

## Hydroformylation of olefins catalysed by dichloro-bis(salicylaldehyde)-*o*-phenylenediiminoruthenate(III)

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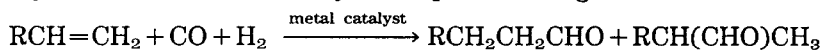
### Abstract

The kinetic study of hydroformylation of 1-hexene, cyclohexene and cyclooctene was performed using  $\text{Ru}^{\text{III}}(\text{saloph})\text{Cl}_2^-$  (saloph = bis(salicylaldehyde)-*o*-phenylenediimine) as a catalyst in ethanolic medium at 130 °C and 21 atm  $\text{CO} + \text{H}_2$  (1:1). Hydroformylation of 1-hexene gave the products 1-heptaldehyde (75%) and 2-methylhexaldehyde (25%) at the turnover rate of 14 mol product per mol catalyst per hour. Cyclohexene and cyclooctene gave cyclohexanecarboxyaldehyde and cyclooctylcarbinol, respectively.

The rate of hydroformylation of these olefins showed first-order dependence with respect to catalyst, substrate and dissolved  $\text{CO} + \text{H}_2$  (1:1) concentration, respectively. The activation energies evaluated for 1-hexene, cyclohexene and cyclooctene are 19.0, 24 and 21.0 kcal mol<sup>-1</sup>, respectively.

### Introduction

The oxo reaction has achieved great importance from both academic and industrial viewpoints [1–4]. It is one of the oldest [1] and most widely used homogeneous catalytic reactions and is used mainly in the petrochemical industry for the synthesis of  $\text{C}_{n+1}$  alcohols from  $\text{C}_n$  olefins. The hydroformylation of the olefin may be expressed in general terms as:



The primary products are thus both linear (l) and branched (b) aldehydes, the ratio l/b depending on the nature of the catalyst, temperature and reaction conditions.

There are several reports on the hydroformylation of olefins [5–9] using metal complexes such as cobalt carbonyls [10] and phosphine-coordinated cobalt carbonyls [11] to give the corresponding aldehydes with different l/b ratios [12]. The hydroformylation reaction is generally conducted in the temperature range 50–200 °C and  $\text{CO} + \text{H}_2$  (1:1) pressures of 100–400 atm.

Earlier, we reported the hydroformylation of 1-hexene by  $[\text{Ru}^{\text{II}}(\text{EDTA})(\text{CO})]^{2-}$  complex to give mostly 1-heptaldehyde as product [13].

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Since then we have been screening other ruthenium(II) carbonyl species for the hydroformylation of olefins. The present paper describes the kinetics of hydroformylation of 1-hexene, cyclohexene and cyclooctene in ethanolic medium catalysed by  $[\text{Ru}^{\text{II}}(\text{saloph})(\text{CO})]$  complex at 130 °C and 21 atm  $\text{CO} + \text{H}_2$  (1:1) pressure. 1-Hexene gave 1-heptaldehyde (75%) and 2-methylhexaldehyde (25%); cyclohexene and cyclooctene gave cyclohexanecarboxaldehyde and cyclooctylcarbinol, respectively.

## Experimental

### *Materials*

1-Hexene, cyclohexene and cyclooctene were obtained from Aldrich Chemicals and were used as such without further purification. The complex  $\text{K}[\text{Ru}^{\text{III}}(\text{saloph})\text{Cl}_2]$  was prepared according to reported procedure [14]. Synthesis gas  $\text{CO} + \text{H}_2$  (1:1) was procured from Indian Oxygen Ltd., Bangalore, India.

### *Apparatus and procedure*

The hydroformylation of 1-hexene, cyclohexene and cyclooctene was conducted in a 300 ml stainless steel pressure reactor (Parr Instruments Co., USA). In a typical experiment, the hydroformylation run was carried out by charging the substrate in 100 ml of ethanol along with a known amount of catalyst at 130 °C and 21 atm  $\text{CO} + \text{H}_2$  (1:1) partial pressures.

