

## A dynamic-route study of solution reactions: ring closure of a hexadienone

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 11423

(<http://iopscience.iop.org/0953-8984/14/44/493>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 17:20

Please note that [terms and conditions apply](#).

# A dynamic-route study of solution reactions: ring closure of a hexadienone

Yoshitaka Goto<sup>1</sup>, Yasushi Ohga<sup>1</sup>, Tsutomu Asano<sup>1</sup> and  
Noam N Weinberg<sup>2</sup>

<sup>1</sup> Department of Applied Chemistry, Faculty of Engineering, Oita University, 700 Dannoharu, Oita 870-1192, Japan

<sup>2</sup> Department of Chemistry, University College of the Fraser Valley, 33844 King Rd, Abbotsford, Canada BC V2S 7M9

Received 1 June 2002

Published 25 October 2002

Online at [stacks.iop.org/JPhysCM/14/11423](http://stacks.iop.org/JPhysCM/14/11423)

## Abstract

Pressure effects on the thermal rate process from *trans*-**1** to **2** shown in scheme 1 were studied in ethanol and highly viscous 2-methylpentane-2, 4-diol. In the former, the reaction was moderately accelerated as expected from the transition state theory (TST). In the latter, the TST became invalid at high pressures and low temperatures and a so-called dynamic solvent effect was observed. The results clearly demonstrated that the medium and the chemical coordinates have to be treated independently.

## 1. Introduction

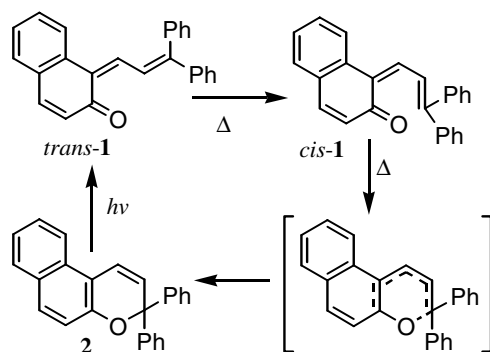
We have been studying kinetic effects of pressure on relatively slow thermal isomerizations ( $k < 1000 \text{ s}^{-1}$ ) in common and highly viscous solvents [1]. The main purpose of such studies is to elucidate how the solvent molecules are involved in the activation step.

From measurements in a common solvent, pressure effects expected from the transition state theory (TST) are obtained. In highly viscous solvents, solvent viscosity rapidly increases with increasing pressure and thermal fluctuations become too slow to maintain the thermodynamic equilibrium between the initial and the transition states. Under such circumstances, the reaction rate is limited by the rate of solvent thermal fluctuations and dynamic solvent effects are observed.

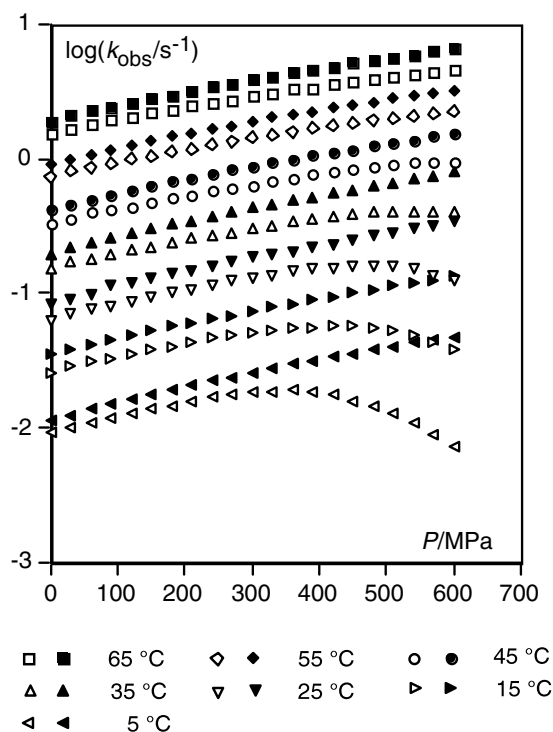
In this paper, dynamic solvent effects will be reported for cyclization of a hexadienone **1** to form **2**, 2-diphenylbenzo[f]2*H*-chromene **2** (scheme 1).

## 2. Experimental details

The hexadienone **1** was photochemically generated *in situ* from **2**. The solvents used were ethanol and 2-methylpentane-2, 4-diol (MPD). At all of the conditions studied, the reaction obeyed the first-order rate law and the rate constant could be determined unequivocally.



**Scheme 1.** Cyclization of a hexadienone **1** to form 2,2-diphenylbenzo[*f*]2*H*-chromene **2**.



**Figure 1.** Pressure dependences of the cyclization rate of **1** in EtOH (filled symbols) and MPD (open symbols).

### 3. Results and discussion

Pressure dependences of the first-order rate constant are illustrated in figure 1.

In ethanol, the reaction was accelerated by an increase in pressure throughout the whole pressure range. Moderately negative (about  $-8 \text{ cm}^3 \text{ mol}^{-1}$ ) activation volumes  $\Delta V^\ddagger$  are in agreement with scheme 1 because the activated complex has much smaller internal freedom of motion than the open-chain reactant *trans*-**1**. Very small solvent dependence of the reaction rate ( $0.15 \text{ s}^{-1}$  in hexane and  $0.083 \text{ s}^{-1}$  in ethanol at  $25 \text{ }^\circ\text{C}$  and  $0.1 \text{ MPa}$ ) is consistent with this

**Table 1.** Isoviscous activation energies obtained from  $k_{obs}$  ( $Ea_{obs}$  ( $\text{kJ mol}^{-1}$ )) for the cyclization of *trans*-**1** in MPD at various viscosities ( $\eta$  (Pa s)).

