RSC Advances



View Article Online

View Journal | View Issue

PAPER



Cite this: RSC Adv., 2014, 4, 54558

Received 1st September 2014 Accepted 14th October 2014

DOI: 10.1039/c4ra09599e

www.rsc.org/advances

1. Introduction

Storage of solar energy in the form of chemical energy is of profound importance. A much sought after goal is the splitting of water into hydrogen and oxygen.^{1,2} Photoelectrolytic conversion in a system wherein amorphous FeOOH was coupled to an amorphous Si solar cell reportedly gave an efficiency of 4.3% in a recent study.³ Solar thermochemical splitting of water is also of interest. Starting with its splitting on a zirconia surface at temperatures exceeding 2500 K, several improvements have been realized over the years through a two-step approach involving reduction and reoxidation of suitable metal oxides.⁴ An important advance made recently is the development of an isothermal water splitting route employing the hercynite cycle based on cobalt ferrite, which overcomes the drawbacks of temperature swing.⁵ However, the high temperature (1350 °C)

Solar driven uphill conversion of dicyclopentadiene to cyclopentadiene: an important synthon for energy systems and fine chemicals[†]

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The retro Diels–Alder conversion of *endo*-dicyclopentadiene to cyclopentadiene (Cp) – which is thermodynamically uphill under ambient conditions ($\Delta G = +9.7$ kcal mol⁻¹; values based on computation at 273 K following CBS-QB3 methodology) – was carried out at 175–190 °C in neat state using solar energy. The reaction is thermodynamically favorable at elevated temperature. Considering heat release from the reverse reaction ($\Delta H = -23.4$ kcal mol⁻¹), the energy storage efficiency was computed to be *ca.* 5.5% with respect to the IR component in concentrated solar radiation. Solar energy was further utilized for preparation of a model 2,5-norbornadiene derivative (75% isolated yield) through the cycloaddition reaction of Cp with 4-phenylbut-3-yn-2-one at 150–185 °C. The norbornadiene– quadricyclane system has been proposed for solar energy storage, and its solar assisted synthesis would help reduce its carbon footprint over its life cycle. Norbornadiene synthesis using solar energy may also be of interest for greener processing of fuels derived from this compound. Cookson's cage ketone, which too has been proposed as an energy storage medium, was additionally synthesized from the Diels–Alder adduct of Cp and *p*-benzoquinone employing concentrated solar photo-thermochemical conditions. The reaction proceeded rapidly (15 min) and gave the desired product in 96% isolated yield. Besides the above applications, Cp is an important synthon in the preparation of fine chemicals.

required in the process poses the challenge of cost-effective reactor design besides the significant problem of higher levels of reradiation. Many other solar thermochemical schemes based on inorganic chemicals have also been proposed for energy storage but these too are high temperature processes for the most part.⁶ Schemes operating at relatively lower temperatures have also been investigated, for example the thermal dehydration of inorganic hydroxides such as Ca(OH)₂, which can release heat on rehydration.⁷

Organic systems are also reported for energy storage. In particular, photochemical conversion of 2,5-norbornadiene (1) to quadricyclane (2) (eqn (1)) has been studied extensively.⁸ ΔH for the process was reported to be 21.4 kcal mol⁻¹.⁹ Solar energy is not an ideal light source for the reaction since photons in the ultraviolet region are required. However, efforts have been made to employ sensitizers that extend the absorption to longer wavelengths.¹⁰ 2 can interconvert thermally to 1 releasing the strain energy as usable heat, and studies are reported on substituent effects to maximize the harvesting of solar energy in this manner.¹¹ 1 has also been employed for the preparation of a missile fuel.¹² The process involved synthesis of the *endo-endo* homodimer (3), followed by its acid-catalyzed isomerization at elevated temperature to the fuel, 4 (eqn (2)). The fuel reportedly has a density of 1.02 g mL⁻¹, calorific value of 160 000 BTU

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[†] Electronic supplementary information (ESI) available: Analytical data; NMR, FT-IR and HR-MS data of some selective compounds. See DOI: 10.1039/c4ra09599e

gallon⁻¹, and freezing temperature below -45 °C, making it well suited for the intended application.