The bomb was pressurized by  $\text{CO} + \text{H}_2$  (1:1) at the desired value when the desired temperature was attained. The reaction was initiated by starting the agitation. Liquid samples were withdrawn from the reactor at fixed time intervals and analysed by GLC (Shimadzu, GC-9A) with a 2 mm long SS column (Poracil C, 80/100 mesh) and a FID detector. The progress of the reaction was monitored by following the moles of substrate consumed with time. The other conditions of GLC analysis were column temperature 100 °C, injection temperature 150 °C, nitrogen carrier gas flow rate 40 ml  $\text{min}^{-1}$ . The products were characterised by  $^{13}\text{C}$  NMR spectroscopic studies (Jeol FX 100 FT-NMR).

In a typical run, the hydroformylation of 1-hexene, cyclohexene and cyclooctene was carried out under optimised conditions in ethanol for a total contact time of 6 h. Samples of the reaction mixture were withdrawn from the reactor at fixed time intervals. The  $^{13}\text{C}$  NMR spectra of the products were taken and the spectra compared with standard samples produced from Aldrich Chemicals USA. In the case of 1-hexene, the spectrum of the reaction mixture showed peaks corresponding to 1-heptaldehyde ( $^{13}\text{C}$   $\delta$  176 ppm for  $\text{C}=\text{O}$ ,  $\delta$  114 and 138 ppm for alkene carbons of unreacted 1-hexene and  $\delta$  17.9–35 ppm for  $-\text{CH}_2$  carbons) and 2-methylhexaldehyde ( $\delta$  164 ppm for  $\text{C}=\text{O}$  and  $\delta$  17.9–35 ppm for  $-\text{CH}_2$  carbons). The spectrum of cyclohexene reaction mixture showed a peak corresponding to cyclohexanecarboxaldehyde

( $^{13}\text{C}$   $\delta$  200.2 ppm for C=O;  $\delta$  127.3 ppm for alkene carbons of unreacted cyclohexene and  $\delta$  20–40 ppm for  $-\text{CH}_2$  carbons). In the case of cyclooctene, the spectrum of the reaction mixture showed a peak corresponding to cyclooctylcarbinol ( $^{13}\text{C}$   $\delta$  50 ppm for  $-\text{CH}_2\text{OH}$ ,  $\delta$  130 ppm for alkene carbons of unreacted cyclooctene and  $\delta$  20–30 ppm for  $-\text{CH}_2$  carbons).

## Results and discussion

### *Hydroformylation of 1-hexene*

Under the reaction conditions studied, hydroformylation of 1-hexene catalysed by complex **1** in ethanolic medium gave 1-heptaldehyde (75.0%) and 2-methylhexaldehyde (25.0%). The effect of catalyst, 1-hexene, dissolved CO and  $\text{H}_2$  concentrations and temperature on the rate of reaction was determined from the plots of moles of 1-hexene consumed *vs.* time.

The solubility data for CO required under the reaction conditions were separately determined [15] and used in kinetic interpretation. The hydrogen solubility data required under the reaction conditions were calculated employing the temperature-dependent exponential form of the solubility equation, using the known value at the specified temperature [16].

### *Effect of catalyst concentration*

The effect of catalyst concentration (varied from 0.5 to  $2 \times 10^{-4}$  M) on the rate of hydroformylation of 1-hexene was studied at 130 °C, 0.016 M 1-hexene concentration and 21 atm CO +  $\text{H}_2$  (1:1) partial pressure. The effect of catalyst concentration on the rate of hydroformylation of 1-hexene is shown in Fig. 1, which shows first-order dependence with respect to catalyst concentration.

### *Effect of 1-hexene concentration*

1-Hexene concentration was varied in the range 0.008 to 0.024 M, and its effect on the rate of hydroformylation was studied at 130 °C,  $1 \times 10^{-4}$  M of catalyst concentration, 0.34 M dissolved CO concentration and 0.108 M dissolved  $\text{H}_2$  concentration. The results, shown in Fig. 2, indicate a first-order dependence of reaction rate on 1-hexene concentration.

### *Effect of dissolved CO concentration*

Figure 3 shows the effect of dissolved CO concentration on the rate of hydroformylation of 1-hexene. The dissolved CO concentration was varied between 0.17 and 0.34 M, keeping other parameters constant: catalyst concentration  $1 \times 10^{-4}$  M, 1-hexene concentration 0.016 M and dissolved  $\text{H}_2$  concentration of 0.108 M at 130 °C. The reaction shows a first-order dependence with respect to dissolved CO concentration (Fig. 3).

