Effects of Pressure on the Thermal Back Electron Transfer in a Dibenzylbipyridinium Salt. Solvent Reorganizations and Dynamic Solvent Effects

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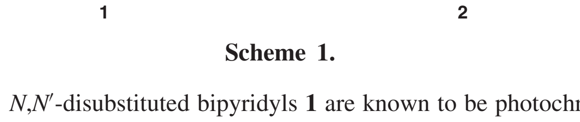
Kinetic effects of pressure on a decay of a radical pair produced by UV irradiation of *N*,*N*′-dibenzyl-4,4′-bypyridinium dichloride were studied in acetonitrile (AN) and propylene carbonate (PC). Both in AN and PC, the process was accelerated by an increase in pressure indicating a considerable contraction of the solvation sphere during the activation. Furthermore, in PC, pressure-induced retardation was observed at $P > 200$ MPa and it was attributed to slow solvent thermal fluctuations at high pressures.

There have been many reports on pressure dependence of electron transfer rate processes and most of the results could be rationalized on the basis of the transition state theory (TST).[1] Namely, the results could be rationalized in terms of the activation volume $\Delta V^{\ddagger}$. For example, the reduction of $Co(NH_3)_5(H_2PO_4)^{2+}$ by $Fe(CN)_6{}^{4-}$ was retarded by an increase in pressure, $\Delta V^{\ddagger} = 17\,cm^3\,mol^{-1}$ at 25 °C in H_2O, and it was attributed to desolvation caused by the charge neutralization.[2] In other words, solvent thermal fluctuations were fast enough to maintain the thermodynamic equilibrium between the initial and the transition state. Since applying pressure results in an increase in viscosity and it, in turn, slows down solvent thermal fluctuations, it is conceivable that solvent reorganization process itself becomes rate-limiting at high pressures, namely, a reaction may change its kinetic nature from the "activation-limited" to the "fluctuation-limited" at high viscosities. To the best of our knowledge, however, there has been no report of a case in electron transfer where the TST was valid at 0.1 MPa and it turned invalid with increasing pressure. In this letter we would like to report possibly the first observation of induced invalidation of the TST in an electron-transfer rate process.



Scheme 1.

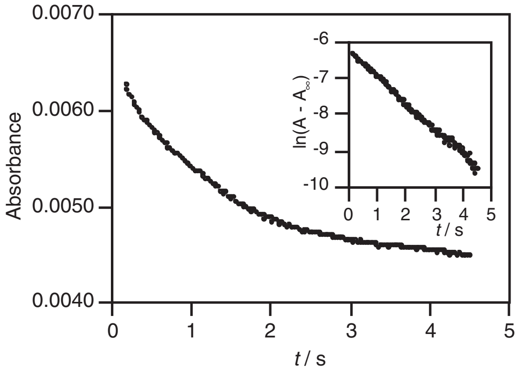


Figure 1. Absorbance change and the plot of first-order rate law (inset) monitored at 600 nm in PC at 10 °C (90 MPa).

N,*N*′-disubstituted bipyridyls **1** are known to be photochromic and it is well proved that the colored species is a radical cation **2**.[3] In solution, this species decays rapidly by thermal back electron transfer (Scheme 1). We studied pressure dependence of this thermal reaction rate in *N*,*N*′-dibenzyl-4,4′-bipyridyl dichloride ($R = PhCH_2$, $X = Cl$) in acetonitrile (AN, 4×10^{-4} M) and propylene carbonate (PC, $4\text{–}5 \times 10^{-4}$ M) by flash photolysis using Xe lamp. The reaction was followed by the absorption decrease at λ_{max} in the visible region, 570 nm (AN) and 600 nm (PC). Figure 1 shows an example of a kinetic reaction profile and the first-order plot constructed from it. The reaction followed the first-order rate law at all of the conditions studied as in the example and we could safely assume that this electron transfer took place within a radical pair and the translational diffusion of the radicals did not play an important role in the present reaction. Figures 2 and 3 illustrate pressure dependence of the first-order rate constant k_1 in AN and PC, respectively. In both of the solvents, the reaction was accelerated by an increase in pressure at lower pressures, $P < 100$ MPa. The activation volumes were estimated by fitting the results to a quadratic equation and the values at zero pressure, $\Delta V_0{}^{\ddagger}$, were estimated to be -17 and $-57\,cm^3\,mol^{-1}$ at 25 °C in PC and AN, respectively. Since a pair of charges was generated in this reaction, a volume contraction during activation is more or less pressure-expected. Solvent molecules have to be reorganized to stabilize the charged species. Kondo and co-workers[4–7] measured reaction volumes ΔV in several nucleophilic substitutions in methyl iodide at 30 °C and the values were -63 to -40 in AN and -36 to -21 $cm^3\,mol^{-1}$ in PC depending on the nucleophiles. The large volume contraction results from electrostrictions around the cation and the anion and the magnitude was always larger in AN because of its larger compressibility than PC. Similarly, in our reaction, the charged species, pyridyl cation and chloride anion, were generated from the corresponding neutral radicals by electron transfer. Comparing these values with our activation volumes, it may be concluded that solvent reorganizations were almost complete at the transition state in AN but they were still underway in PC.

