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The reaction between 2-methoxyfuran and dimethylacetylenedicarboxylate: Thermochemical and kinetical data[☆]

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Abstract

The Diels-Alder reaction between methoxyfuran and dimethylacetylenedicarboxylate, leading to a substituted oxanorbornadiene, has not yet been studied in terms of its thermodynamic and kinetic properties, in order to use this liquid phase reaction for storage and release of thermal energy.

Here, the reaction enthalpy and kinetic parameters are determined by dynamic modelling which uses only the experimental temperature of the reaction mixture versus time and the known kinetic law (second order). NMR spectroscopy is used for structural identification of the adduct and for determining the relative ratio of reactants and product, allowing the kinetic constant to be obtained.

Results obtained by modelling are compared with those of other Diels-Alder reactions currently studied. This reaction has suitable thermodynamic and kinetic properties for thermal energy storage and release. We discuss the conditions of such an application.

Keywords: Diels-Alder reaction; Kinetics; Modelling; NMR; Reaction enthalpy

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List of symbols

T	temperature of the system in °C
T_a	room temperature in °C
MC_p	water equivalent mass of the entire system in JK^{-1}
K	exchange coefficient of the system in $JK^{-1} s^{-1}$
V	volume of the reaction mixture in l
ΔH	reaction enthalpy in $J mol^{-1}$
[A]	concentration of reactants (diene and dienophile) in $mol l^{-1}$ at time t
$[A]_0$	initial concentration of reactants in $mol l^{-1}$
E_a	activity energy in $J mol^{-1}$
K_0	preexponential factor in $l mol^{-1} s^{-1}$
R	gas constant in $JK^{-1} mol^{-1}$
k^*	rate constant $l mol^{-1} s^{-1}$
[MF]	concentration of 2-methoxyfuran

1. Introduction

The possibility of using solar energy to generate substantial amounts of power appears attractive for the future. However, since this source of energy is intermittent, a convenient storage material, capable of storing energy for extended periods of time, would be a very welcome component in a renewable energy system [1,2].

Reversible reactions can be used for photochemical or thermal storage of solar energy [3,4]. However, although a great variety of reversible reactions are known, only a few are technically acceptable as candidates. Wentworth and Chen [5] and Lenz et al. [6] stated several criteria which could serve as guidelines in the selection of such reactions. Among these criteria, they noted that: ΔH of the reaction should be as large as possible to maximize storage capacity; reaction rates should be rapid in order to minimize residence time in the reaction vessel; and a liquid system with a moderate pressure in the relevant temperature range would be useful.

Diels-Alder and retro-Diels-Alder reactions ([4 + 2] cycloadditions and cycloreversions) have been extensively studied [7,8]. Some of them, which are exothermic at room temperature and reversible in the temperature range available with concentrated solar energy, might be used for thermal energy storage and release of heat at moderate temperature [6,9,10].

As part of our on-going work, relative to the study of thermal (solar) energy storage and release, we investigated several liquid-phase Diels-Alder reactions [11,12].

We observed that the [4 + 2] cycloaddition between 2-methoxyfuran (MF) and dimethylacetylenedicarboxylate (DMAD) is exothermic and very fast. Therefore it could be considered as the energy release step of a storage-release cycle, the storage step being the thermal cycloreversion.

The aim of this study is to determine the thermodynamic and kinetic data of this reaction, using dynamical modelling and nuclear magnetic resonance spectroscopy (NMR).

The validity of the dynamic method was demonstrated on other reactions. The enthalpies determined by the modelling are close to those given in the literature. For example, the enthalpy of the Diels-Alder reaction between 2-methylfuran and maleic anhydride deduced by modelling is 10% from the literature value [10], and the enthalpy of the reaction between acetic acid and triethylamine is 2% from the enthalpy measured by classical calorimetry [13].

We have also tested our method in the determination of kinetic parameters of well-known reactions and the results are concordant, e.g. the catalytic decomposition of hydrogen peroxide [14].

The kinetic study of Diels-Alder reactions by NMR is monitored by the rate constant provided the solutions are properly diluted [15].

