Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Electronic Supporting Information

Can a Diels-Alder Reaction Accelerate in a Supersaturated Solvent at Room Temperature?

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1. The detailed GC method:

The following parameters were set for a typical kinetic analysis for Scheme 1

Column make: CP SIL 5CB

Column length: 15m

Internal diameter: 0.25 mm

Film thickness: 0.25-micron

Flow rate: 0.8 ml/min of nitrogen

Injector temperature: 200 °C

Detector temperature: 250 °C.

Total run time 18.51 min (Hold at 70 °C for 5 min., ramp at 4°C, then maintain at 100 °C for 0 min., ramp at 79 °C and then maintain at 180 °C for 5 min.)

Internal Standard (IS): Chlorobenzene

Typical Retention Times of the compounds analyzed:

Compound Retention time (min)

Compound	Time (min)
IS	**3.48**
3(a)	**15.95**
3(b)	**16.02**

The GC method was calibrated with respect to the product concentrations using pure samples of the products. The amount of product formed as a function of time gave the extent of the reaction (x).

From the gas chromatographic analysis the extent of the reaction (x) can be monitored by plotting the amount of product as a function of time. Since for the reaction (Scheme **1**), products have been formed due to reactions between the two reactants in 1:1 ratio; the concentration of the remaining reactants would be equal with respect to time. It implies that if 'a' is initial concentration of both the reactants [1M of each of **1** and **2** have been used in the case of Scheme 1]. Now (a-x) will give the remaining reactants in the solvent at time 't' after commencing the reaction at t=0. The plot between x/a(a-x) vs. t gives the value of k_2 in each case.

2. Determination of second order rate constant:

The determination of k_2 was done according to the standard kinetic procedure, when initial concentrations of the reactants are same. The expression to determine k_2 = (1/at) x [x/(a-x)], where a plot between x/(a-x) and t. For example, The k_2 value was determined from the slope of the graph as $k_2 = 5.61 \times 10^{-5}\ M^{-1}s^{-1}$ ($r^2 = 0.991$).

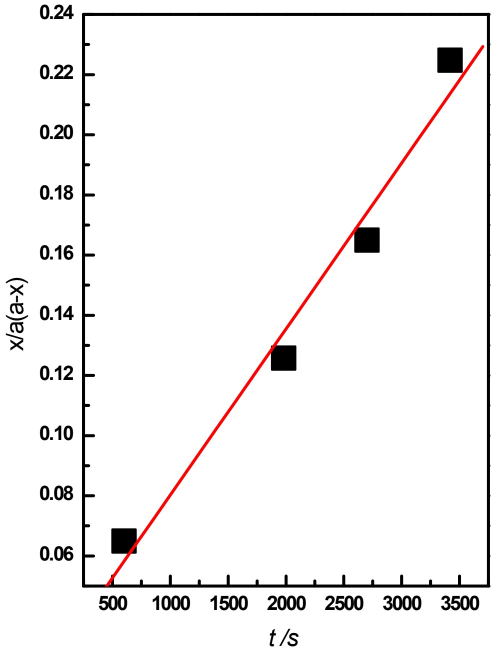


Figure S1: Plot of [x/(a(a-x))] against time, *t* for the reaction of **1** with **2** in Honey at 298.15 K.

3. Preparation of New supersaturated solvent

A. New supersaturated solvent (with gluconic acid) has been prepared by using percentage composition described in Table 1. For the preparation of 10 g of artificial honey, we have taken 1.81 g of water, 3.89 g of fructose, 3.182 g of glucose, 0.144 g of sucrose, 0.81g of maltose, 0.127g of gluconic acid, 0.037 g of gluconolactone in sealed tube (M/s. Sigma Aldrich Co.). It was already made sure that all carbohydrate added to sealed tube are dried under vacuum for ~6 h prior to their use. Then the mixture of carbohydrate is heated at temperature 120 °C under vigorous stirring for 4 h.