Figures 2 and 3 reveal another significant difference between the two solvents. In AN, the reaction was accelerated throughout the whole pressure range studied,[8] while in PC the pressure effect was reversed somewhere between 100 and 300 MPa. The sign of the activation volume changed from negative to positive with increasing pressure. This sort of behavior is

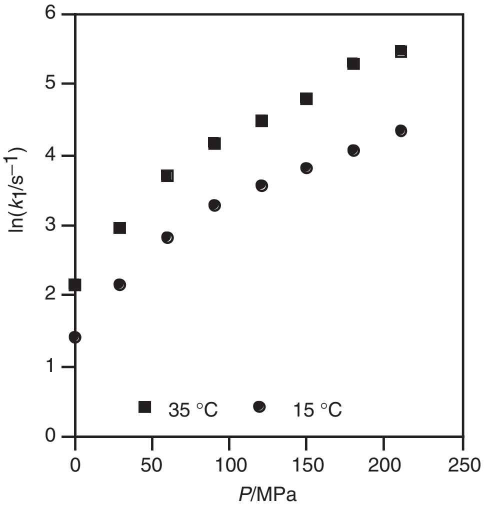


Figure 2. Pressure dependence of the first-order rate constant (k_1/s^{-1}) in AN.

usually an indication of a shift of the rate-determining step, however, the present reaction is a one-step rate process and the pressure-induced retardation was difficult to understand if we assume fast solvent thermal fluctuations at all pressures. The most reasonable explanation would be that solvent thermal fluctuations became too slow to maintain the thermodynamic equilibrium between the initial and the transition state and so-called dynamic solvent effects[9] were observed. The rate-controlling factor might have changed from the activation free energy, $\Delta G^{\ddagger}$, at low pressures to the rate of solvent thermal fluctuations at high pressures.

As a measure of relative solvent fluctuation rate, the bulk solvent viscosity is often used. Although high-pressure viscosity of the present solvents are not available, the viscosity of PC and AN are 2.53×10^{-3} Pa s and 3.41×10^{-4} Pa s, respectively at 25 °C, and their pressure coefficients would be larger in PC which has a five-membered ring with a methyl substituent and a carbonyl oxygen than in linearly shaped AN. Therefore, it would be reasonable to observe dynamic solvent effects in PC but not in AN. The fact that the pressure where the maximum rate constant was observed shifted from 210 MPa at 40 °C to 150 MPa at 10 °C supports this view.

Further kinetic measurements at other temperatures and in other solvents are under way and the results will be reported when they are completed.

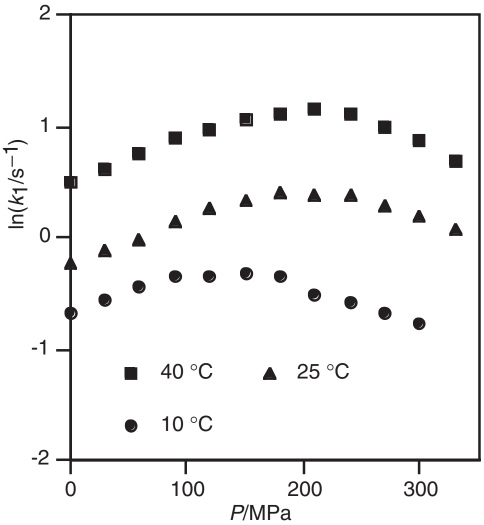


Figure 3. Pressure dependence of the first-order rate constant (k_1/s^{-1}) in PC.

References and Notes

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