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Determining the feasibility and mechanisms of chemical reactions as a basis for heat transfer media

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14. ABSTRACT

We sought to test the hypothesis that endothermic chemical reactions could be used as the basis for heat transfer media with effective thermal conductivity and response times that were larger and faster than current media. This hypothesis was tested by synthesizing reactive cooling media, based upon the intramolecular endothermic rDA reaction and then testing this media's ability to cool a restively heated wire and comparing these results to theoretical and simulated predictions of the effect of accessing the chemical reaction. We found that, while both theory and simulation predicted significant effects, we did not determine measurable effects using our experimental approach.

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1 Project Summary

Objective: We sought to test the hypothesis that endothermic chemical reactions could be used as the basis for heat transfer media with effective thermal conductivity and response times that were larger and faster than current media.

Significance: Many modern technologies output large amounts of waste heat, and so require significant cooling. Some applications, such as pulsed lasers, generate large amounts of thermal energy over short time periods, and so also require the ability to respond to this fast generation of waste heat. Advances in, and the ultimate utility of, these technologies will require accompanying advances in management of waste heat.

Rationale: The core concepts of the proposed work can be broken up in to two key hypotheses:

1. *Activating endothermic chemical reactions will increase the observed thermal conductivity of a medium by a factor related ot the enthalpy of reaction.*
   The support for this hypothesis comes from considering the equation for thermal conductivity:

   $$\kappa = \frac{1}{3} n \nu c_p l \tag{1}$$

   where κ is the thermal conductivity, n is the number density of particles, ν is the average velocity of these particles, c_p is the heat capacity of a substance, and l is the mean free path of the particles. The idea here was to increase the effective c_p by accessing an activated endothermic reaction and, hence, the amount of energy that could be absorbed by the medium during the heat transfer process. Given typical values of reaction enthalpy (100 kJ / mol) and heat capacity for liquids (< 10 J g^{-1} K^{-1}), as well as temperature changes of 10s of kelvin, such an approach to increasing the effective heat capacity might provide more than a 10-fold increase in the effective thermal conductivity.

2. *Using endothermic chemical reactions as the basis for heat transfer will provide sub-nanosecond responsivity to changes in temperature.*
   The ability for heat transfer media to respond to a change in temperature ultimately lies in the quickness by which the system can respond to a temperature change. Using thermally activated chemical reactions to absorb heat means that the limit for accessing these reactions will rest on the kinetics of these reactions. For a chemical reaction, the ultimate rate is limited by the frequency factor—or the rate at which the barrier to the reaction is approach. For intermolecular reactions, where the rate is limited by encounters between reactants, this can be as slow at 10s of nanoseconds. However, for intramolecular reactions, where the rate is determined by bond stretching, the ultimate rates are picoseconds, or faster. Thus, using an endothermic intramolecular interaction should provide fast response times to the heat transfer media.

Approach: The general approach to testing our hypotheses can be summarized in four steps.

1. Identify and synthesize chemical species that are liquid and undergo intramolecular endothermic chemical reactions.

2. Using the reaction parameters of the above chemicals, simulate the expected cooling power of the material.

3. Design and construct a cell that will allow for us to test the cooling of a bulk metal wire using our synthesized chemicals.
4. Using both femtosecond and nanosecond time-resolved spectroscopy, determine the response of the chemical system to heating on the sub-nanosecond timescale.

The results obtained for each of these steps are summarised in Section 2, and detailed in Section 3.

2 Accomplishments

The major accomplishments of this project were:

- *We tested our hypotheses.*
  Though under some of our conditions (see section 3) we found significant improvements in the measured thermal conductivity, under other conditions we found no significant effects of employing reactive media. Thus, overall, our experimental design produced inconclusive results. Given the large enhancement we were expected from reactive media, I feel it likely that our inconclusive results constitute a falsification of our hypotheses and we can likely rule out the utility of endothermic chemical reactions as a source to greatly improve thermal conductivity of liquid media. While this is a negative result, it does help narrow the parameter space that must be explored when attempting to improve heat transfer media.