B. New supersaturated solvent (without gluconic acid) has been prepared by using percentage composition described in Table 1. For the preparation of 10 g of artificial honey, we have taken 1.81 g of water, 3.89 g of fructose, 3.309 g of glucose, 0.144 g of sucrose, 0.81g of maltose, 0.037 g of gluconolactone in sealed tube (M/s. Sigma Aldrich Co.). It was already made sure that all carbohydrate added to sealed tube are dried under vacuum for ~6 h prior to their use. Then the mixture of carbohydrate is heated at temperature 120 °C under vigorous stirring for 4 h.

C. For the preparation of saturated solution of glucose first 6.9 g of glucose was added to 10 g of water in a sealed tube and then the mixture was heated at 120 °C under vigorous stirring for ~4 h. Supersaturated solution of glucose was prepared by the addition of 7.5 g of glucose in to 10 g of water and consequent heating at 130 °C under vigorous stirring for ~4 h. Similarly, saturated solution of fructose has been prepared by addition of 38 gm of fructose in to 10 g of water in sealed tube followed by heating at 120 °C under vigorous stirring for ~4 h. Supersaturated solution of fructose was made by addition of 40 g of fructose to 10 g of water in sealed tube followed by heating at 130 °C under vigorous stirring for ~4 h.

4. Measurement of E_N^T polarity parameter

E_N^T values of the solvent medium in question were measured via the standard solvatochromic methods.[1] For the measurement of E_N^T parameter of Honey, Reichardt's dye no. 30 (**Figure S2**), is used as a probe molecule. The minute amount of Reichardt's dye no. 30 was added to Honey at 40 °C with vigorous stirring. Samples containing probe molecules was then transferred to the cuvette for the measurement of $\lambda_{\max}$ (in nm). A representative spectra obtained is shown in **Figure S3.**

Temperature of the sample was kept constant at 298.15 K using the Peltier setup with an accuracy of ±0.01 K. $E_T(30)$ value for the Honey were calculated from the molar transition energy (in kcal mol^{-1}) of Reichardt's dye using equation (1).

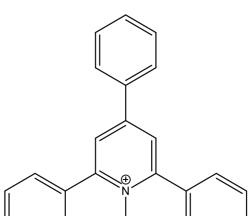


Figure S2. Structures of Reichardt's dye no. 30.

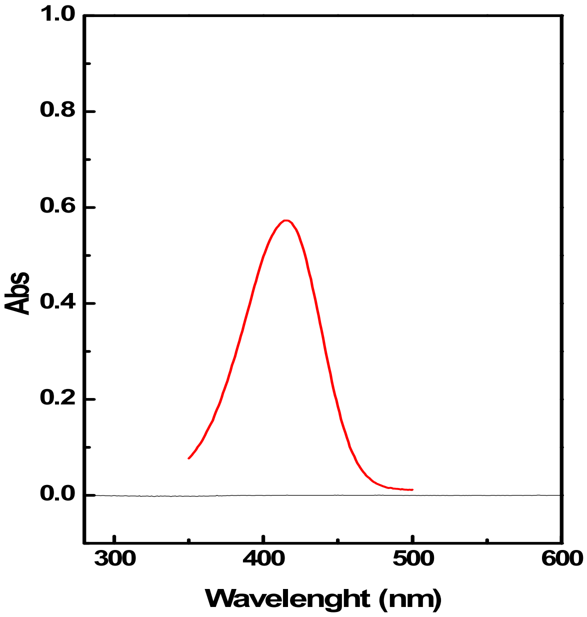


Figure S3: A representative UV-vis spectra obtained.