### *Effect of dissolved $\text{H}_2$ concentration*

The effect of dissolved  $\text{H}_2$  concentration (varied from 0.05–0.11 M) on the rate of hydroformylation of 1-hexene was studied at 130 °C, catalyst

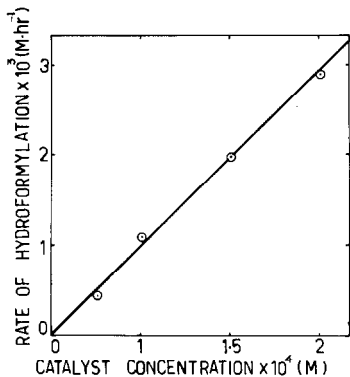


Fig. 1. Effect of catalyst concentration on the rate of hydroformylation of hexene.

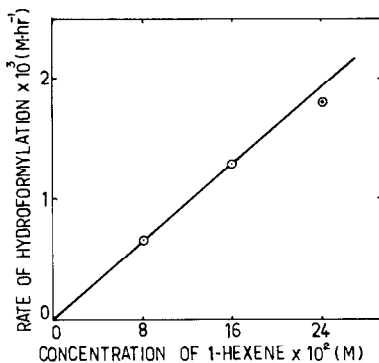


Fig. 2. Effect of 1-hexene concentration on the rate of hydroformylation of 1-hexene.

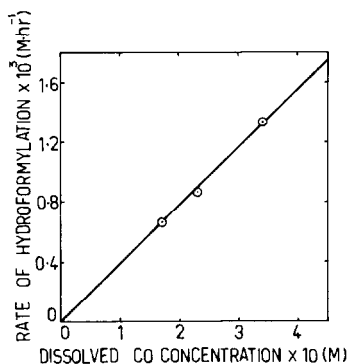


Fig. 3. Effect of dissolved CO concentration on the rate of hydroformylation of 1-hexene.

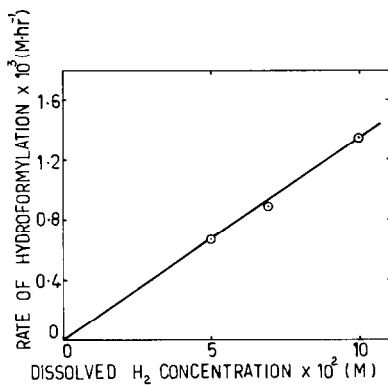


Fig. 4. Effect of dissolved H<sub>2</sub> concentration on the rate of hydroformylation of 1-hexene.

concentration of  $1 \times 10^{-4}$  M, 0.016 M 1-hexene concentration and dissolved CO concentration of 0.34 M. Figure 4 shows a first-order dependence of reaction rate on dissolved H<sub>2</sub> concentration.

#### Effect of temperature

The effect of temperature on the rate of hydroformylation of 1-hexene was studied in the temperature range 120–140 °C, at a catalyst concentration of  $1 \times 10^{-4}$  M, 1-hexene concentration of 0.016 M and dissolved CO+H<sub>2</sub> concentration of 0.34 and 0.108 M, respectively. A plot of  $-\ln$  rate *vs.*  $1/T$  is shown in Fig. 5, from which the value of the activation energy,  $E_a$ , evaluated was 19.0 kcal mol<sup>-1</sup>.

#### Mechanism and rate law

Based on the products formed and kinetic observations for the hydroformylation of 1-hexene, the probable mechanism proposed is shown in