$\eta$	0.01	0.1	1	10	100	1000
$Ea_{obs}$	70.2	74.2	75.6	75.5	74.8	74.4

consideration. A small volume increase by desolvation must have been overshadowed by a volume decrease of the reactant itself. Similar pressure-induced accelerations were observed in MPD at lower pressures, clearly indicating the validity of TST even for this viscous solvent up to a few hundred megapascals (MPa). At higher pressures and lower temperatures, however, pressure-induced retardations were observed. Since this retardation was observed only in MPD, it is reasonable to assume that the TST became invalid because of high viscosities at high pressures.

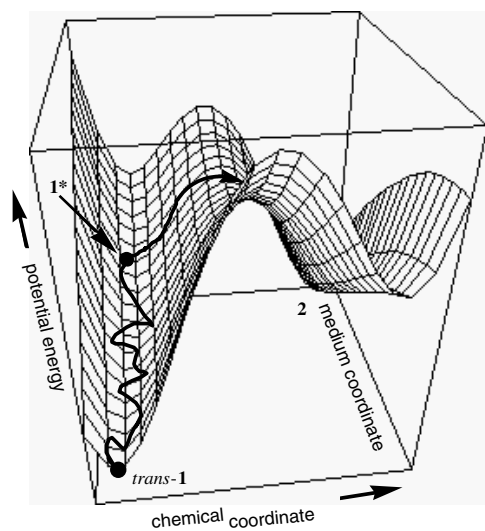
Two fundamentally different models were proposed for solution reactions. The first model was proposed by Kramers [2] and modified later by Grote and Hynes [3] (KGH model). In this model, a movement of a reactant particle along the reaction coordinate is assumed to be Brownian motion and, therefore, the medium and the chemical coordinates are fully concerted. The second model, originally proposed by Agmon and Hopfield [4] (the AH model), assumes that the two coordinates are independent to each other. The two models make totally different predictions regarding the viscosity dependence of the activation energy. In the KGH model, the reactant particle is pushed back and forth by solvent molecules and gradually climbs up the energy barrier. Therefore, if the viscosity of the medium is kept constant, the temperature dependence of the reaction rate is solely determined by the barrier height. In other words, the isoviscous activation energy would be independent of the viscosity. In the AH model, on the other hand, a movement along the medium coordinate, i.e., solvent reorganization in the initial state, becomes rate-limiting at high viscosities. The situation is schematically illustrated in figure 2 where the reaction starts from the lower left corner and the reactant moves back and forth along the medium-coordinate valley up to point **1\***. If the reactant molecule acquires enough energy to surmount the barrier, one fast movement along the chemical coordinate takes place as shown by a curly arrow. At high viscosities, the isoviscous temperature dependence of the reaction rate reflects the height of the position **1\***. Since this position is lower than the saddle point, a shift from the TST-valid viscosity region to the TST-invalid one is characterized by a decrease in the isoviscous activation energy. As can be seen from this discussion, it is possible to examine the validity of these models on the basis of the viscosity dependence of the isoviscous activation energy.

Figure 3 illustrates the viscosity dependence of  $k_{obs}$  in MPD at various temperatures. From these plots, rate constants at a constant viscosity were estimated for different temperatures and isoviscous Arrhenius plots were constructed. The activation energies thus obtained are listed in table 1.

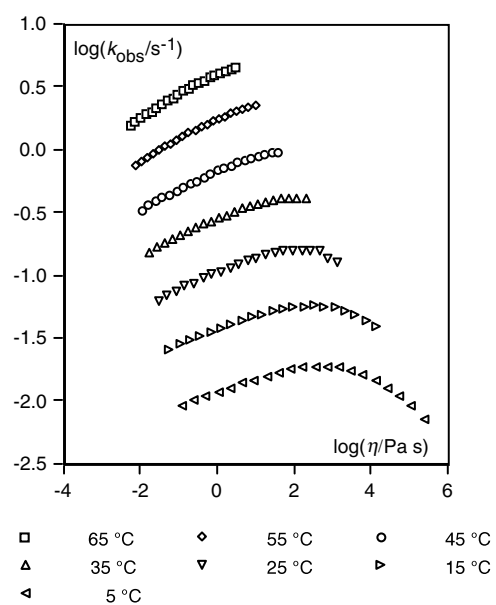
The activation energy decreased with increasing viscosity at viscosities above 10 Pa s. This can be considered a clear indication of validity of the AH model.

#### 4. Conclusions

Kinetics in a common and a viscous solvent again proved to be an effective tool for studying dynamic routes of solution reactions. It was shown that the medium and the chemical coordinate have to be treated separately in the present system.



**Figure 2.** A schematic illustration of the AH model applied to the present reaction.



**Figure 3.** Viscosity dependence of the cyclization rate of **1** in MPD at various temperatures.

## References

- [1] Asano T 1999 *Pure Appl. Chem.* **71** 1691 and earlier papers cited therein
- [2] Kramers H A 1940 *Physica* **7** 284
- [3] Grote R F and Hynes J H 1980 *J. Chem. Phys.* **73** 2715
- [4] Agmon N and Hopfield J J 1983 *J. Chem. Phys.* **78** 6947  
Agmon N and Hopfield J J 1983 *J. Chem. Phys.* **79** 2042