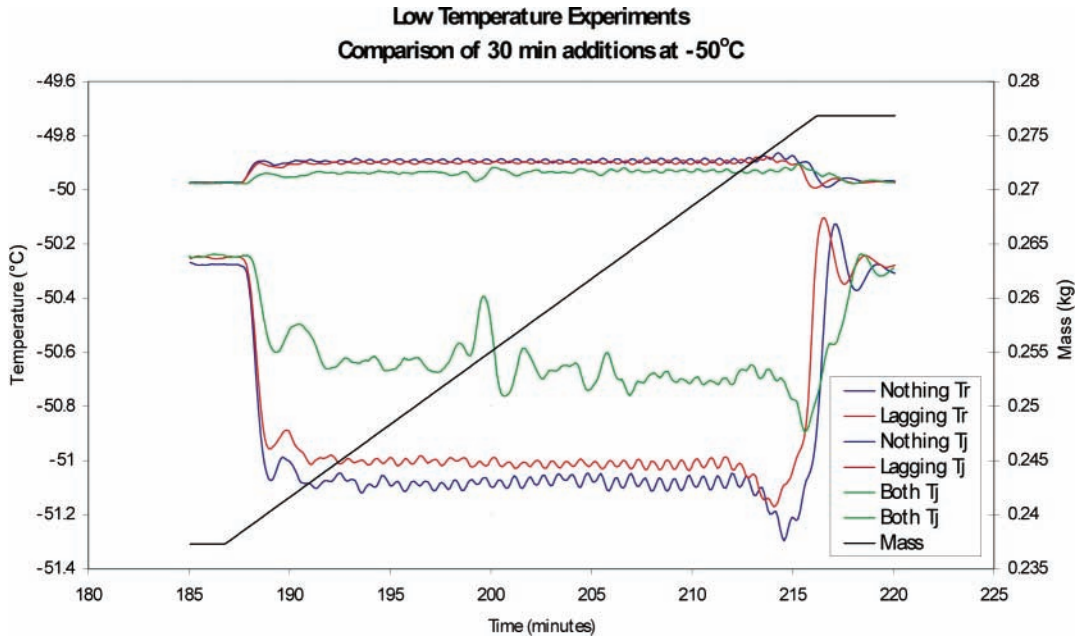

Figure 10. **30 min addition at −50 °C.**

Table 4. **Heat output from additions at −30 °C**

configuration	heat output excluding heat of dosing (kJ)
standard	3.013
lagging	2.953
lagging and MT01 head	2.377

Table 5. **Heat output from additions at −50 °C**

configuration	heat output not including dosing (kJ)
standard	4.108
lagging	3.835
lagging and MT01 head	2.276

temperature is much lower with no vessel lagging or the MT01 head. This lower jacket temperature is also shown by the heat output from the addition, excluding heat of dosing; see Table 4. The measured heat output is less when the MT01 head and lagging are fitted.

As with the addition at −30 °C, the addition at −50 °C was easily controlled by the calorimeter, ∼0.1 °C of a temperature rise; see Figure 10 . Again the overall measured heat output is less when the vessel lagging is fitted; see Table 5.

It was again possible to control the heat output resulting from the addition at −70 °C, with only a ∼0.15 °C temperature rise in the batch; see Figure 11. The measured heat output when the lagging is fitted is also less at this temperature; see Table 6.

4. Example Process

An actual chemical process was carried out between −70 and −60 °C. This involved the condensation of a gas and