The preparation of $\underline{1}$ involves the use of cyclopentadiene (Cp) (eqn (3)).¹³

$$Cp + \parallel \longrightarrow 1$$
 (3)

Cp, in turn, is obtained from *endo*-dicyclopentadiene (5) through a retro Diels-Alder reaction at elevated temperature (eqn (4)).

$$\underbrace{4}_{\underline{5}} \underbrace{\longrightarrow}_{2 \operatorname{Cp}} 2 \operatorname{Cp}$$

The kinetics of the forward reaction of eqn (4) was investigated by Khambata and Wassermann.14 Studies were carried out at atmospheric pressure in the temperature range of 50-175 °C, both in paraffin solution and in pure liquid state. The nonexponential factor of the velocity coefficient was found to be of the same order of magnitude $(4 \times 10^{13} \text{ s}^{-1})$ as the interatomic vibrational frequency, leading the authors to propose a unimolecular reaction pathway. The rate constant, k, in paraffin solution was estimated to be 4.8 \times 10 $^{-5}$, 7.2 \times 10 $^{-4}$ and 8.0 \times 10^{-3} min⁻¹ at 120, 145 and 175 °C, respectively, and the values were similar for neat liquid. Practical conversion rates are thus feasible only for $T \ge 175$ °C. The ΔH of the process has been estimated to be 21.4 kcal mol⁻¹ experimentally.¹⁵ The rate constant, k, of the reverse reaction of eqn (4) has been computed to be 2.71×10^{-4} , 5.84×10^{-3} and 6.75×10^{-2} L mol⁻¹ min⁻¹ at 40, 80 and 120 °C, respectively.16 The moderately good kinetic stability of Cp at lower temperatures makes it amenable to storage.

Solar photo-thermochemical C(sp³)–H bromination, conducted efficiently in a specially designed reactor, was reported by us recently.^{17*a*} The scope of the reaction was expanded subsequently to include the solar syntheses of more complex organic molecules such as 2,5-oxazole derivatives from simple building blocks.^{17*b*} Several publications also reported the application of similar solar thermochemical reactions for the preparation of heterocycles.¹⁸ The present work reports the solar driven synthesis of Cp from **5**. Solar assisted preparation of Cookson's cage ketone and a compound akin to **1** from Cp is also reported. Production of energy systems in this manner would reduce the overall carbon footprint, providing the motivation for this study.

2. Experimental section

2.1. Materials and methods

All reagents were of commercial grade and purified according to established procedure. ¹H and ¹³C NMR were recorded in CDCl₃ with TMS as the internal standard using Model BrukerAvance II spectrometer. FT-IR spectra were recorded in KBr using Perkin Elmer spectrometer. Melting point was recorded using Mettler Toledo instrument and the data were uncorrected.

2.2. Temperature and weather related measurements

The thermal imager used for temperature profiling was TESTO 876. It gave the temperature distribution on the surface of the round bottom flask and condenser assembly. It had a wide angle lens with $32^{\circ} \times 23^{\circ}$ field of vision. The thermal sensitivity of this device was < 80 mK at 30 °C. The spectral range was 8-14 μ m and it could measure the range of temperature from 0° to 280 °C. The accuracy of the instrument was ± 2 °C. A microcontroller based automatic weather station with data logging facility was used to capture the weather data during the course of the experiment. Global radiation was measured on CM4 pyranometer having spectral range of 305-2800 nm and nominal sensitivity of 15 µV Wm⁻². Diffused and infrared radiation were measured using a CMP22 pyranometer with shaded ring and CGR4 pyrgeometer (4500-42 000 nm spectral range), respectively. Air temperature in the weather station was recorded with a digital sensor having measurement range of -40 to 123.8 °C. A 3 cup anemometer measured the wind speed and had the range of measurement from 5 kph to 200 kph. The sensing was done by a reed switch/magnet and provided 1 pulse per rotation. The wind direction was sensed using a magnetic Hall Effect sensor having range 360° (zero dead band). The accuracy was ± 0.3 to 0.5 % of signal range. The wind direction was considered in terms of angle with respect to the North direction, measured clockwise. The air pressure sensor was a barometer of piezo-resistive silicon membrane type having range of measurement as 0.150 Bar to 1.15 Bar. The temperature at the focus of the parabolic dish was determined by K-type thermocouple of ± 0.5 °C accuracy.

