An Experimental Attempt to Identify a Moving Molecular Moiety in a Solvent Matrix

Yoshitaka Goto, Keijiro Sugita, Toru Takahashi, Yasushi Ohga, and Tsutomu Asano*
Department of Applied Chemistry, Faculty of Engineering, Oita University, 700 Dannoharu, Oita 870-1192

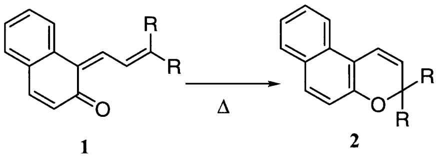
(Received April 23, 2003; CL-030343)

It was experimentally demonstrated that microscopic friction between a reactant molecule and the surrounding solvent during a unimolecular structural change increased with increasing bulkiness of substituents and it is suggested that this dependence can be used to identify a moving molecular moiety in the reactant inside of a solvation shell.

In unimolecular reactions, at least two reactant moieties change their relative positions in the activation step. For vapor phase reactions, it would suffice if we determine the amount of the energy increase during the intramolecular geometrical transformations along the reaction coordinate. In solution reactions, however, another question has to be answered, i.e., which part of the reactant molecule changes its position in a solvent matrix. Moments of inertia and microscopic frictions must be dominant factors controlling the relative mobilities of various atomic groups of a reactant in a solvent matrix. If one half of the reactant has a smaller mass and feels smaller friction than the other, it would change its position while the rest of the molecule remains more or less in the same position. To the best of our knowledge, however, this sort of question has never been asked explicitly and nobody has tried to get an answer to this potentially important question.

We have been studying kinetic effects of viscosity on the rate of slow thermal unimolecular rate processes. Usually viscosity shows no effect on the rate of such reactions because the reaction rate is solely determined by a free energy difference between the initial and the transition states $\Delta G^{\neq}$. In order to invalidate this fundamental assumption of the transition state theory, we adopted viscous liquids as the reaction media and applied high external pressures in order to increase the viscosity further. As expected, we observed strong viscosity-induced retardations in various unimolecular reactions.[1,2] Obviously, movements of the reactant molecules along the reaction coordinate became rate-determining. High viscosities suppressed thermal fluctuations of the solvent and the rate of supply of the reactant molecules to the transition state became rate-controlling. These results imply that we now have a tool to study relative mobilities of molecular moieties of a reactant in the activation step. Suppose we installed sterically larger substituent(s) on one side of the reactant molecule and observed an appearance of viscosity-induced retardation at a lower viscosity. Then it would be reasonable to conclude that major solvent reorganizations along the reaction coordinate took place in the neighborhood of the modified part. In other words, the modified part changed its relative position in the solvation shell in the activation step although it does not exclude a possibility that the rest of the molecule also changed its position. In this letter, we are going to report the first experimental application of this idea to a real reaction system.

The reaction that we studied is shown in Scheme 1 where photochemically generated 1-prop-2-enylidenenaphthalen-2-one derivatives **1a** and **1b** thermally regenerate 3*H*-naphtho[2,1-*b*]pyrans **2a** and **2b**, respectively.[2]



1 **2**

Scheme 1. **1a** : R = Me, **1b** : R = Ph.

We introduced two methyl and phenyl groups on a carbon next to the oxygen atom in **2** and studied kinetics of the thermal return of **1** to **2** in viscous 2-methylpentane-2,4-diol (MPD) and nonviscous ethanol (EtOH) at various temperatures and pressures. Since methyl and phenyl group are different not only in their steric bulk but also in their electronic properties, it is desirable to examine whether the nature of the reaction was not affected by the substituents. The observed rate constants k for **1a** and **1b** in ethanol are plotted against pressure in Figure 1 and activation parameters are listed in Table 1. The activation volumes are the values at $P = 0$.

The reaction was slower in **1b** than in **1a** because of a larger activation enthalpy and a more negative activation entropy. However, the activation parameters did not show any dramatic dependence on the substituent. The acceleration by an increase in pressure was slightly larger in **1b**. All of these parameters strongly suggest that the influence of the substituents were mostly steric.

Now let us compare the viscosity effects in the two compounds. The rate constants for **1a** and **1b** in MPD are plotted against the solvent viscosity in Figures 2 and 3, respectively. The measurements were performed from 0.1 MPa to 600 MPa

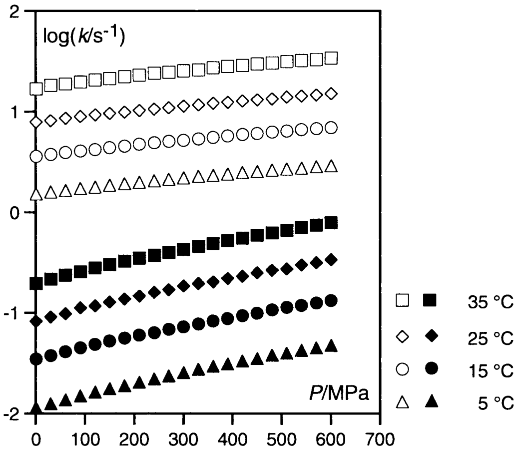


Figure 1. Pressure effects on the reaction of **1a** (open keys) and **1b** (closed keys) in ethanol.