2. Experimental

2.1. Dynamic calorimetry

The apparatus used is similar to that presented in earlier papers [11, 13, 16]. The temperature of the mixture, contained in a 100 ml glass reactor, is measured by a thermocouple connected to an acquisition system. The sampling rate is one acquisition every second and the plot of the temperature versus time is obtained. Calorific capacity is measured by a differential calorimeter (DSC 200 Netzsch). The equivalent mass of the empty system is estimated by relaxations with variable masses of water according to the method of dynamic modelling perfected by our team [17, 18].

A solution of 10 ml of MF, prepared in chloroform at 1 and 2 $\mathrm{mol\,l^{-1}}$, is added to the same volume of DMAD at equal concentration in the same solvent. A series of experiments at different concentrations is carried out to assure reproductibility, here only representative results are shown. The equimolar mixture concentrations are respectively 0.5 and 1 $\mathrm{mol\,l^{-1}}$.

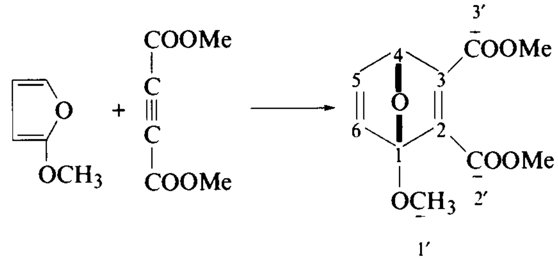
2.2. Nuclear magnetic resonance analysis

All NMR spectra were recorded on a Bruker AC 200 Fourier transform spectrometer operating at 200.132 MHz for ^{1}H and 50.323 MHz for ^{13}C in deuterated chloroform, with all shifts referenced to internal tetramethylsilane (TMS). Carbon and proton NMR spectra were recorded respectively with the following parameters: pulse width (PW), 3.2 μs (flip angle 45°) and 2 μs (flip angle 25°); acquisition time 1.3 and 2.3 s for 32 and 16 K data table with spectral widths (SW) of 250 and 13 ppm. Carbon-13 spectra were recorded with CPD mode and a digital resolution of 0.736 Hz/pt. Exponential multiplication of free induction decay (FID) with a line broadening of 1.0 Hz was used before Fourier transformation.

For kinetic measurements, MF and DMAD are mixed in $CDCl_3$ so as to obtain equimolar solutions of concentrations equal to 0.5 and 1 $\mathrm{mol\,l^{-1}}$. The reaction occurs in the NMR probe and it is followed by proton NMR until complete disappearence of the reactants.

3. The reaction between MF and DMAD

The reaction of equimolecular amounts of MF and DMAD in $CHCl_3$, $CDCl_3$ or CCl_4, led quantitatively to 1-methoxy-2,3-dicarbomethoxy-7-oxabicyclo[2.2.1]hepta-2,5-diene (oxanorbornadiene, ON) which has been fully characterized sepctroscopically [19].



MF DMAD ON

Spectral characteristics of ON

IR: 3010, 1720, 1640, 1435, 1270, 1120, 1080 cm^{-1}.

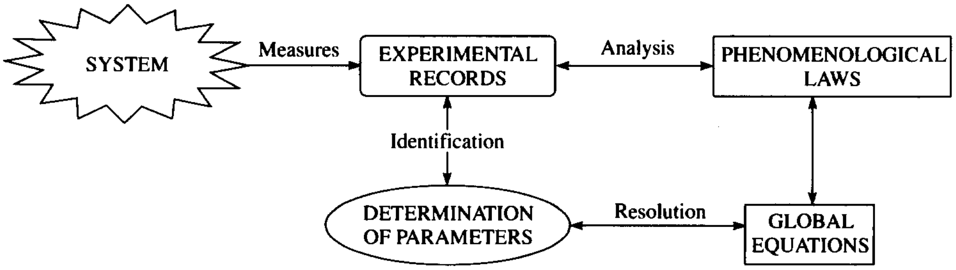
^{1}HNMR: H–C-4 (5.55, d, 2.0 Hz);
H–C-5 (7.23, dd, 5.4 and 2.0 Hz)
H–C-6 (7.01, d, 5.4 Hz);
esters (3.78, s et 3.87, s); OCH_3 (3.58, s).