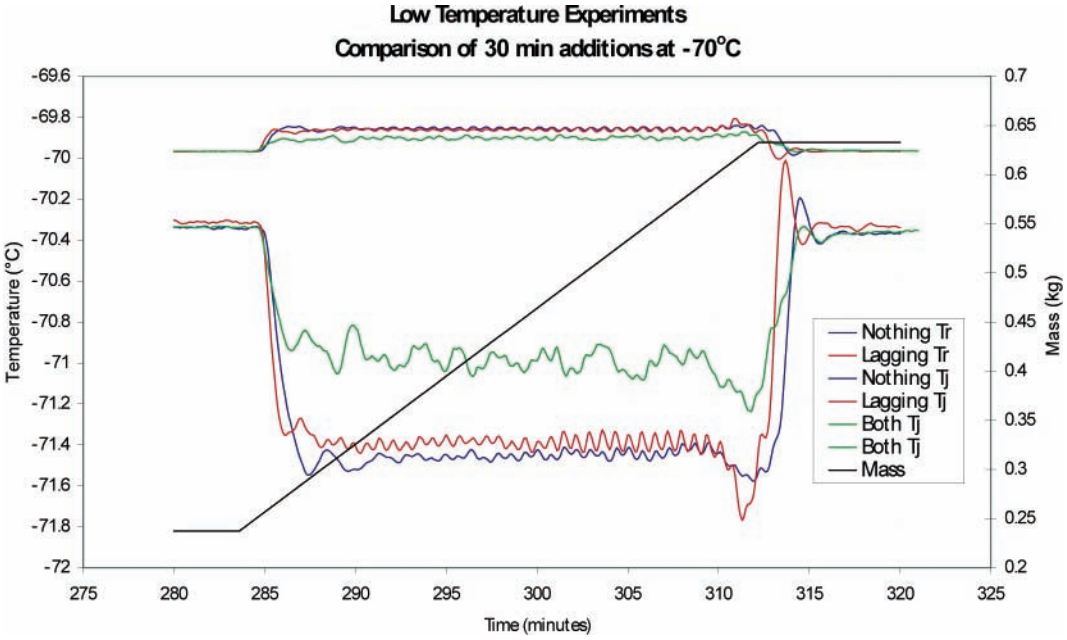

Figure 11. **30 min addition at −70 °C.**

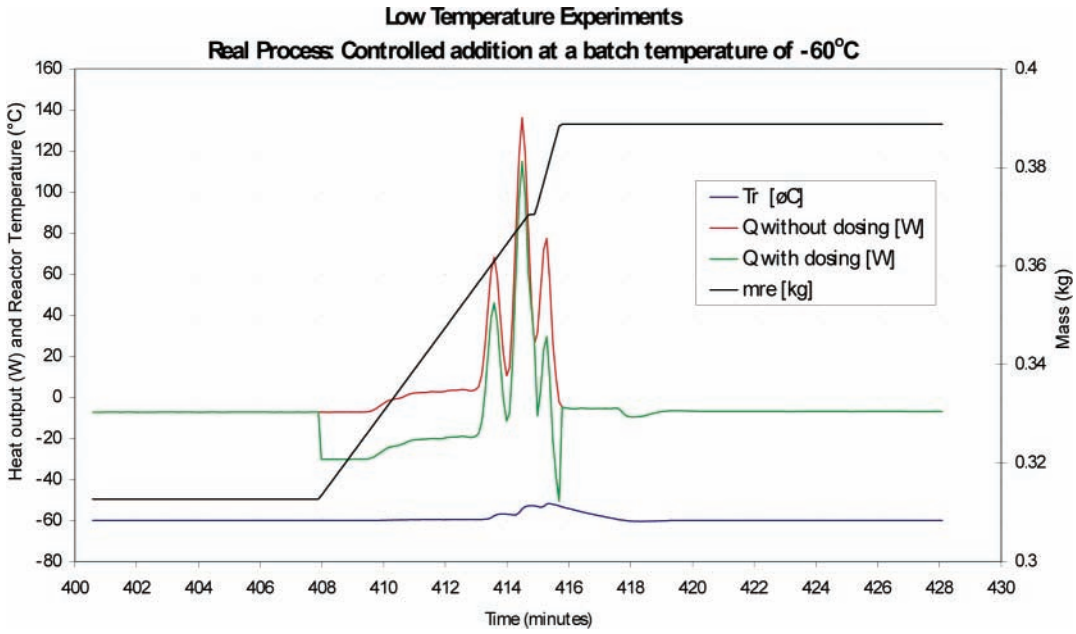

Figure 12. **Real process, addition at −60 °C.**

Table 6. **Heat output from additions at −70 °C**

configuration	heat output not including dosing (kJ)
standard	5.05
lagging	4.824
lagging and MT01 head	2.979

several subsequent liquid additions at temperatures between −70 and −60 °C. These are for illustrative purposes to show what can happen during a real experiment.

4.1. Experimental Section. These experiments involved carrying out controlled additions over several minutes to a reactor at a batch temperature of between −60 and −70 °C.