Table 1. Activation parameters for the reaction of **1a** and **1b** in ethanol

	P/MPa	**1a**	**1b**
$\Delta H^{\neq}$/kJ mol^{-1}	0.1	54.7	63.2
	300	55.4	62.2
	600	55.5	61.0
$\Delta S^{\neq}$/J K^{-1} mol^{-1}	0.1	−44.4	−53.6
	300	−38.6	−50.7
	600	−35.9	−49.8
$\Delta V^{\neq}$/cm^3 mol^{-1}	(298 K)	−3.7	−8.8

at every 30 MPa as in EtOH. As observed for other unimolecular reactions,[1] we observed pressure-induced accelerations both in **1a** and **1b** at lower pressures (P < 200 MPa) even in this viscous solvent, showing the thermodynamic equilibrium was maintained between the initial and the transition states. However, viscosity-induced retardations were observed at higher pressures despite the negative activation volume. The high viscosities retarded thermal fluctuations of the solvent molecules and these slow motions became rate-determining. Figures 2 and 3 reveal that these viscosity-induced retardations appeared at a lower viscosity in **1b** than in **1a** compared at the same temperature. Obviously, sterically smaller methyl groups felt lower friction than the phenyl groups. As discussed in the preceding paper,[2] the activation step of this reaction consists of two major motions. A rotation around the carbon–carbon single bond connecting the vinyl substituent to the naphthalenone skeleton takes place first and this conformational change is followed by a carbon–oxygen bond formation. Considering the large movement with a large dihedral angle change in the first step (see Figure 1 in Ref. 2), microscopic friction would have affected mainly this rotation step. The fact that **1a** felt lower friction clearly indicated that the vinyl moiety changed its position in the solvation shell during this conformational change.

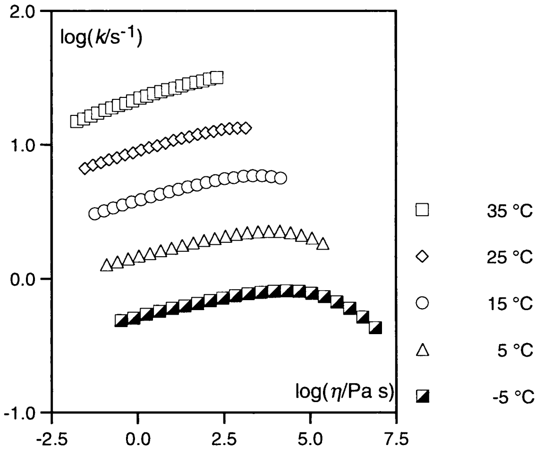


Figure 2. Viscosity dependence of the reaction of **1a** in MPD.

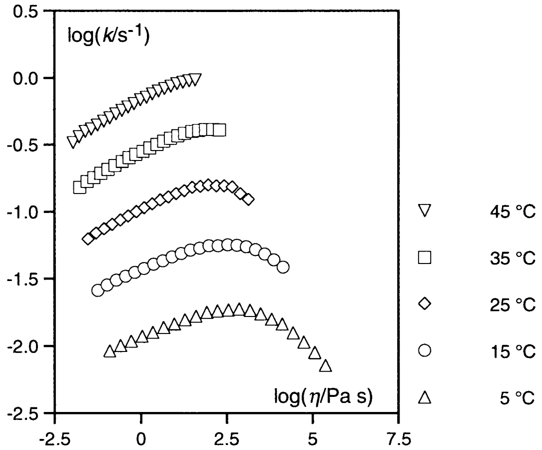


Figure 3. Viscosity dependence of the reaction of **1b** in MPD.

The present experiment did not tell whether the 2-naphthalenone group also changed its position simultaneously in the activations step. In order to obtain information on the relative mobility of the vinyl and the naphthalenone moieties, we also need to examine the influence of substituent(s) on the naphthalenone ring. Experiments along this line are under progress and the results will be reported when they are completed.

References

1 J. C. Kim, Y. Ohga, T. Asano, N. N. Weinberg, and A. V. George, *Bull. Chem. Soc. Jpn.*, **74**, 103 (2001) and earlier papers cited therein.

2 Y. Goto, T. Takahashi, Y. Ohga, T. Asano, M. Hildebrand, and N. Weinberg, *Phys. Chem. Chem. Phys.*, **2003**, 1825.

Published on the web (Advance View) June 17, 2003; DOI 10.1246/cl.2003.618