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Friedel–Crafts Acylation Using Solar Irradiation

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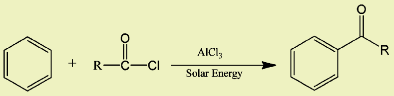

ABSTRACT: In recent decades, scientists have attempted to make more environmentally friendly chemical synthesis procedures. One area of environmental concern is the amount of electricity required to complete an experiment. An effective means for minimizing the amount of electricity needed to drive chemical reactions to completion is proposed through the use of solar parabolic reflectors. The proposed solar reflectors are assembled by covering unused satellite dishes with Mylar tape, giving the satellite dish reflective properties when the dish is directed at the sun. The ability to use the solar reflector as the sole heat source for organic synthesis reactions is being considered. Comparative studies will be conducted using electrical supplies to compare the solar reflectors ability to generate heat to drive the chemical reactions to completion. Analysis of the products of the reactions will be analyzed using NMR and GC-MS. Preliminary research has shown that the solar reflector is capable of heating a substance to a temperature over 300 °C, which is more than capable to drive most organic synthesis reactions to completion. The synthesis of isobutyrophenone, which is synthesized through a Friedel–Crafts acylation of benzene, has been attempted using the solar reflector.

KEYWORDS: *Solar organic synthesis, Solar reflector, Friedel–Crafts acylation, Green chemistry, Solar energy, Reactions and methods*

INTRODUCTION

Green chemistry is generally defined as any attempt to reduce or eliminate the synthesis or use of hazardous substances, especially organic chemicals.[1] The birth of green chemistry is often associated with the recent recognition of the irreversible damage done to the environment through man-made materials and the economic incentives of avoiding the high cost of polluted air and water recovery.[2] The United States Environmental Protection Agency (EPA) has established the Office of Pollution Prevention and Toxics (OPPT) to analyze methods of developing new or improving existing chemical procedures to make them less hazardous to human health and the environment.[3]

Electricity is needed for most synthetic chemical procedures. Most of the electricity in the United States is generated from fossil fuels. All forms of electricity generated through the use of fossil fuels have some form of environmental impact associated with it. Nearly two-thirds of the total greenhouse gas emissions result from the use of fossil fuels for energy.[4]

Solar and water-based energy generation processes have been engineered and implemented in various parts of the United States over the past decade and are virtually greenhouse gas emission-free sources of electricity.[5] Recently, the introduction of the solar oven as a possible heat source for chemical reactions has been examined.[6] A solar oven is a device that uses directed sunlight to generate a concentrated beam heat. Unfortunately, solar ovens have been observed to only heat to approximately 170 °C, far less than some known synthetic reactions.[7]

The development of a solar concentrator constructed out of ionized aluminum sheets was recently studied in attempt to develop a solar autoclave. The autoclave was attached to a metal ring of the solar concentrator, which focused sunlight onto the autoclave, allowing it to gain heat. During the winter season, the solar concentrator was observed to have reached a maximum temperature of 134 °C in a time period of approximately 45 min.[8]

The goal of this study is to design a high-power solar heat source that has the capability of performing high-temperature chemical reactions. Once developed, the power of the solar heat source will be examined through boiling point analysis of several common organic solvents. Also, a full scale chemical reaction will be conducted with the solar heat source, with analysis of the results compared to the same reaction performed in-lab and using an electrical heat source.

EXPERIMENTAL SECTION

Development of the Solar Heat Source. We have designed a solar reflector through the repurposing of an unused satellite dish into a reflective parabolic mirror that will serve as the sole heat source to drive synthetic chemical reactions to completion (Figure 1). An oval, high-definition Direct TV Slimline satellite dish (32 in. × 22 in.) was completely covered with metalized mylar tape to attain the reflective properties needed to generate heat. Because the feed horn of the dish is located at the focal point, it was removed, and reaction flasks were placed in this position in order to achieve maximum intensity from the sunlight. An aluminum heating block was added in this position to act as a heat sink.

Boiling Point Analysis. To gather data on how much heat the solar dish could generate, several high-boiling organic compounds were tested to determine whether enough heat could be generated to get the organic solvents to boil (Table 1). A 20 mL disposable scintillation vial containing 10 mL of solvent was attached to the aluminum heating block on the solar heat source. The satellite dish was then proportioned in the sunlight such that the focal point was directly centered on the bottom of the aluminum block. A Fisher Scientific thermocouple (with a temperature range of −200 °C to +1370 °C) was used to monitor the temperature for each solvent. It

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Figure 1. Repurposed satellite dish heat source.

Table 1. Solvent Boiling Point Analysis Using Satellite Dish Heat Source

	water	propylene glycol	ethylene glycol	diethylene glycol
time to begin boiling	20 min	59 min	36 min	90 min
solvent temperature at boiling	99.8 °C	187.3 °C	196.1 °C	235.7 °C
average outside temperature	25.6 °C	26.9 °C	27.8 °C	28.4 °C
average solar irradiation to reach boiling temperature	671 W/m^2	805 W/m^2	909 W/m^2	789 W/m^2
average heat energy[a]	3193.9 Joules	4147.9 Joules	3665.4 Joules	5000.2 Joules

[a] Heat energy calculated from $Q = mCs\Delta T$.

was observed that by moving the position of the flask, we are capable of attaining various time rates to desired temperature ranges. If the flask is positioned directly in the focal point, for instance, boiling temperatures can be obtained quite rapidly. Repositioning the flask to a position that is off center will allow for a much slower and somewhat controlled heating process.