^{13}C NMR: C-1 (118.5); C-2 (153.3); C-3 (151.5);
C-4 (78.5); C-5 (146.5); C-6 (140.9);
C-2′/C-3′ (162.2, 164.3);
$COO\underline{C}H_3$ (52.4); OCH_3 (55.0).

4. Determination of kinetic and thermodynamic parameters by dynamic modelling

4.1. Principle of the method

The chosen method, of dynamic and phenomenological modelling is one which has already been used and validated in the thermodynamic and kinetic study of liquid phase exothermic reactions [11, 18]. We can sum it up in the following scheme



4.2. *Modelling*

4.2.1. *Construction of the model*

The model is built from the calorimetric experimental set-up mentioned above.

The exothermicity of the reaction between MF and DMAD is evidenced by the experimental records obtained, which present a phase of temperature rise followed by a classic phase of relaxation. The kinetics of this Diels-Alder reaction, as for all [4 + 2] cycloadditions, obeys a second-order kinetic law.

In order to build the model with this experimental information, we use the global thermic balance (the system (apparatus + reactants) is considered to be global and then to be uniform at temperature T) and the rate equation.

The model is represented by a non-linear system with two state variables, the temperature and the concentration

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\frac{K}{MC_p}(T - T_a) + \frac{\Delta H V}{MC_p} K_0 \, \mathrm{e}^{-[(E_a/R(T+273))]} [\mathrm{A}]^2 \tag{1}$$

$$\frac{\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = -K_0 \mathrm{e}^{-[(E_a/R(T+273))]} [\mathrm{A}]^2 \tag{2}$$

with $\alpha = K/(MC_p)$ and $[\mathrm{A}] = [\mathrm{MF}] = [\mathrm{ADCM}]$, α varies slightly with concentration because the water equivalent mass of the system (MC_p) is the sum of the water equivalent mass of the empty system and the thermic mass of the reactants, which depends slightly on the concentration.

This system of equations, whose numerical resolution is the only one suitable, can be written in the form

$$T(t) = T(t-h) + h(-\alpha(T(t-h) - T_a)) + \frac{\Delta H V}{MC_p} K_0 \mathrm{e}^{-(E/R[T(t-h)+273]} [\mathrm{A}]^2(t-h) \tag{3}$$

$$[\mathrm{A}](t) = [\mathrm{A}](t-h) - hK_0 \mathrm{e}^{-(E/R[T(t-h)+273]} [\mathrm{A}]^2(t-h) \tag{4}$$

where h is the step (time/number of simulations).

The aim of modelling is the determination of the reaction enthalpy ΔH and of the kinetic parameters (activation energy and frequency factor) such that the solution $T(t)$ of the system coincides as well as possible with the experimental curve; then identification problems of the parameters α, K_0, E_a, and ΔH must be resolved.

4.2.2. *Identification*

Every identification method requires the initialization of the parameters to be determined. Having no idea of their value, we have to estimate them by simplifying the problem (with simplifying assumptions) and by using the experimental data.

Determination of the initial values. We assume that the rate constant is independent of temperature. We thus obtain a linear model represented by the equation

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\alpha(T - T_a) + \frac{\Delta H V}{MC_p} k^* [\mathrm{A}]^2 \tag{5}$$

After integration of the kinetic law and after a change of variables relation (5) becomes

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\alpha(T - T_a) + \frac{a}{(1+bt)^2} \tag{6}$$

with

$$a = \frac{\Delta H V k^* [\mathrm{A}_0]^2}{MC_p} \quad \text{and} \quad b = k^* [\mathrm{A}_0].$$

The three parameters α, a, and b are evaluated from experimental data and curves. The value α is calculated by logarithmic linearization in the phase of the reaction (identified in this part of the curve). The parameter a is obtained by measuring the slope at the origin. As the slope is null at $t = t_{\max}$ (at the top of the curve $T = f(t)$), we can easily establish that the constant b is obtained from

$$b = \frac{1}{t_{\max}} \left[\sqrt{\frac{a}{\alpha(T(t_{\max}) - T_a)}} - 1 \right].$$

The rate constant k^* and the reaction enthalpy ΔH are easily deduced from these three parameters.

In our earlier papers [11,13], we showed that this first linear model was sufficient for a correct estimation of the reaction enthalpy which can be taken and eventually changed for a better simulation of the experimental record.