4.2. Results. It is clear that the RC1 was unable to control the reactor temperature during the addition at −60 °C, a rise of ∼8 °C; see Figure 12. This was mainly due to the short addition time of ∼8 min and to the dosed material being at ambient temperature.

It can be seen from this trace that the heat of dosing masked the initial endothermic heat of reaction. Problems may arise at these temperatures as a reaction may stall, and when the batch is subsequently warmed to ambient temperature, it may then run away. One possible method to determine if the reaction has occurred would be to estimate the amount of heat of dosing there would be from carrying out the addition and then to compare the amount of heat observed on-line with this value. It would not be easy to determine if the reaction has taken place analytically, as the sample would naturally warm to ambient temperature before the analysis is carried out. One possible method would be

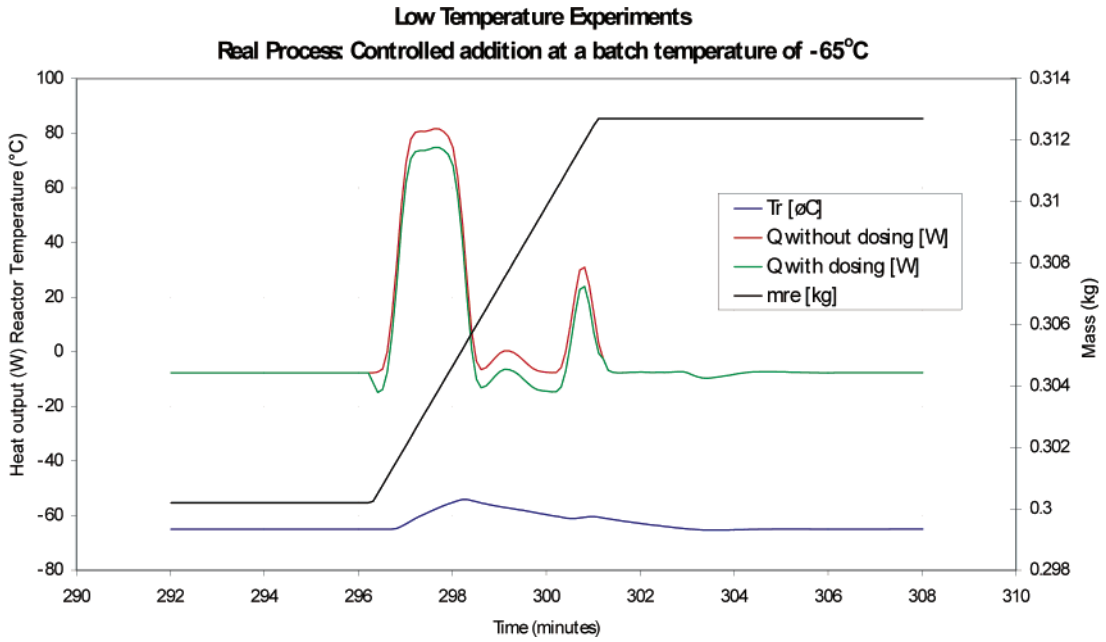

Figure 13. **Real process, addition at −65 °C.**

Table 7. **Cool down times and minimum temperatures**

configuration	−30 °C (min)	−50 °C (min)	−70 °C (min)	min jacket (°C)	min reactor (°C)
standard	3	8	46	−72.5	−71.5
lagging	3	7.5	36.5	−73	−72
MT01 and lagging	3	8.7	42.8	−74.5	−73.5

to follow the reaction using FTIR spectroscopy. A new way of establishing whether the reaction had occurred would be with the WinRC-NT software, as it is now possible to carry out on-line evaluations. This would allow the heat of reaction to be quantified before the batch was warmed.

Again, there was a significant rise in the reactor temperature, over 10 °C, during the addition at −65 °C; see Figure 13. Therefore, the addition time would have to be increased.

5. Conclusions

5.1. Cool Down Rates. Table 7 shows how quickly the calorimeter was able to cool to reach the target temperature and also the minimum temperatures achievable.

All three configurations are able to cool to −30 °C in the same time. A slight improvement is gained with the lagging fitted to the vessel and MT01 head when cooling to −50 °C. But a large improvement in time is gained when cooling to −70 °C. As can be seen in the Table 7, the time to −70 °C with the MT01 head and lagging was actually longer than that with the standard head. This is likely due to experimental problems.