We found that the solar heat source was capable of attaining temperatures well above that of most known chemical reactions. Because of the positive results with the boiling point tests, we believed that the solar heat source was capable of generating enough heat to drive chemical reactions to completion. The Friedel−Crafts acylation of benzene using isobutyryl chloride was chosen as the first reaction to be performed with the newly developed solar heat source. To analyze the outcome of each reaction, analyses using NMR and GC/MS are going to be conducted.

Experimental Methods. NMR spectra were obtained on a Varian Mercury VX-300 multi-nuclear FT-NMR spectrometer operating at 300 MHz. Chemical shifts were measured in parts per million (ppm) relative to tetramethylsilane (TMS).

A Varian CP-3800 gas chromatograph was used with a Varian Saturn 2200 GC/MS/MS detector and a Varian VF-5MS 30MX0.25 mm ID DF = 0.25 column (Catalog No. CP8944) and CombiPAL auto sampler to obtain GC/MS spectra. Dilutions of all of samples analyzed were necessary due to the observance of extremely high peak counts when undiluted samples were analyzed. Acetonitrile was determined to be a suitable solvent for all of the samples. A mixture of sample and acetonitrile in a 1:1000 dilution ratio was found to be the best concentration of the samples. The mass detector was set to detect only ions with a mass over 40 m/z in order to avoid the appearance of nitrogen, oxygen, and water vapor in the spectra.

Friedel−Crafts Acylation of Benzene Using Isobutyryl Chloride. A solution of benzene (390 mmol), isobutyryl chloride (100 mmol), and aluminum chloride (110 mmol) was placed into a 25 mL round-bottomed flask. The flask was then placed in an aluminum heating block that was attached to the solar heat source near the point at which the focal point was going to be located. Because the reaction was required to reflux for a certain amount of time, a condenser was filled with cold water and capped with pipet bulbs to ensure that the water stayed in the condenser (Figure 2). To keep the condenser at a low enough temperature that reflux would persist for the stated time period, condensers were kept on ice and exchanged periodically during the experiment. The solar heat source was then moved into a position in which it was reflecting sunlight. The focal point of the sunlight was directed at the bottom of the aluminum block. The sunlight heated the aluminum block, just as a hot plate would heat the aluminum block. The solution was allowed to reflux at a temperature of 88−90 °C for a period of 4 h. After an acid workup, pure isobutyrophenone was obtained through vacuum distillation. The in-lab study of this chemical reaction was conducted using the same molar amounts of each reactant, but the reaction was heated using a Fisher Scientific hot plate.

Figure 2. Solar reflux set up.

A 66% yield (9.70 g) of isobutyrophenone was obtained when the Friedel−Crafts acylation of benzene was performed with the solar reflector, while a comparative study using an electric heat source only had a 44% yield (6.73 g) of isobutyrophenone. Spectral analysis using ^{1}H and ^{13}C NMR and GC-MS identified the products. ^{1}H NMR ($CDCl_3$): δ 7.891 (doublet, $J = 5.4$), 7.67−7.31, 3.490 (septet, $J = 9.0$), 1.14 (doublet, 6.9). ^{13}C NMR ($CDCl_3$): δ 204.202, 136.150, 132.700, 128.537, 128.221, 35.227, and 19.67. GC: 7.42 min. MS: 51.0 m/z, 77.0 m/z, 105.1 m/z (base peak), and 148.0 m/z (m^+ peak).

Seasonal and Weather Limitations. In order to examine the seasonal and weather limitations of the solar heat source, the Friedel−Crafts acylation of benzene using isobutyryl chloride was performed in all four seasonal periods (Table 2, Figure 3). Each reaction was performed on the same mole scale. The only conditions changed were the outside weather conditions. All weather conditions were obtained from the weather station located at the Millard Oakley STEM Center in Cookeville, TN, on the campus of Tennessee Technological University.[10]

Our work demonstrates that the solar heat source we developed can be used successfully during any time of the year. However, there are

Table 2. Seasonal Variations for Solar Friedel–Crafts Acylation of Benzene

	spring (3/22/13)	summer (6/26/12)	fall (11/18/12)	winter (2/18/13)
time to begin reflux	19 min	8 min	20 min	15 min
reflux temperature	89 °C	89 °C	89 °C	88 °C
average outside temperature	7 °C	27 °C	16 °C	14 °C
outside conditions	partly cloudy, wind gusts (1–3 mph)	sunny, wind gusts (3–7 mph)	partly cloudy, wind gusts (5–8 mph)	partly cloudy, wind gusts (5–15 mph)
average solar irradiation	670	901	540	626
percent yield	63%	66%	60%	78%

several factors that affect its efficiency. As long as there is enough sun present to produce at least approximately 600 W/m^2 of solar irradiation, efficient heating can be obtained in a reasonable amount of time. Therefore, on days that are mostly cloudy, there typically is not enough solar irradiation to produce enough energy to heat a chemical reaction. Passing clouds occasionally provided losses in heat; however, the use of the aluminum heating block provided enough insulation that the reaction continued while the clouds passed, unless the cloud period lasted for longer than approximately five to ten minutes.