The linear model leads to the rate constant, from which we can estimate the initial value of E_a and K_0 calculated by linear regression of the Arrhenius plot.

Results. We first estimate the parameters useful for the initialization of the identification program according to the method presented above, and these are obtained for all experimental records with different initial concentrations of reactants. Table 1 presents the results of two series of experiments.

Then, an identification data program searches for K_0 and E_a so as to minimize the quadratic error between the solution of the system Eqs. (3) and (4), obtained by the Euler method [20], and the experimental data. The kinetic and thermodynamic parameters that lead to the best optimization of the system behaviour are presented in Table 2.

Fig. 1 shows the difference between the experimental graphs and solutions of the model found with the characteristic values of the Diels-Alder reaction between 2-methoxyfuran and dimethylacetylenedicarboxylate.

Table 1
Data determined from the linear model

$[\mathrm{MF}]_0$ (mol l^{-1})	a (K s^{-1})	α s^{-1}	MC_p (kg K^{-1})	k^* (l mol^{-1} s^{-1})
1	0.04	5.0×10^{-4}	143	2.3×10^{-3}
0.5	0.013	3.2×10^{-4}	141	2.9×10^{-3}

Table 2
Kinetic and thermodynamic data

$[MF]_0$ ($mol\,l^{-1}$)	K_0 ($l\,mol^{-1}\,s^{-1}$)	E_a ($kJ\,mol^{-1}$)	k (293 K) ($l\,mol^{-1}\,s^{-1}$)	ΔH ($kJ\,mol^{-1}$)	standard deviation
1	10^{10}	71.7	1.6×10^{-3}	150	0.225
0.5	10^{10}	70.6	2.4×10^{-3}	110	0.038