- *The research supported two graduate students.*
  These students gained valuable scientific training in the testing of hypotheses, use of lasers, time-resolved spectroscopy, data analysis, computer coding, Labview^{TM}, and the synthesis, purification, and characterization of chemical species. Of these two students, one has defended her thesis (Dr. Andrea Widstrom) and the other (Mr. Anthony Katona) is finishing up his thesis work.

3 Research Activities and New Findings

3.1 Synthesis and characterization of chemical compounds

For the proposed work, we ultimately selected retro Diels-Alder (rDA) reactions as the basis for our intramolecular endothermic reactions (Figure 1. This is a well-known and studied class of reactions that proceed cleanly. The basic chemical framework can be modified in order to tune the barrier to reaction as well as the degree of endothermicity. Thus, by alteration of the chemical species, we could change the parameters we felt would be relevant to both the thermal conductivity (Hypothesis 1) and the responsibility to temperature change (Hypothesis 2). An additional advantage of these chemicals is that the unsaturated chemical bonds can be hydrogenated, removing the rDA pathway. Thus, a non-reactive analog is readily obtained, in order to compare to the reactive species.

We synthesized three different species for rDA reactions (Figure 1) and also purchased several other species that undergo rDA. In order to ensure that we understood their behavior, we also followed the rDA reaction under several different conditions, in order to obtain information regarding their activation barrier and enthalpy of reaction. These results are summarized in Figure 1 for the chemical species that we had synthesized.