2.3. Computational method

Full geometrical optimizations were carried out in the gas phase employing the complete basis set CBS-QB3 method at the temperature 273 K, unless mentioned otherwise.^{19,20} Frequency calculations were performed at the same level of theory to confirm that each stationary point is a local minimum with zero imaginary frequency. ΔG and ΔH of reactions were computed by complete basis set CBS-QB3 method. All calculations were performed with Gaussian 09 suite of programmes.²¹

2.4. Solar mediated retro Diels-Alder reaction of 5

The retro Diels–Alder reaction of 5 was carried out using a solar parabolic dish concentrator with geometrical concentration ratio of 20 *X* (Fig. S1†). Experiments were conducted during 11.15 am to 2.15 pm on a typical sunny day in March. Details of the concentrator and ambient conditions on the day of the experiment are provided under Section S1 of ESI.† 500 g of 5 was charged into a 1 L RB flask placed at the focus of the dish. A PV panel was used to operate a pump to circulate cool water through a condenser to facilitate condensation of Cp. The distillate was collected in a 250 mL RB flask placed inside an ice bag. It was stored in the refrigerator and used as required.

2.5. Solar mediated synthesis of 1-(3-phenylbicyclo [2.2.1] hepta-2,5-dien-2-yl) ethanone (7) (see eqn (5))

An offset parabola of concentration ratio 59 X (Fig. S2^{\dagger}) was employed for the synthesis and the reaction was conducted over 5.5 h (10.00 am to 3.30 pm) on a typical day in March. Details of the concentrator and ambient conditions on the day of the experiment are provided in Section S1.[†] 0.46 g of Cp prepared above was added along with 1 g of 4-phenylbut-3-yn-2-one (6) and 15 mL of diphenyl ether (solvent) into a 25 mL single neck RB flask. The flask was placed at the focal point of the concentrator which served as source of thermal energy. The reaction temperature over the reaction period was in the range of 150-185 °C. After termination of the reaction the contents were charged on a silica gel column and eluted with 5% ethyl acetate in hexane. 1.1 g (75% isolated yield) of pure 7 was obtained. ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.35 (d, 2H), 7.33-7.31 (m, 1H), 7.29-7.28 (d, 2H), 6.98 (s, 1H), 6.88 (s, 1H), 4.09 (s, 1H), 3.77 (s, 1H), 1.99 (s, 3H); 13 C NMR (125 MHz, CDCl₃) δ 196.5, 166.5, 149.4, 143.7, 141.2, 137.0, 128.5, 127.1, 70.3, 59.3, 52.2, 29.1; IR (in KBr, cm⁻¹) 3435, 2931, 2362, 1651, 1443, 1359, 1237, 1022, 759, 699; HRMS (ESI): found 211.1135 (calcd for $C_{15}H_{14}O[M + H], 211.1123).$

2.6. Solar mediated synthesis of pentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-8, 11-dione (9) from 8 (see eqn (6)).

8 was prepared as a yellow crystalline solid from solar generated Cp and benzoquinone following literature procedure.²² 1 g of **8** was taken in 10 mL of ethyl acetate and placed in a quartz RB flask positioned at the focus of an 8× parabolic dish.^{17*a*} **9** was obtained as a brown solid (m.p. 240 °C) in 96% yield within 15 min. The reaction temperature was *ca.* 90 °C. 1H NMR (500 MHz, CDCl₃) δ 3.18 (s, 2H), 2.94 (s, 2H), 2.82 (d, 2H), 2.71 (s, 2H), 2.06–2.04 (d, 1H), 1.90–1.88 (d, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 212.1, 54.7, 44.6, 43.7, 40.4, 38.7; IR (in KBr, cm⁻¹) 3448, 2990, 2930, 2868, 1753, 1728, 1454, 1267, 1224, 1191, 1056, 966, 911, 860, 823, 755, 600, 525, 453. Observed mass (M + H) 174.96, calculated mass (M + H) 175.08.