$$E_T(30) = hc\,\nu_{max}(30)N_A = 28591/\lambda_{max} \qquad (1)$$

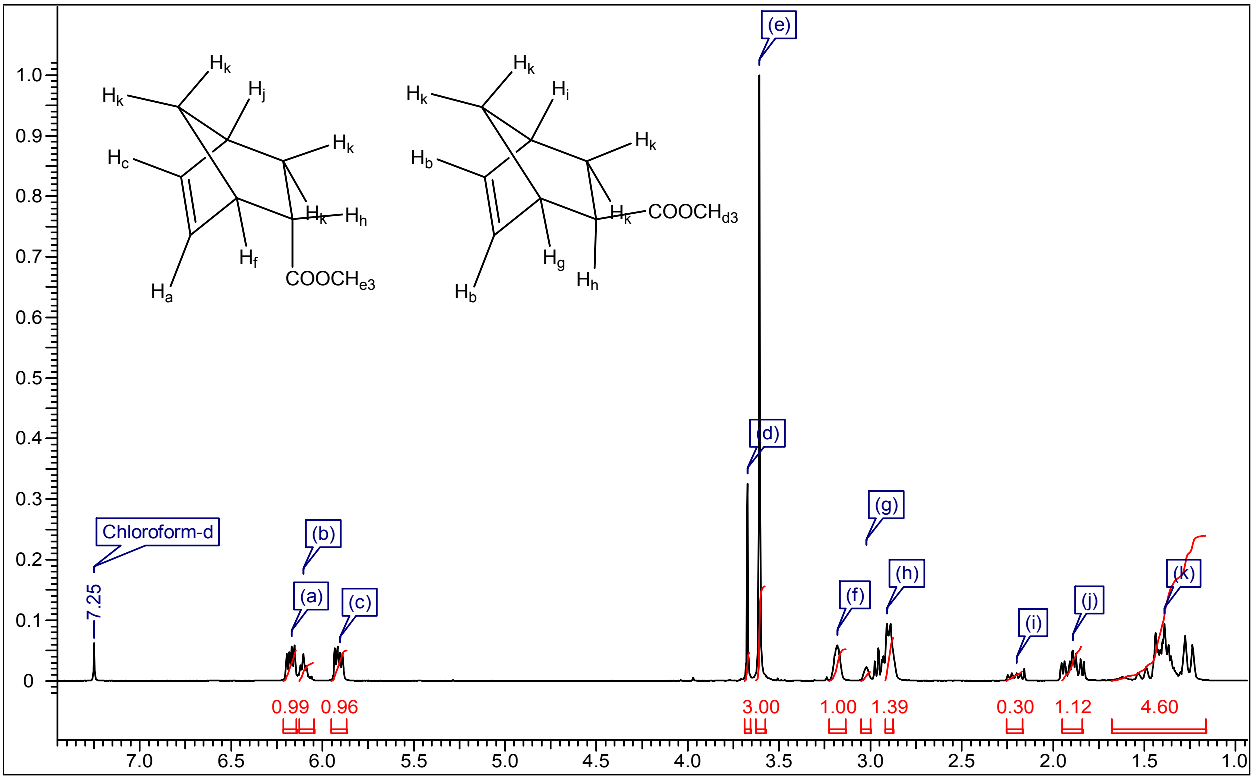
The E_N^T values of Honey was calculated via the normalization of $E_T(30)$ parameter, using water ($E_N^T = 1$) and TMS ($E_N^T = 0$) as reference solvents.

$$E_N^T = [E_T(30)_{solvent} - E_T(30)_{TMS}]/[E_T(30)_{water} - E_T(30)_{TMS}]$$

$$= [E_T(solvent) - 30.7]/32.4 \qquad (2)$$

5. ^{1}H-NMR spectra:

The ^{1}H-NMR spectra of the product of the reaction of cyclopentadiene (**1**) with methyl acrylate (**2**): Methyl bicyclo[2.2.1] hept-5-ene-2-carboxylate **(3a, b**) ^{1}H-NMR (200 MHz, $CDCl_3$).