A lower minimum temperature was achieved when the lagging was fitted, and an even lower temperature achieved when the MT01 head was fitted.

Cooling the reactor from −70 °C to the minimum takes a significant time.

5.2. Calibrations. *5.2.1. −30 °C.* Calibrations at this temperature are possible with standard setup, but when the lagging is added, the temperature the jacket has to cool to is less. There is a greater improvement when the MT01 head is added. The reactor temperature only rose by ∼0.25 °C.

5.2.2. −50 °C. Similar results were found at this temperature, as it is well within the capabilities of the calorimeter. Again, the reactor temperature only rose by ∼0.25 °C.

5.2.3. −70 °C. Calibrations at this temperature are unsatisfactory. The jacket is unable to cool fast enough to control the reactor temperature, a rise of 0.9 °C. With the vessel lagging, there is an added improvement, a rise of 0.6 °C, but the shape of the profiles are not the same as those at the higher temperatures. The 5 W heating energy from the heater appears too much for the calorimeter to control.

5.3. Additions. *5.3.1 −30 °C.* A 30 min addition of acetone to a batch of acetone at −30 °C is possible in all configurations. As with the calibrations, the jacket had to work less when the lagging was added and even less when the MT01 head was added. A maximum temperature rise of ∼0.1 °C was observed.

5.3.2. −50 °C. Again, it was found that it was possible to carry out this addition at −50 °C. The reactor temperature rise was found to be ∼0.1 °C in this case.

5.3.3. −70 °C. Even at this low temperature, an addition at the same rate was possible with only an ∼0.15 °C temperature rise observed.

5.3.4. General Points. In general, if the dosed material is added too quickly, then a significant temperature rise will be observed at any temperature. This is however more noticeable as the temperature decreases. When working at −70 °C, there is only a maximum 4.5 °C of cooling capacity, which will not be achieved straight away. Therefore, when working at these temperatures, addition rates must be carefully planned.

5.4. Real Processes. It is possible to carry out real chemical processes at temperatures of −70 °C. However, careful experiment planning is required to ensure the reactor temperature is controlled within the desired range. Care is

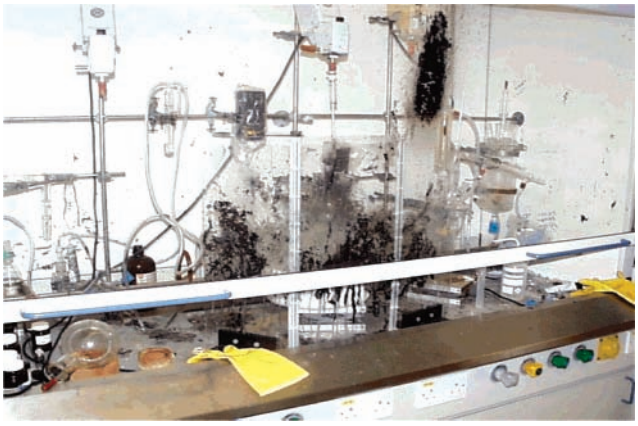

Figure 14. **Fume cupboard after low-temperature Grignard ran away during warm-up.**

also required when warming the batch back to ambient temperature, as reactions may stall at these low temperatures; see Figure 14 for an example. As the heat of dosing is so great, it is possible that reactions can be masked by the dosing effect.

5.5. Operational Recommendations. From experience of using the calorimeter at these low temperatures, several operating issues were highlighted.

1. The RC1 must be stirred at ambient temperature for ∼30 min, to enable the Tc reservoir to cool to a temperature similar to that of the chiller. This will eliminate the "*T*j − *T*c > 5 °C" warning.

2. It is recommended that the chiller be set at a temperature at least 40 °C less than the required *T*r, to avoid any oscillation in the d*T*r/d*t* and Qr curves.

3. Before operating at temperatures around −70 °C, ensure there is adequate oil in the system, as significant contraction of the oil occurs.

4. Beware of the condensation from the hoses causing safety issues (slip hazard) in the lab.

5. Ensure that the indirect heat exchanger is dry at all times, to avoid any possible damage to the RC1 coil.

6. No significant improvement is seen when the MT01 head is fitted instead of the lagging.

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