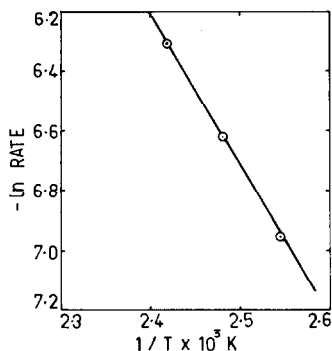
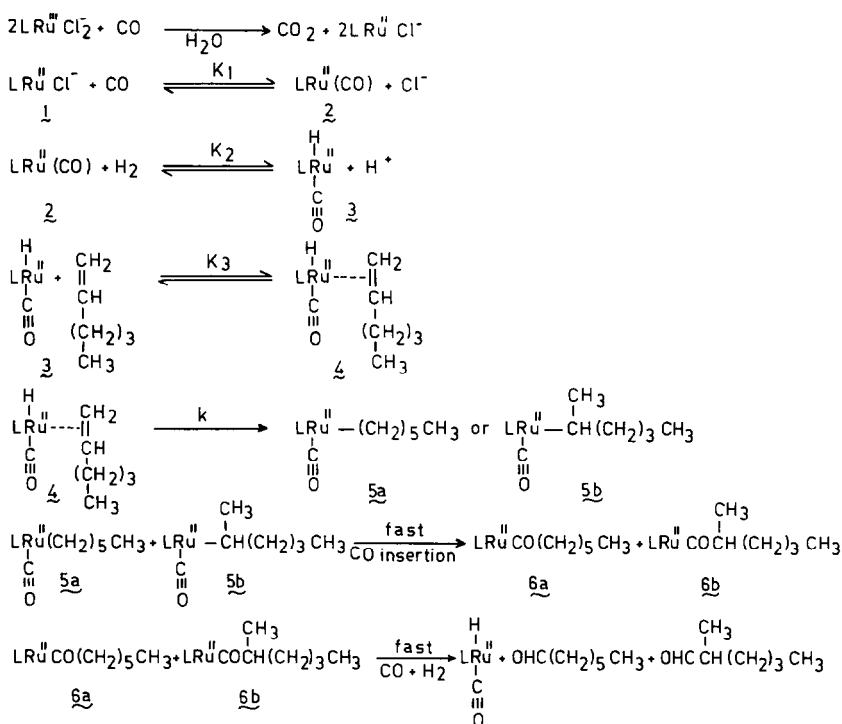


Fig. 5. Effect of temperature on the rate of hydroformylation of 1-hexene.



Scheme 1.

Scheme 1. In the proposed mechanism, complex **1** reacts with a molecule of CO to give  $[\text{Ru}^{\text{II}}(\text{saloph})(\text{CO})]^-$  species **2** in a pre-equilibrium step. The solution spectrum of the hydroformylation experiment, conducted in the absence of substrate 1-hexene, showed a peak at 370 nm which is attributed to the LMCT band of the carbonyl complex [17–19]. In the second pre-equilibrium step, complex **2** reacts with  $\text{H}_2$  with heterolytic cleavage of the latter to form the monohydrido species **3**. The hydride NMR spectrum of

the sample withdrawn from the reactor during the course of the reaction, showed a multiplet in the region  $-20.0$  to  $-30.0$  ppm. In a third pre-equilibrium step  $K_3$ , the hydrido complex **3** forms an intermediate mixed ligand-olefin complex **4**. The suggested rate-determining step involves the transfer of H to the olefin to form the alkyl complexes **5a** and **5b**. Fast insertion of CO in **5a** and **5b** results in the formation of acyl complexes **6a** and **6b** [5, 20–22], which undergo hydrogenolysis in the presence of CO + H<sub>2</sub> to form the hydride **3** and the products 1-heptaldehyde and 2-methylhexaldehyde from **6a** and **6b**, respectively. Transfer of hydride in step 5 to the  $\beta$ -carbon atom results in the formation of 2-methylhexaldehyde.

From the proposed mechanism and kinetic observations for the hydroformylation of 1-hexene, the rate equation can be written as:

$$\text{Rate} = kK_1K_2K_3[\text{Cat}]_T[\text{CO}][\text{H}_2][\text{S}] \quad (1)$$

where  $[\text{Cat}]_T$  = total catalyst concentration;  $[\text{CO}]$  = dissolved CO concentration;  $[\text{H}_2]$  = dissolved hydrogen concentration;  $[\text{S}]$  = 1-hexene concentration;  $K_1$ ,  $K_2$ ,  $K_3$  are equilibrium constants and  $k$  is the rate constant.

