

Fig. 1. The UV/V spectrum of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide in methyl acetate(a) and acetonitrile(b).

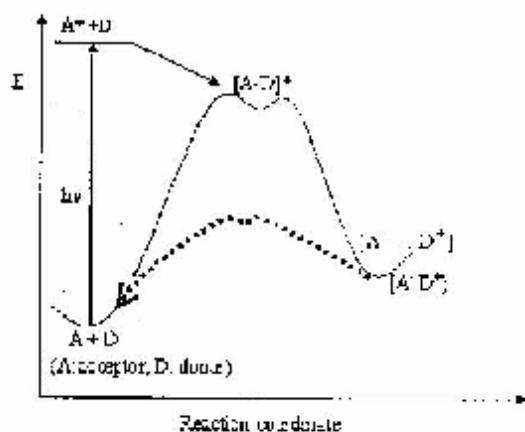
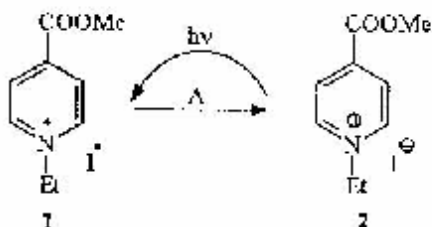


Fig. 2. The photochromism via electron transfer.

### Results and discussion

We measured the rate of (ET) reaction of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide as shown in scheme (2) in several different solvents at different pressures and temperatures.



Scheme 2

The pyridinyl radical **1** was photochemically generated *in situ* **2**. The absorption spectra of **2** before and after irradiation in acetonitrile are illustrated in Fig. 3. Decay of **1** was followed by monitoring the absorbance at its  $\lambda_{max}$  the reaction obeyed the first order law. Pressure dependences

of rate constant in three organic solvents (acetonitrile, ethyl acetate and ethanol) at different temperatures are shown in Figs.4-6 and representative values are listed in Table 1.

Fig. 3 shows the changing in the spectrum of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide in acetonitrile before and after irradiation which explains formation of the radical **1** within about a second and the decay of **1** showed first order law and could assume that (ET) took place within a radical pair and the translation diffusion of radicals did not play an important role in the present reaction. Figures 4-6 illustrate pressure dependence of first order rate constant  $k_1$  in acetonitrile, ethyl acetate and ethanol, respectively up to 100MPa. In all solvents, the thermal (ET) reaction did not show any systematic dependence of the rate constant on the solvent, temperature, or pressure. By fitting the result to a quadratic equation to calculate the values of volume of activation,  $\Delta V^\ddagger$ , were estimated to be about (zero  $\pm 1$  cm<sup>3</sup>.mol<sup>-1</sup>) at 25°C in all solvents. In contrast of the preceding thermal (ET) reaction of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide, the thermal (ET) reaction in dibenzylbipyridinium salt demonstrated dependence of pressure, temperature and solvent on the rate constants and showed solvent reorganization with volume of activation ( $\Delta V^\ddagger = -57$  cm<sup>3</sup>.mol<sup>-1</sup>) at 25°C in acetonitrile[7]. The results of the thermal (ET) reaction of 1-ethyl-4-methoxycarbonyl)pyridinium iodide suggest: 1) structure of the solvation sphere in the transition state is very close to that in initial state, and 2) the solvent reorganization involves concerted movements of a large number of solvent molecules. ET process, like other chemical reactions, can be discussed as motions on the potential energy surfaces [9], therefore, the energy profile in Fig.7 would rationalize our observation.

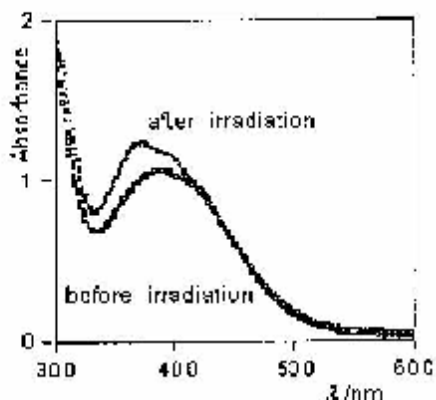


Fig. 3. Absorption spectra of 2 before and after irradiation in acetonitrile

Table 1. First-Order Rate Constants ( $k/s^{-1}$ ) for the Electron Transfer in 1 in Various solvents with standard deviation  $\pm 1.6$ .

P/MPa	MeCN			AcOEt				EtOH			
	5°C	15°C	25°C	15°C	20°C	25°C	30°C	15°C	20°C	25°C	30°C
0.1	5.8	5.6	5.2	4.5	4.2	4.5	5.2	4.2	4.9	4.2	4.9
10	5.0	4.7	5.6	5.0	4.9	3.5	4.8	4.3	5.0	4.1	5.0
20	6.5	5.9	5.6	5.3	6.7	4.4	5.3	4.0	4.5	3.8	4.2
30	4.3	5.4	4.8	5.0	4.4	4.3	4.8	4.4	5.1	4.5	4.3
40	5.6	4.5	5.6	4.6	3.8	5.0	4.0	4.3	5.5	4.5	4.8
50	5.5	5.3	4.2	4.9	3.8	4.3	3.8	4.8	5.1	4.6	4.7
60	5.8	4.3	4.2	5.0	5.5	5.6	4.8	4.6	4.6	4.7	5.1
70	5.5	5.5	4.2	4.8	4.6	5.1	4.0	4.2	4.2	4.3	6.2
80	5.0	6.6	5.5	5.7	4.6	3.9	4.6	4.6	4.6	4.7	5.2
90	5.2	3.4	4.3	5.3	4.6	5.2	4.2	5.0	5.0	4.6	5.0
100	5.1	5.1	3.5	5.7	4.8	3.9	4.8	4.7	3.9	4.7	4.8