Note: safety precautions must be taken while performing experiments with concentrated solar radiation.

3. Results and discussion

CBS-QB3 method was employed to calculate the changes in ΔH and ΔG of the various reactions considered in the present study. The data are compiled in Table 1. The method was tested initially for the formation of quadricyclane from norbornadiene. The calculated ΔH of 22.8 kcal mol⁻¹ was in good agreement with the experimental ΔH value of 21.4 kcal mol⁻¹ reported for this process.9 The free energy of reaction was computed to be 22.7 kcal mol⁻¹. The reaction of eqn (4) was studied next. The computed ΔH of 23.4 kcal mol⁻¹ at 273 K was again in good agreement with the experimentally determined value of 21.4 kcal mol⁻¹.¹⁵ Corresponding value of ΔG was 9.7 kcal mol⁻¹. The computed ΔG reduced to 2.0 kcal mol⁻¹ at 423 K (Table 1), suggesting that the equilibrium of eqn (4) moves to the right at higher temperature, in line with the reported observations. Since the values of ΔH were similar at 273 K and 423 K, the shift in ΔG is due to changes in the $T\Delta S$ term in the free energy equation ($\Delta G = \Delta H - T\Delta S$). This term would be expected to increase with temperature on account of the positive ΔS expected from the cracking of one molecule of 5 into two molecules of Cp.

Drawing on the kinetics data reported earlier on the retro Diels–Alder reaction of 5,14 the parabolic dish of Fig. S1† was designed and fabricated to achieve 175 °C $\leq T \leq$ 200 °C under peak insolation condition (850–1000 W m⁻²) prevailing in the summer months in the western part of India. Initially, the reactor assembly of Fig. S1(A)[†] was taken, and entries 1 and 2 in Table 2 provide data for experiments conducted on cracking of 5 on two separate sunny days during March 2014. The second set of data were taken for further analysis. Fig. S3(A)[†] provides data on global insolation, ambient temperature and temperature in the reaction zone during 10.00 am to 2.00 pm on the day of the experiment pertaining to entry 2, Table 2. Other weather related data are presented in Table S1.† The reaction temperature rose gradually from 11.15 am to 12.00 noon and thereafter remained in the range of 175-190 °C. A thermal image recorded during this period is shown in Fig. 1. The total volume of Cp collected over 3 h was 154 mL which worked out to an average hourly collection of 51.3 mL h^{-1} (Table 2). Although hour-wise data were not collected, the output was highest during 12.30 pm to 1.00 pm. Based on the collector aperture area (1.83 m^2) and average global insolation (857 W m⁻²) during the duration of the experiment, the total energy captured by the parabolic dish was 1344 kcal h⁻¹. However, the energy available at the reaction zone was only 5142 kcal h⁻¹ based on pyranometer reading of the concentrated radiation. This was ascribed to the following reasons: (i) diffuse radiation (*ca.* 100 W m^{-2}) was not concentrated and (ii) there were considerable reflection losses during concentration. Further, in the experiment as conducted using a glass RB flask, heating would have been effected mainly by the infrared component (4500-42 000 nm) in the concentrated radiation. This component was estimated to be 2424 kcal h⁻¹ based on measurement of IR intensity in the solar insolation. Taking

Table 1 Free energy and enthalpy values of substrates and products computed by CBS-QB3 method, along with data on free energy and enthalpy changes for reactions of interest^a