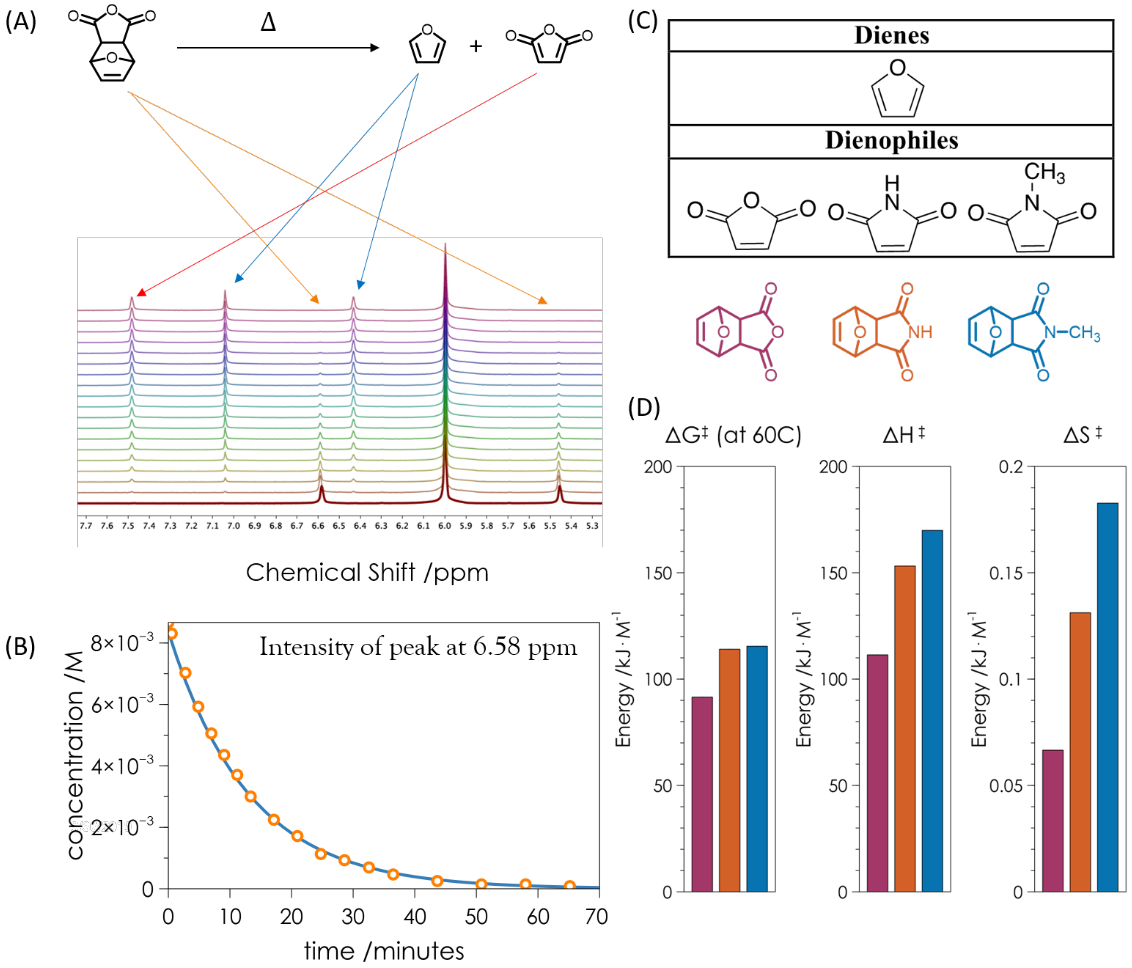

Figure 1: Summary of the chemical species prepared and used in the work being reported on. (A) The basic reaction was a retro Diels-Alder reaction, based upon an adduct formed between furan a dienophile. In general, these provide unique spectroscopic signatures (shown here is ^{1}H NMR), which can be used to follow the course of the reaction. (B) An example of the spectroscopic response over the course of an reaction. (C) The other dienophiles used in this study. (D) By following the course of the reaction at different tempreatures, we extracted the different kinetic parameters for the species. This indicated that we might expect different changes to the heat transfer ability for these different reactive species.

In general, we were able to show that the rDA reaction did undergo the clean cycloreversion that was expected, that the reaction was endothermic, and that we had significant control over the activation parameters for the reaction. In addition, the reaction was straightforward to follow, and produced clean reaction kinetics.Thus, these chemical species were judged appropriate for testing the proposed work.

3.2 Simulation of cooling effects

With appropriate chemical species identified, we also simulated the expected behavior under extreme and rapid heating. This was done using a in-house developed Python code that provided numerical simulation of heat transfer around a nanoparticle that was heated from room temperature to as much as 5000 K over the course of 8 ns. The core details of the simulation were previously published (*Molecules*, **2018**, v. 23, p. 1234). The code described in that publication was modified to allow chemical reactions to occur during the heat transfer and to account for the thermal energy consumption / production that resulted from the chemical reactions.

Using the density of our chemical species and the values of the activation barrier and enthalpy of reaction (as determined in the work describe in Section 3.1), we obtained simulated results of the cooling effects from the chemical reaction. These are seen in Figure 2. These simulations produced 2 key insights:

1. *Reactive media are expected to produce significantly better cooling effects than their non-reactive counterparts.* Examination of Figure 2 shows that the reactive media can increase the conductivity to a point that the media can handle 7.2 MW / cm^2 of additional thermal flux, or exhibits up to 3.36 times the thermal conductivity of the non-reactive species.
2. *The effectiveness of the cooling is dependent on the temperature of the system.* This is an expected result, if we are relying up on a thermally activated chemical reaction. In fact, we expect an exponential dependence on the temperature of the system. This also implies that we should expect the reactive media to provide benefits only for case of extreme heating. Given our simulations, we predicted that reactive media at room temperature cooling objects with ΔTs of around 500 K would exhibit about a 20% increase in thermal conductivity over their non-reactive analogs. We judged this to be significant enough to produce a measurable result.

3.3 Instrumentation for testing cooling media

3.3.1 Commercial instrumentation

We purchased an instrument (Hot Disk TPS 500 S, Thermtest) for measuring thermal conductivity using the transient hot disc or transient hot wire method. These methods can produce rapid and accurate determinations of thermal conductivity, but the ΔT employed during the measurement. Nevertheless, we felt it a good idea to be able to measure thermal conductivity using commercial instrumentation to validate any observations measured using the home-built instrument described next.