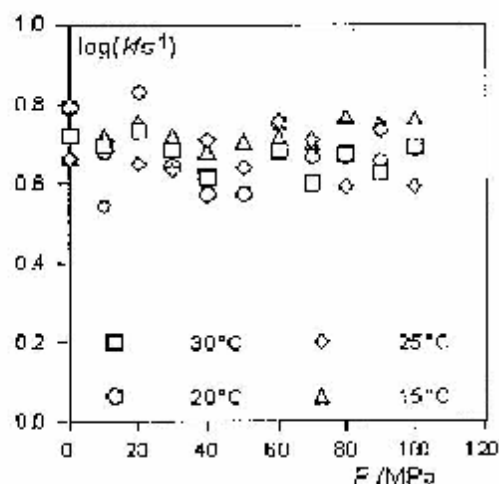


Fig. 5. Plots of  $\log k$  against pressure in acetonitrile for thermal (ET) 1.

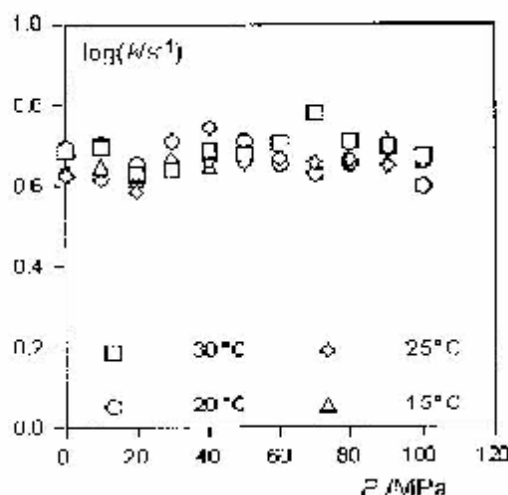


Fig. 6. Plots of  $\log k$  against pressure in ethanol for thermal (ET) 1.

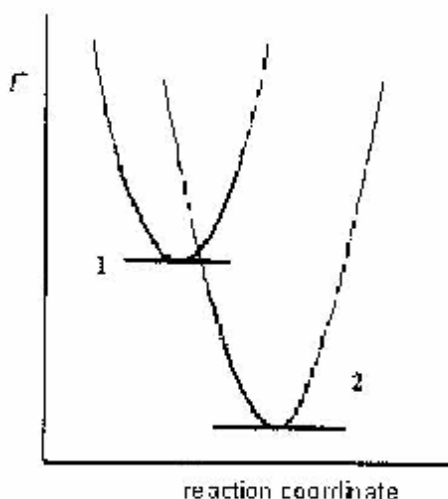


Fig. 7. A schematic illustration of a possible energy profile for the (ET) reaction in scheme 2.

### Conclusion

The thermal electron transfer (ET) process of **1** could not demonstrate any systematic dependence of the rate constant on the solvent, temperature, or pressure. These results may suggest that the structure of the solvation sphere in the transition state is very close to that in the initial state.

### Experimental Section

1-ethyl-4-(methoxycarbonyl) pyridinium iodide was purchased from Aldrich without further purification. Solvents were purified and dried according to methods described in the literature [8]. The pyridinyl radical **1** was photochemically generated *in situ* from **2** by using flash photolysis (Xe lamp) and its decay was followed spectrophotometrically at 395 nm, and the original spectrum was recovered within a second. High-pressure optical measurements are shown in Fig. 8. The optical pressure vessel is described elsewhere [10]. The inner sample cell consists of a transparent quartz spherical shape and a hypodermic syringe and they are connected together with a teflon coupler. Since the pressure is transmitted to the sample solution by means of syringe. The pressure-transmitting fluid is hexane. The online calculations of the rate constants based on Guggenheim method were performed by a computer. The finding obeyed first order law and the rate constants could be determined unequivocally. Before measurements the solutions of 1-ethyl-4-(methoxycarbonyl)pyridinium iodide (Conc.  $1.10^{-3}$ - $1.10^{-2}$ M) in all solvents were degassed by using thaw cycles with a high vacuum pump.

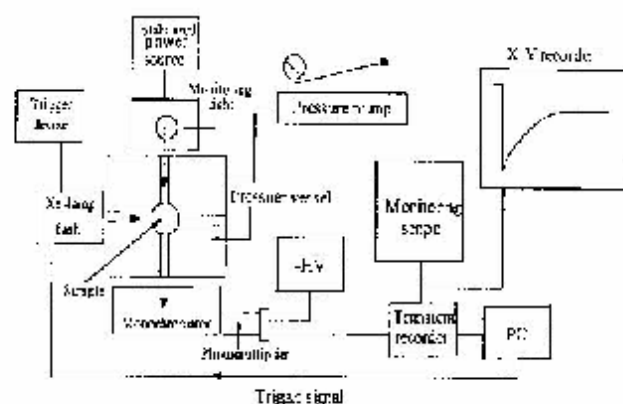


Fig. 8. Block diagram of high pressure flash photolysis equipment.

### Acknowledgments

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