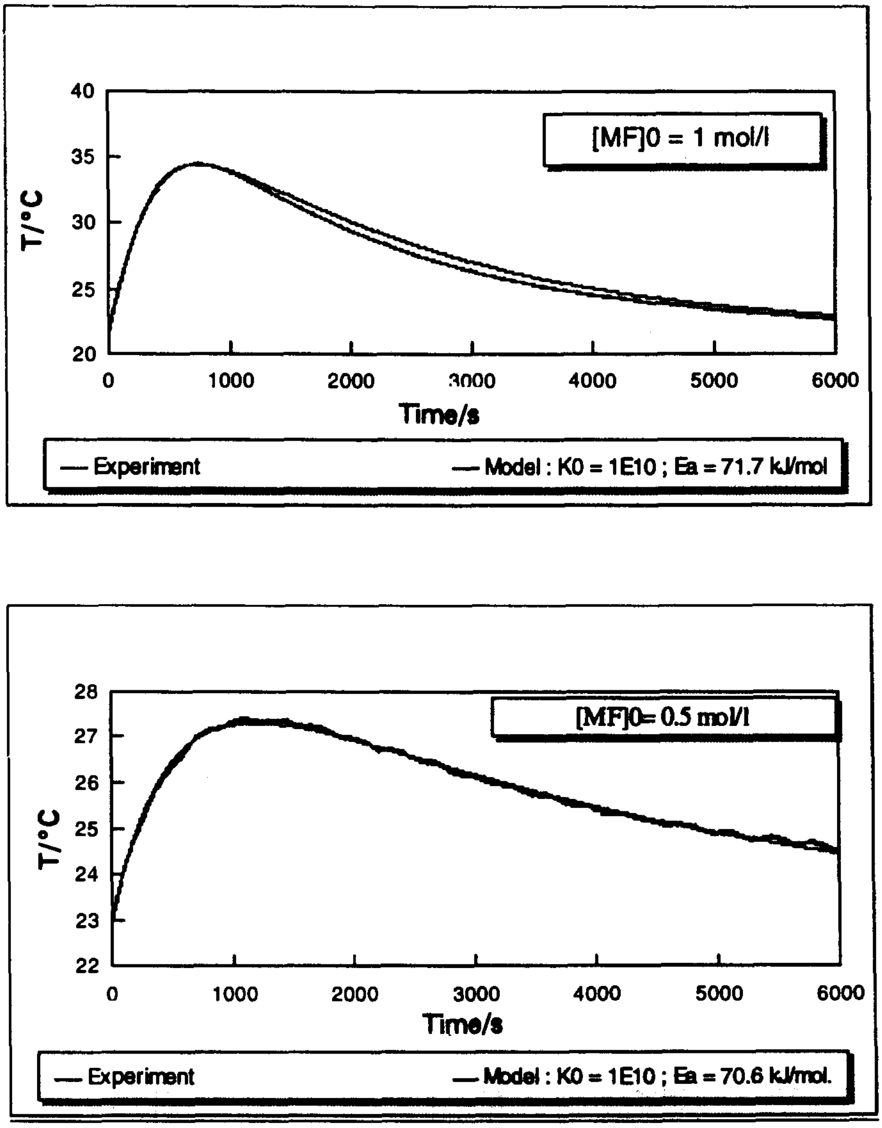


Fig. 1. Comparison between the model and the experimental graphs.

The respective means of the enthalpy and activation energy for the reaction between MF and DMAD are 130 kJ mol^{-1} and 71.15 kJ mol^{-1}.

The activation energy has the same order of magnitude as those reported for other Diels-Alder reactions [6].

The rate constant calculated at 293 K from the Arrhenius law is around 2×10^{-3} l mol^{-1} s^{-1}. This last parameter is now determined from spectroscopic measurements (NMR) in order to confirm this result.

5. Determination of the rate constant by NMR analysis

5.1. Kinetic study

We proceed as before. All the kinetic studies were made at 20°C directly in the NMR tube and the initial concentration $[\mathrm{MF}]_0$ of diene and $[\mathrm{DMAD}]_0$ of dienophile were exactly the same. Several experiments were carried out at two concentrations: 0.5 and 1 mol l^{-1}.

The rate constant is obtained from the equation

$$kt = \frac{1}{([\mathrm{MF}]_0 - x)} - \frac{1}{[\mathrm{MF}]_0}$$

where $([\mathrm{MF}]_0 - x]$ is the concentration of the methoxyfuran at time t.

The concentrations of the reactants and the adduct are calculated from the relative ratio of these compounds. This ratio is obtained by integration of the ^{1}H NMR signals of -vinylic hydrogens of the MF and -vinylic and bridgehead hydrogens of the adduct. The reaction was followed for 90 min and 14–18 ^{1}H NMR spectra were recorded.

5.2. Results

Integration of the selected NMR signals gives the relative ratio of the reactant and the adduct from which the concentrations are calculated. From these data we can plot $(1/[\mathrm{MF}]) - (1/[\mathrm{MF}]_0) = f(t)$ and deduce the slope which is the rate constant of the reaction. The results of two experiments obtained from the plots in Fig. 2 are given in Table 3.

Table 3
Rate constants determined by NMR

$[\mathrm{MF}]_0$ (mol l^{-1})	k (293 K) (l mol^{-1} s^{-1})
1	1×10^{-3}
0.5	1×10^{-3}