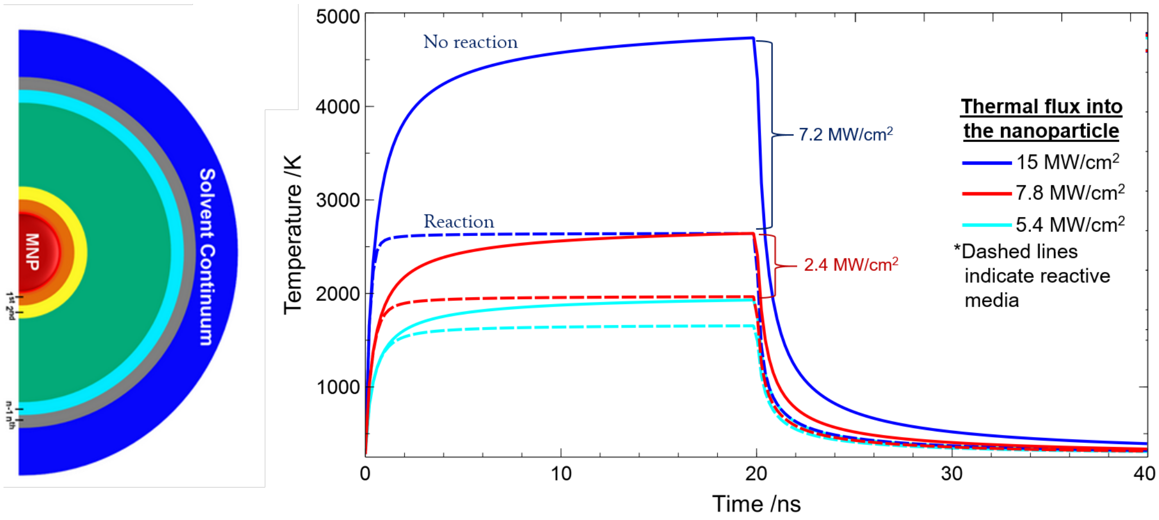

Figure 2: Results of simulation of cooling effects. Left: We used a model in which a metal nanoparticle (MNP) experienced a flux of thermal energy that raised the temperature of the particle. The thermal energy was then allowed to diffuse through successive layers of media out to a continuum, numerically simulating thermal conductivity using discrete timesteps. The number of layers was dynamically controlled to ensure the layer prior to the continuum remained at the initial temperature of the system. The layers of media could be reactive or not reactive in nature. for reactive media, reaction progress during each timestep was modeled using standard Arrhenius kinetics and the impact on the final temperature accounted for using the enthalpy of reaction. Right: Simulations of the nanopaticle temperature in reactive and non-reactive media predict that the reactive media can provide significant cooling enhancement, though this enhancement is dependent on the temperature (i.e., the reactivity is thermally activated). These results are shown for activation energies and reaction enthalpies of 100 KJ / mol.

3.3.2 Home-built instrument

To test the ability of our reactive media to enhance the cooling of a real world object, we designed and constructed a sample cell that would flow this media past a restively heated wire. The cell was designed using COMSOL, to simulate flow and ensure that the wire would experience good flux of chemical species around it. Figure 3 shows a sketch-up of the instrument, COMSOL simulation, and photograph of the cell.

By monitoring both the current (I) and voltage (V) across the wire, we could determine the

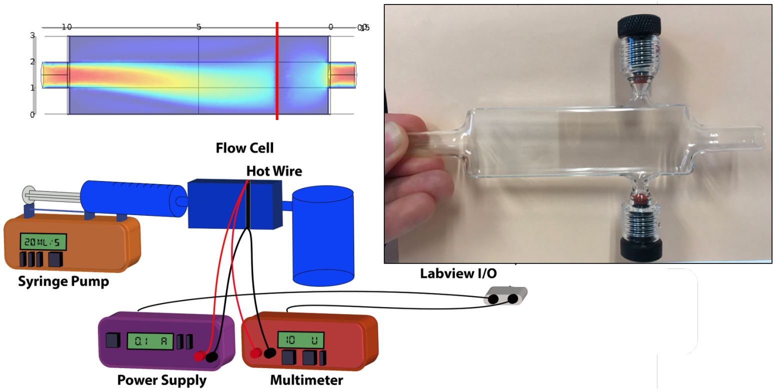

Figure 3: Design of the home-built instrument for monitoring the cooling of a wire by our reactive media. The sample cell consists of a rectangular rube of glass, through which is passed a wire. The wire is connected to a power supply and a multimeter. The power supply provides a constant current, while the multimeter measures the voltage. A syringe pump is used to flow the reactive media past the wire. Also shown are simulations of the media flow past the wire (red) and a photograph of the final cell.