| Compounds | $G(\times 10^{-3}$ kcal mol ⁻¹) | $H(\times 10^{-3} \text{ kcal mol}^{-1})$ | Reaction and remarks | ΔG (kcal mol ⁻¹) | ΔH (kcal mol ⁻¹) |
|-----------------------------------|---|---|---|--------------------------------------|--------------------------------------|
| (1) | -170.037 | -170.018 | hv | +22.8 | +22.9 |
| Δ | -170.014 | -169.995 | ⊥ <u>2</u> light-driven thermodynamically uphill conversion | | |
| (2) | $-121.572 \\ -121.582^{b}$ | $-121.554 \\ -121.551^b$ | Ň | +9.7 | +23.4 |
| (Cp) | -243.153 -243.166^{b} | -243.131 -243.125^{b} | solar thermal driven thermodynamically uphill conversion | +2.0 ^b | +23.0 ^b |
| (5) H────H Cp | -48.446 -121.572 | -48.433 -121.554 | $\langle \rangle$ + \parallel Δ | -19.2 | -31.3 |
| | -170.037 | -170.018 | H solar thermal mediated thermodynamically spontaneous reaction | | |
| (1) (5) | -288.82 | -288.793 | c_{p} + $solar \Delta$ | | |
| | -410.411 | -410.381 | solar thermal mediated thermodynamically spontaneous reaction | -19.7 | -35.0 |
| | -360.599 | -360.573 | $\frac{1}{\sqrt{0}}$ Solar hv $\sqrt{1}$ | -8.1 | -10.4 |
| | -360.607 | -360.584 | <u>8</u> <u>9</u> solar photon-mediated thermodynamically spontaneous reaction | | |
| لع) ^a Unless otherw | vise stated all c | alculations wer | e at 273 K ^b Calculations at 423 K | | |

the computed ΔH of 23.4 kcal mol⁻¹ for the forward reaction of eqn (4), the re-formation of *endo*-dicyclopentadiene from 51.3 mL of Cp (specific gravity = 0.8) would release 7.27 kcal of heat, corresponding to an energy storage efficiency of

2.97% [energy storage efficiency (%) = (heat output from dimerization of Cp)/(energy supply by concentrated IR radiation incident on the reactor) \times 100] for the experiment of entry 2, Table 2. To improve the capture of the solar radiation

 Table 2
 Retro Diels–Alder reaction of 5 undertaken using the parabolic dish concentrator in Fig. S1

| Entry no. | Time period | Amount of 5 charged/mL | Amount of Cp collected/mL | Yield/ mL h ⁻¹ |
|----------------|------------------|---------------------------|------------------------------|------------------------------|
| 1^a | 12.30 pm–2.00 pm | 500 | 60 | 40.0 |
| 2^{b} | 11.15 am–2.15 pm | 500 | 154 | 51.3 |
| 3 ^c | 12.30 pm–1.30 pm | 500 | 94.8 | 94.8 |

^a 1 March, 2014. ^b 3 March, 2014. ^c 30 September, 2014.



Fig. 1 Thermal image recorded during solar driven retro Diels–Alder reaction of 5 (entry 2, Table 2) using a parabolic dish having $20 \times$ concentration ratio.

and to reduce heat losses, the RB flask was painted black and inserted in a wooden box with transparent bottom and other interiors of the box painted black, as shown in Fig. S1(B).† An experiment conducted on 30 September, 2014 with this assembly gave a much higher yield of 94.8 mL of Cp during the 1 h period between 12.30 pm and 1.30 pm (entry 3, Table 2), even while the average global insolation during the period of the experiment [Fig. S1(B)†] was comparable to that recorded for the experiment of entry 2, Table 1 [Fig. S1(A)†]. Maintaining the same basis of computation as above, the energy storage efficiency was 5.49%.

As mentioned above, the norbornadiene–quadricyclane system holds promise for energy storage. Synthesis of **1** from Cp (eqn (3)) using solar energy was of interest. However, due to difficulties in handling acetylene, the substituted acetylene, 4-phenylbut-3-yn-2-one (**6**), was chosen as a model substrate for the experiment (eqn (5)). Studies were conducted initially in the laboratory under neat condition using an oil bath. No reaction was observed either at room temperature or at 100 °C. When the temperature was raised further to *ca.* 160 °C and the reaction left overnight, the 2,5-norbornadiene derivative, **7**, was obtained in satisfactory yield and purity. The reaction was thereafter attempted using an offset-parabolic dish (Fig. S2†), which was found to be well suited to small scale reactions at 150–200 °C. Diphenyl ether was taken as high boiling solvent.