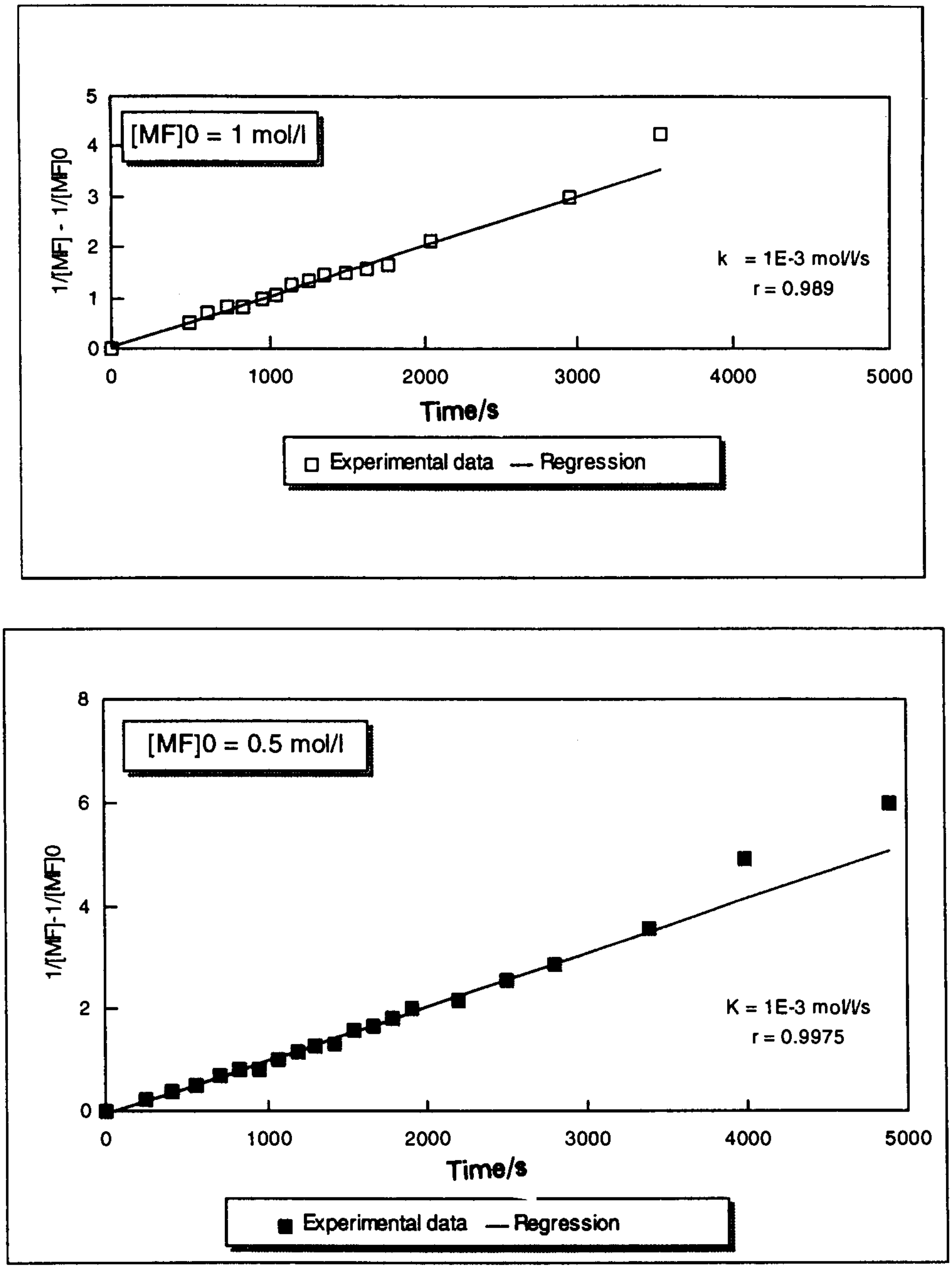


Fig. 2. Linear regression of the experimental data.

6. Conclusion

The results for the rate constant (at 293 K) obtained by the two methods may appear very different ($1 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ from NMR and $2 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$ from modelling). However, this kind of deviation is found in the literature at present and can be explained by the underlying differences of the two approaches which do not have the same objectives.

The NMR analysis provides the rate constant at a given temperature but only for low concentrations and volumes ($0.5\,\mathrm{cm^3}$).

The dynamic calorimetry simultaneously provides the enthalpy and the rate constant for every temperature (the kinetic parameters K_0 and E_a being known) for a larger range of concentrations and with a greater volume ($20\,\mathrm{cm^3}$ in this case).

The low volume used in NMR may be the reason for the noticeable relative error on the initial concentrations of the reactants which should be absolutely equal. Dynamic calorimetry does not yield a great precision, rather an overall approach so as to control the process is provided.

The aim of this study was to check the thermochemical and kinetic capacities of the cycloaddition between MF and DMAD for thermal energy storage (release step). The results are encouraging because the enthalpy (approximatively $130\,\mathrm{kJ\,mol^{-1}}$) and the rate constant (1×10^{-3}–$2 \times 10^{-3}\,\mathrm{l\,mol^{-1}\,s^{-1}}$) of this reaction are very high, compared with other reversible liquid-phase reactions [6, 9, 10].

Work is in progress to examine other criteria which allow this reaction to be a good candidate for thermal (solar) energy storage and release. Among these criteria, the possibility of carrying out the reverse reaction (thermal cycloreversion) at relatively moderate temperatures and the absence of side reactions in both cycloaddition and cycloreversion steps have to be studied in detail.

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