Taking into consideration the total catalyst concentration present in the form of different species formed *in situ* at steady-state conditions, the final rate law is written as:

$$\text{rate} = \frac{kK_1K_2K_3[\text{Cat}]_T[\text{CO}][\text{H}_2][\text{S}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{H}_2] + K_1K_2K_3[\text{CO}][\text{H}_2][\text{S}]} \quad (2)$$

To evaluate the kinetic constants, the above eqn. (2) can be rearranged into slope and intercept form as:

$$\frac{[\text{Cat}]_T}{\text{rate}} = \frac{1}{[\text{S}]} \left( \frac{1}{kK_1K_2K_3[\text{CO}][\text{H}_2]} + \frac{1}{kK_2K_3[\text{H}_2]} + \frac{1}{kK_3} \right) + \frac{1}{k} \quad (3)$$

The value of  $k$  was calculated from the intercept obtained by plotting a graph of  $[\text{Cat}]_T/\text{rate}$  vs.  $1/[\text{S}]$  from eqn. (3). The values of  $K_1$  and  $K_2$  were calculated spectrophotometrically at room temperature, by monitoring the peak at 370 nm (species **2**, Scheme 1) and shoulder at 290 nm (species **3**, Scheme 1), respectively. Substituting the values of  $k$ ,  $K_1$ ,  $K_2$ , CO and H<sub>2</sub> in eqn. (3), the value of  $K_3$  was evaluated. The kinetic constants determined in the case of hydroformylation of 1-hexene catalysed by complex **1** at 130 °C and 21 atm. CO + H<sub>2</sub> (1:1) are:

$$K_1 = 62.5 \text{ M}^{-1}$$

$$K_2 = 18.0 \text{ M}^{-1}$$

$$K_3 = 6.0 \text{ M}^{-1}$$

$$k = 2.8 \text{ min}^{-1}$$

Hydroformylation of 1-hexene catalysed by  $[\text{Ru}^{\text{II}}(\text{EDTA})(\text{CO})]^{2-}$  to give 1-heptaldehyde was reported earlier [13]. The reaction was conducted at 130 °C and 50 atm CO + H<sub>2</sub> (1:1) in 80:20 ethanol:water mixture. The turnover

rate for the reaction was found to be 12 mol product per mol catalyst per hour. Thus  $[\text{Ru}^{\text{II}}(\text{saloph})(\text{CO})\text{Cl}]^-$  gives a better turnover rate as compared to  $[\text{Ru}^{\text{II}}(\text{EDTA})(\text{CO})]^{2-}$ , though the ratio of  $l/b$  is much higher in the former case as compared to the latter.

#### *Hydroformylation of cyclohexene and cyclooctene*

The hydroformylation of cyclohexene and cyclooctene using  $\text{CO} + \text{H}_2$  (1:1), catalysed by complex 1 was studied in a manner similar to that of 1-hexene. The hydroformylation of cyclohexene and cyclooctene at 130 °C and 21 atm  $\text{CO} + \text{H}_2$  (1:1) gave cyclohexanecarboxaldehyde and cyclooctylcarbinol [23–25], respectively. The kinetics of the reaction using complex 1 was studied by monitoring the consumption of moles of substrate with time. The effects of catalyst (Fig. 6), substrate (Fig. 7), dissolved CO (Fig. 8) and dissolved  $\text{H}_2$  concentration (Fig. 9) were studied on the rates of hydroformylation of cyclohexene and cyclooctene, respectively. It was observed that the rates of hydroformylation of cyclohexene and cyclooctene showed first-order dependence with respect to catalyst, substrate and dissolved  $\text{CO} + \text{H}_2$  concentration. The effect of temperature on the rate of hydroformylation of cyclohexene and cyclooctene was also studied. From the plot of  $-\ln \text{rate vs. } 1/T$  (Fig. 10), the values of activation energy,  $E_a$ , for cyclohexene and cyclooctene hydroformylation are given in Table 1.

Based on the products formed and kinetic observations for the hydroformylation of cyclohexene and cyclooctene, a probable mechanism for the reactions is shown in Scheme 2. The mechanistic steps involved in Scheme 2 are similar to those shown for hydroformylation of 1-hexene (Scheme 1). In the case of cyclooctene hydroformylation, the last step involves the hydrogenation of the aldehyde formed to give the final product cyclooctylcarbinol.