power of the Joule heating (P) as well as the temperature (T) of the wire.

$$
\begin{aligned}
V &= IR \\
P &= VI \\
q &= \frac{P}{A_{wire}} \\
T_{final} &= \frac{1}{\alpha}\left(\frac{R_{final}}{R_{initial}} - 1\right) + T_{initial}
\end{aligned}
$$

In the above equations, R is the resistance of the wire, q is the thermal flux at the surface of the wire, A_{wire} is the cross-sectional area of the wire, and α is the temperature coefficient of resistivity. Thus, if the radius of the wire and the temperature coefficient of resistivity are known, a measurement of I and V will allow for determination of the thermal flux at the wire and the temperature of the wire. If the temperature of the media bath is known (room temperature), the thermal conductivity can be calculated from these values. Performing these measurements for the reactive and non-reactive chemical media, we could isolate the effects of chemical reactivity on κ.

3.4 Testing of cooling media

3.4.1 Measurement of κ using a commercial instrument

Using the transient plane wave instrument, we measured the difference in conductivity for reactive and non-reactive species. Here, we obtained measurable and significant differences between the two species. However, for the non-viscous media we were employing, convection is a serious concern in the measurements. As the two media can have different mass transport properties and the products of the reactive species might be expected to have different convective properties, it was

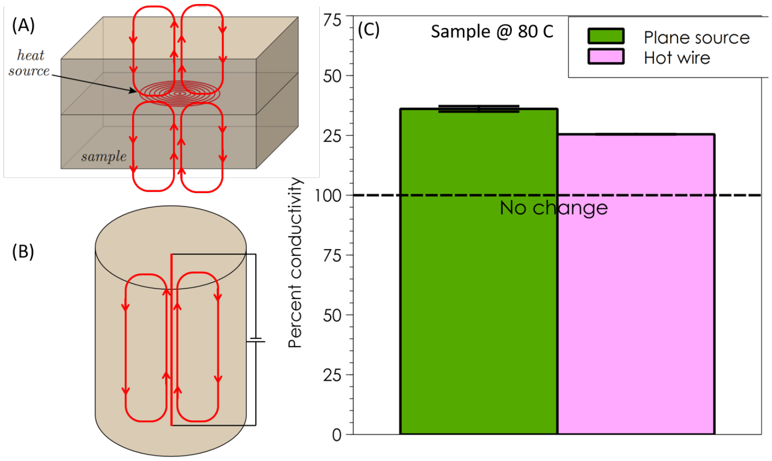

Figure 4: Results of measurements with commercial instrumentation. (A) The plane wave source can introduce convective cooling in non-viscous media that can be difficult to acocunt for. (B) Using a vertically oriented hot wire can alleviate some of the complications associated with convection. (C) For both plane wave and vertical hot wire, we observe significant differences in conductivity (the y-axis is $\frac{\kappa_{reactive}}{\kappa_{non-reactive}} \times 100\%$), though the changes decrease upon mitigating the convective cooling.

not possible to ascribe our observations entirely to changes in κ. To mitigate these problems, we also made measurements using a transient hot-wire geometry. Here we still obtained statistically significant differences in conductivity when comparing reactive and non-reactive species. Given that the temperature changes involved in these measurements are small, we expected more significant observed differences when using our home-built instrument to probe the cooling of a wire heated by several hundred degrees.

3.4.2 Cooling the wire in our home-built cell

We attempted several iterations of the cell and with different chemical species. A typical experiment would involve flowing media past the wire, alternating periods of running large and small amounts of current through the wire, and then monitoring the temperature of the wire during this process. The high current (high power) periods provided measurements of cooling power at high temperatures, while the lower current (low power) regions provided baseline values for the resistance at low temperatures. Figure 5 shows an exemplar of such a run.