The reaction temperature could be maintained in the range of 150-185 °C during the peak insolation period of 10.00 am to 3.30 pm (5.5 h) (Fig. S4[†]). In view of the small scale (1 g of 6) at which the reaction was undertaken, the solvent volume could not be optimized as a minimum reaction volume had to be maintained. 7 was isolated from the crude reaction mixture in 75% yield through column chromatographic separation. The reaction of eqn (5) is thermodynamically favored ($\Delta H = -34.7 \text{ kcal mol}^{-1}$; $\Delta G = -19.7$ kcal mol^{-1} (Table 1), and the role of solar thermal energy was mainly to overcome the activation barrier. Although product isolation in the reaction with the model substrate was through chromatographic separation, a more practical solution would be required in a commercial process. As mentioned above, the ultimate aim is the preparation of 2,5norbornadiene (eqn (3)) which has a boiling point of 89.5 °C. It can thus be isolated through fractional distillation, leaving behind the high boiling diphenyl ether solvent (b.p. 258 °C) for recycle. Further, even if some dicyclopentadiene were to form in the reaction from the dimerization of Cp, it can be cracked at a temperature well below the boiling point of the solvent to regenerate and recover Cp.

Another application of Cp in the context of energy is toward synthesis of Cookson's cage ketone, 9^{22} The Diels–Alder adduct of Cp and benzoquinone, 8, which was formed spontaneously in crystalline form in 94.2% yield at room temperature, was converted rapidly (15 min) under neat condition into 9 through solar driven [2 + 2] photo-cycloaddition (eqn (6)).²² Conversion under photochemical conditions in the laboratory using artificial light source seemingly takes much longer,²³ indicating that the concentrated solar radiation used in the present study was beneficial. Cookson's cage ketone can be employed for solar energy storage, as reported for the cyclic scheme of eqn (7).²²



Besides the above uses, Cp finds numerous other applications in fine chemicals synthesis making it a versatile synthon (Scheme 1).²⁴ Hence its solar driven synthesis from the



Scheme 1 Schematic depiction of various uses of Cp.²⁴

universally employed precursor, 5, would help reduce the carbon footprint of such fine chemicals also.

4. Conclusions

The thermodynamically uphill cracking of neat endo-dicyclopentadiene to Cp using solar thermal energy was demonstrated. The energy storage efficiency was 5.5% with respect to IR component in global insolation during peak period. The efficiency can be enhanced in the future by (i) minimizing losses during concentration of the solar insolation, (ii) improving the absorption of radiation by the reactor assembly and minimizing heat losses from the reactor through better insulation, and (iii) improving the distillation assembly. Compared to the high temperature conditions required typically for solar energy storage through thermochemical conversion routes involving inorganic systems, this transformation required less demanding conditions and, consequently, less sophisticated hardware. The disadvantage, on the other hand, is that the energy storage density is lower than in the case of H₂. A means will also have to be devised to maintain Cp in adequately stable form at room temperature for easy storage, and yet release the thermal energy rapidly on demand. The utility of Cp as a synthon is considerable and its solar driven conversion into a 2,5-norbornadiene derivative and Cookson's cage ketone were demonstrated. These molecules too are of interest for reversible solar energy storage and preparation of specialty fuels such as 4. Cp additionally finds applications in the fine chemicals industry, thereby expanding the scope of the methodology. Although the solar driven synthesis of Cp was demonstrated at multigram scale (*ca.* 100 g h^{-1} during peak insolation), it is to be noted that the procedure is limited considerably by the weather, location and sunshine duration.

Acknowledgements

The referees are acknowledged for helpful suggestions. P. Patel, J. N. Bharadia, P. S. Bapat and J. P. Makwana are acknowledged for fabrication of the solar devices and assistance during solar experiments. Analytical support provided by the Discipline of Analytical Science and Centralized Instrument Facility is gratefully acknowledged. MD, SC and SS thank CSIR for their research fellowships. Authors are grateful to CSIR India for supporting the study as part of an in-house laboratory project. This is communication number 076/2014 from CSIR-CSMCRI.

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