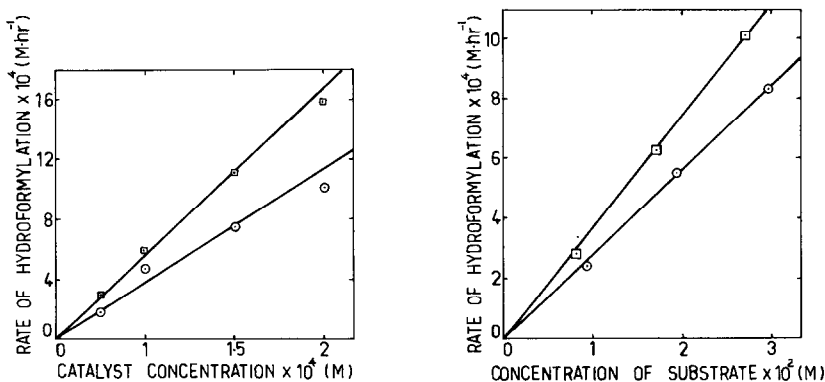


Fig. 6. Effect of catalyst concentration on the rate of hydroformylation of (○) cyclohexene and (□) cyclooctene.

Fig. 7. Effect of (○) cyclohexene and (□) cyclooctene concentration on the rate of hydroformylation of cyclohexene/cyclooctene.

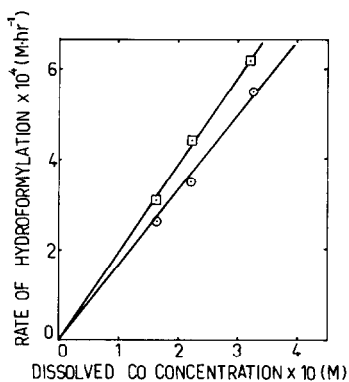


Fig. 8. Effect of dissolved CO concentration on the rate of hydroformylation of (○) cyclohexene and (□) cyclooctene.

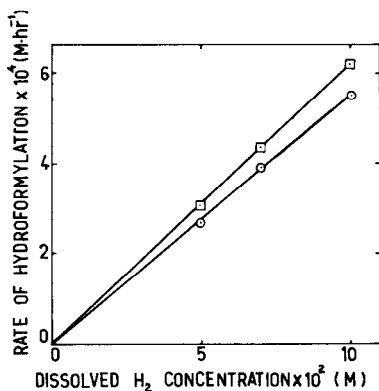


Fig. 9. Effect of dissolved H<sub>2</sub> concentration on the rate of hydroformylation of (○) cyclohexene and (□) cyclooctene.

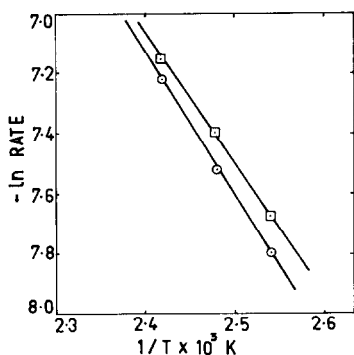


Fig. 10. Effect of temperature on the rate of hydroformylation of (○) cyclohexene and (□) cyclooctene.

The rate data for the hydroformylation of cyclohexene and cyclooctene were obtained in a manner similar to that for 1-hexene. The values of equilibrium constants  $K_1$  and  $K_2$  ( $K_1 = 62.5 \text{ M}^{-1}$  and  $K_2 = 18.0 \text{ M}^{-1}$ ) are the same as those obtained for 1-hexene. The calculated values of equilibrium constant  $K_3$  for cyclohexene and cyclooctene are  $11.7 \text{ M}^{-1}$  and  $7.8 \text{ M}^{-1}$ , respectively. The rate constants  $k$  for the hydroformylation of cyclohexene and cyclooctene are given in Table 1.

The rate constants  $k$  for the hydroformylation of the three olefins decrease in the order 1-hexene > cyclooctene > cyclohexene. The straight chain olefin 1-hexene reacts at a faster rate than the cyclic olefins. In the cyclic olefins cyclooctene, which is less rigid than cyclohexene, reacts at a faster rate than the latter. The same order of reactivity of straight chain *vs.* cyclic olefins has also been observed by other investigators [5, 21, 22, 24].





The formation of alkyl complex **6**, which is proposed as the rate-determining step (Schemes 1 and 2), is significantly endothermic in the case of cyclic olefins, which is shown by positive  $\Delta H^\ddagger$  values (Table 1). The entropies also decrease in the same order cyclohexene > cyclooctene > 1-hexene. The large positive entropy change in the case of cyclohexene compensates for the endothermic  $\Delta H^\ddagger$  and makes the reaction possible.

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