As a first order expectation of behavior, if the reactive media provided enhanced cooling, then the wire would be expected to attain lower steady-state temperatures (lower R) under the high current period, as compared to non-reactive media. This requires us to be able to measure differences in R, within the noise of the experiment.

As can be seen in Figure 5, the measurement of V (from which R is determined) is rather noisy. We were able to reduce the noise of our measurements beyond what is shown in this figure. As a result, we were never able to measure differences in R (and, hence, T and κ) that were outside the

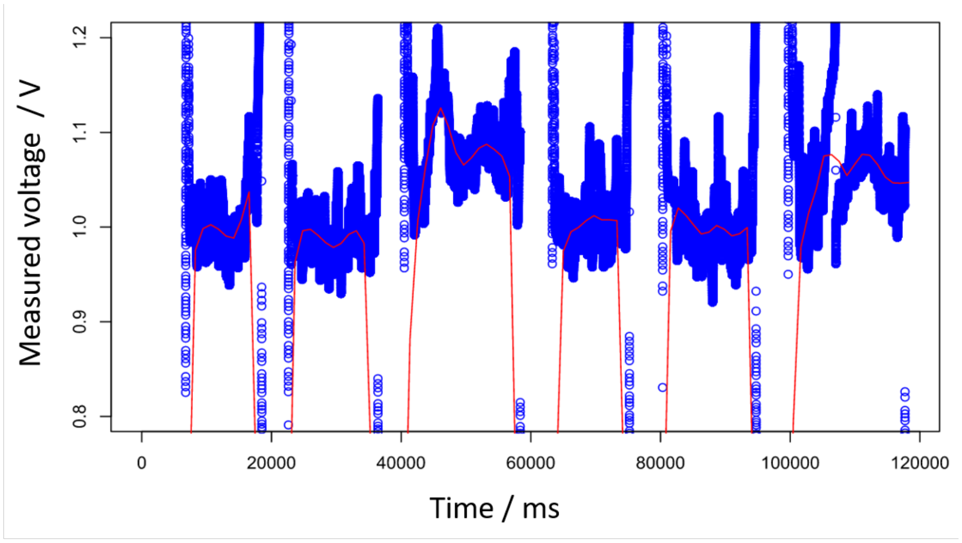

Figure 5: An example of the response of the home-built cell to reactive media. The cell measures the voltage at constant current. Due to the temperature dependence of resistivity, the voltage is related to temperature of the wire under constant current conditions. The blue points are the measured data. The red line is the smoothed data. Shown are the peak voltages. The valleys correspond to low current conditions. The full spread in y is not shown in order to emphasize the results at the peak voltage. The data is relatively noisy. We expected that reactive vs. non-reactive media would have different peak voltages. Based upon the commercial measurements, we might expect ∼20% change in voltage. However, due to the noise in our data, we never measured a statistically significant change.

noise of our instrument. Given the results of our simulation (Section 3.2) and transient thermal measurements (Section 3.4.1), these differences should have been measurable, even given the noise of our instrument. Thus, we concluded that there was likely no effect of the reactive media on the cooling of the bulk hot wire in our flow cell.

3.4.3 Time-resolved measurements

Though time-resolved measurements were proposed, they were ultimately not performed. The reason was that we could never attain bulk-scale measurements of changes in cooling due to reactive media, and so we did not identify a system which we felt warranted the more involved time-resolved measurements. These time-resolved measurements were meant to help verify and explain the observed bulk cooling, which we never observed in a way that satisfied us.

3.5 Conclusions

Both theory and simulation suggested that inclusion of endothermic reactivity into heat transfer media would result in a change in the thermal conductivity of the media. However, experimental measurements of this effect did not yield consistent results. Furthermore, the differences that we were able to measure ($\sim$ 20%) in a statistically significant manner were not the large enhancements ($\sim$10-fold) that originally motivated this study.

4 Publications

As our findings were negative in nature, we have only one publication (under revision) for this project, which details the rDA reactions used.

- A. W. Widstrom and B. J. Lear, “Structural and solvent control over activation parameters for a pair of Diels-Alder reactions” *Scientific Reports*, Under revision.