6. Comparative IR- spectra of unsaturated, saturated and supersaturated aqueous solution of fructose.

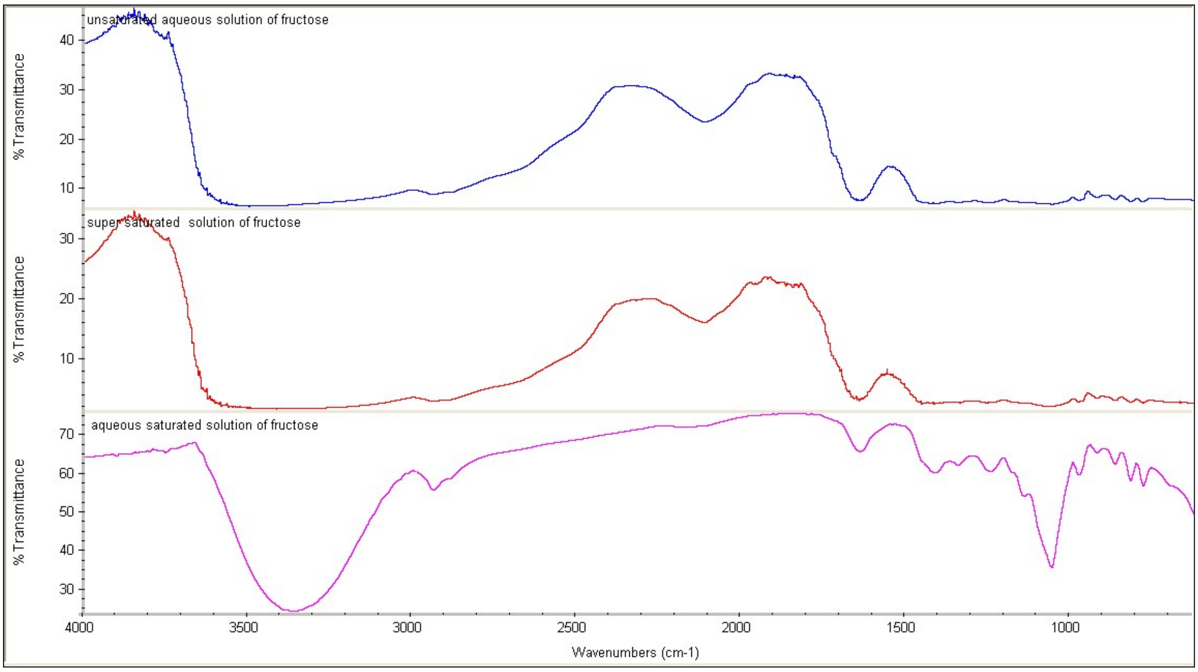


Figure S4. Superimposed FTIR spectra *i.e.,* % Transmittance *vs.* wavelength (cm^{-1}) plots of the aqueous solution of fructose. Here the pink (saturated solution), red (Super saturated solution) and blue (unsaturated solution) give a comparative look.

7. The Arrhenius plots of supersaturated solvent and Carbohydrate-urea melt.

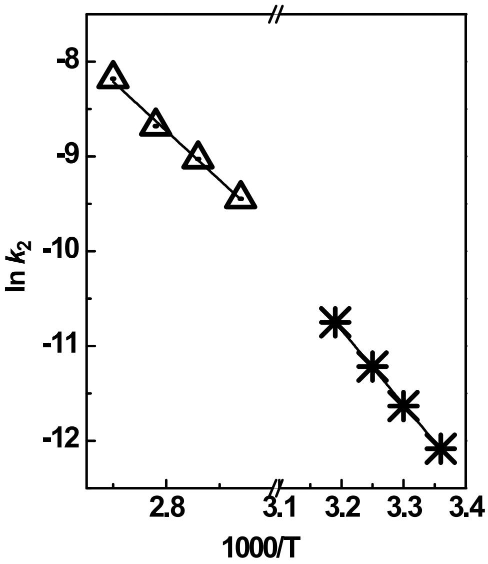


Figure S5. The Arrhenius plots for reaction between **1** and **2** in the presence of new supersaturated solvent (∗) and glucose–DMU (*N*, *N* Dimethyl Urea) mixture (△)

8. ^{1}H NMR of the super-saturated solution used (DMSO-d^6 solvent) at 500 MHz:

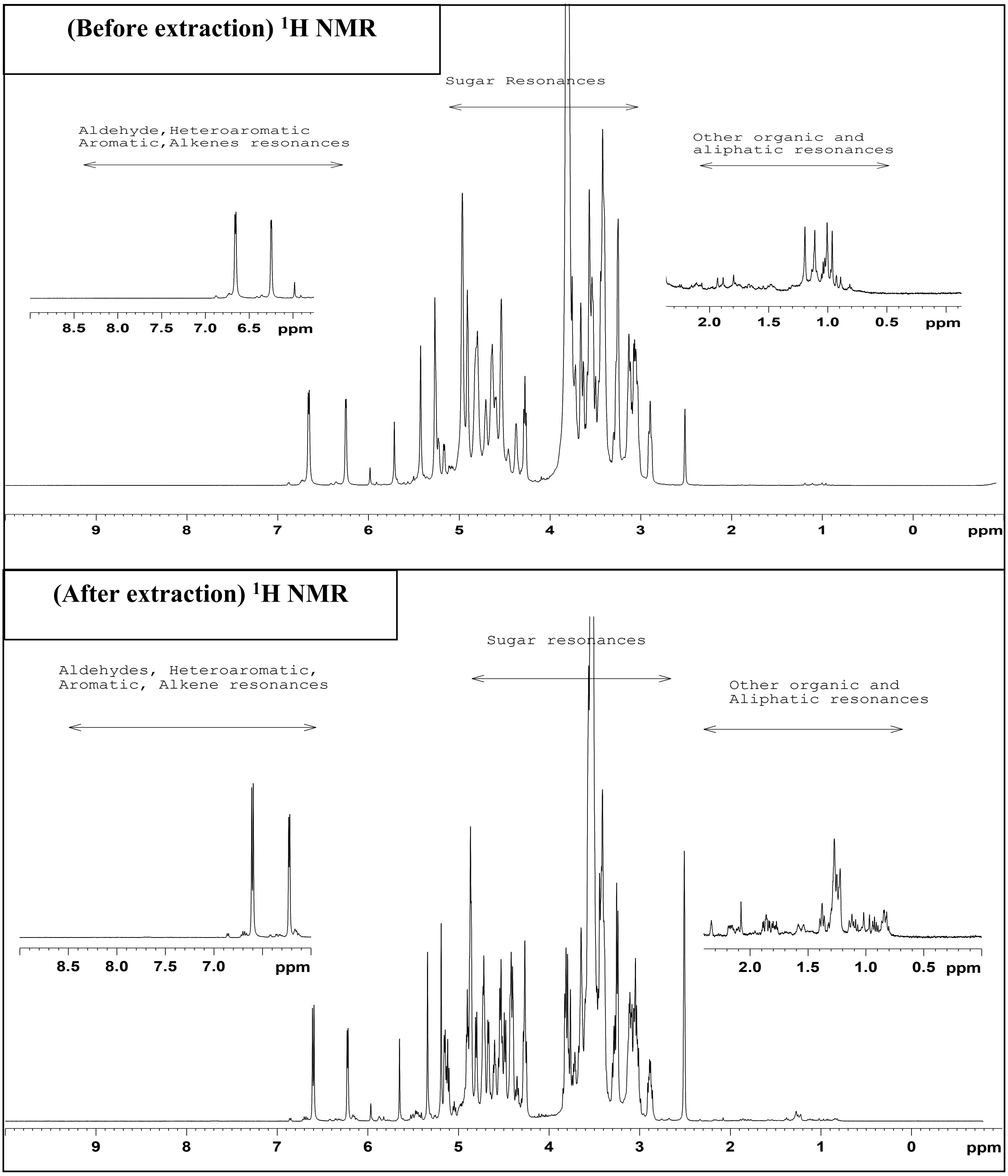


Figure S6. ^{1}H NMR spectra of the new supersaturated solution used in the Diels-Alder reaction (DMSO-d^6 solvent) at 500 MHz with respective peaks.

Reference:

1. C. Reichardt, *Green Chem.*, 2005, **7**, 339–351.