Another trouble area when using the solar heat source is the presence of wind. The presence of wind, especially in the winter and spring, caused notable fluctuations in the reflux temperatures. We were able to solve this problem through the development of a wind blocker that we built and placed around the reaction vessels (Figure 4). A piece of aluminum metal was cut and placed around the reaction vessel such that the top and bottom of the vessel was open, but the sides were blocked. This blocked the reaction vessel from the wind just enough that temperature fluctuations were not observed, even when wind gusts up to 15 mph were present.

■ RESULTS AND DISCUSSION

Upon obtaining data from both the solar (summer 2012) and electrical reactions, it was concluded that the solar heat source was a reliable heating source that produced similar, if not better results, than its electrical counterpart.

A 66% yield (9.70 g) of isobutyrophenone was obtained when the Friedel–Crafts acylation of benzene was performed with the solar reflector during the summer of 2012, while the comparative study using an electric heat source only had a 44% yield (6.73 g) of isobutyrophenone. The in-lab synthesis of isobutyrophenone reported is for one single experiment. Multiple attempts of synthesizing isobutyrophenone in-lab were performed and resulted in similar yields (40–50%). Furthermore, the solar reflector was able to produce a purer product based off of the NMR spectra of the product. This is based off of the observation that the NMR spectra for this reaction using an electric heating source displayed small residual peaks for the presence of initial reacting compounds. There were no observable peaks for these compounds in the NMR spectra of the solar reaction product.

■ CONCLUSION

Our work demonstrates that the solar heat source that has been developed can be used successfully in the place of an electric heating source. The solar heat source was able to successfully synthesize the product from a well-known high-temperature reaction with yields that were comparable to the same scale reaction performed using an electric heat source. Furthermore, it was determined that seasonal variations do not seem to affect the results obtained from the use of the solar heat source. As long as sunlight is present, the solar heat source can be used as the heating source for a chemical reaction, no matter what the outside temperature is.

It is believed that the solar heat source is a viable option for the replacement of electric heating sources and could be used to make these and other chemical reactions greener. By using the solar heat source, none of the waste from using electricity is generated because the only energy being used is the energy from the sun. Currently, data is being collected daily to investigate the effect of seasonal and weather conditions on the solar reflector as a heat source. In addition, more complex chemical reactions are being conducted using the solar reflector heat source. The results of using solar energy as the heat source

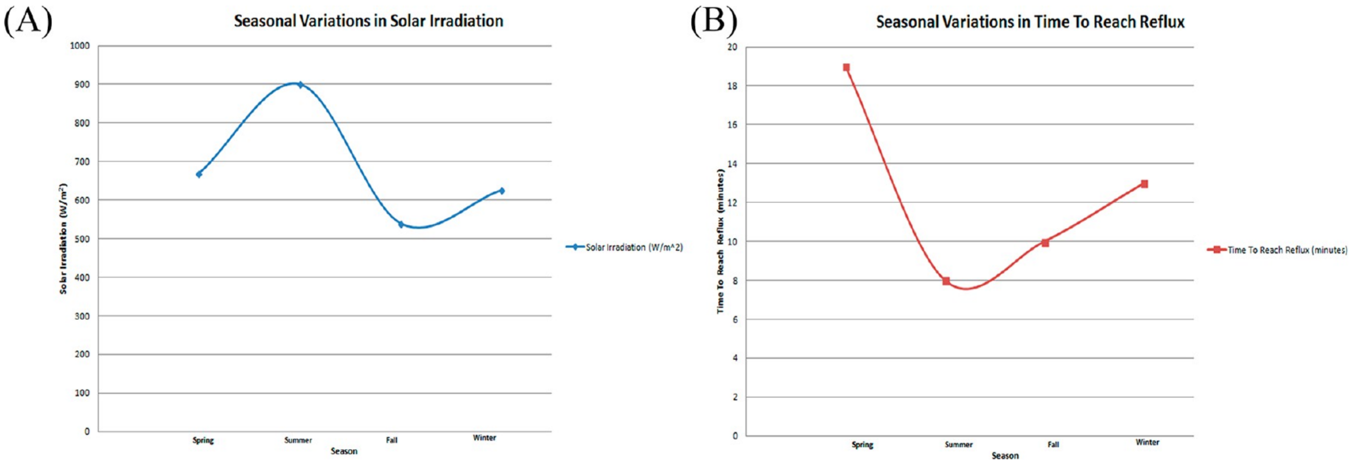

Figure 3. Seasonal variations vs (A) time to reach reflux and (B) solar irradiation.

Figure 4. Wind breaker attachment.

for these synthetic reactions and the yearly investigation on seasonal/weather impacts will be presented in a future publication.[11]

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Notes

The authors declare no competing financial interest.

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