Temperature, Pressure and Solvent Dependence of the Rate of Electron Transfer between Neutral species

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Abstract

I-ethyl-4-carbomethoxypryridinium iodide 2 (Kosower's salt) shows peculiar solvatochromism based on its charge-transfer absorption. As expected, we observed an increase in absorption at around 395 nm after irradiation by xenon flash and the original spectrum was recovered within a second. The thermal electron transfer (ET) process of 1 was followed and the first-order rate constants were determined in different solvents (ethanol, ethyl acetate and acetonitrile) at various pressures $\leq 100 \text{MPa}$. It could not observe 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. Keywords: Kosower's salts; solvent effect; electron transfer

Introduction

Knower's salts[1] have the structures as shown in scheme1 and formally named as salts of 1-alkyl-substituted pyridinium.

Scheme 1. (R: alkyl group, R': substituted group, X': atom or organic moieties)

The pyridinium cation has a relatively electrons affinity and therefore behaves as a good Lewis acid (electron acceptor, A). Accordingly, this species readily forms outer-sphere charge transfer (CT) complexes with Lewis base-type species possessing low ionization potential (electron donor, D)[2] (Eq.1).

Kosower defined his polarity parameter, Z (solvatochromism) as the molar of transition states energy $E_{\rm T}$, for the (CT) absorption band of the Jethyl-4-(methoxycarbonyl) pyridinium iodide [3] in different solvents according to the [Eq. (2)]:

Eq. / (kcalimol -1) = 2.859 .
$$\overline{v}$$
 / em-1 = 2 ------2

Where $\overline{\nu}$ is wave number of photons which produce electronic excitation, and the UV/V spectrum of the i-cthyl-4-(methoxyearbonyl) pyridinium iodide in acetonitrile and methyl

acetate is shown in the Fig. (1). The solvatochromism of 1-ethyl-4-(methoxycarbonyl) pyridinium iodide in different solvents could be explained by (ET) from iodide ion to the pyridinium ring[3]. The (ET) reactions had a let of attention as investigated subjects in different fields of chemistry [4] and the theory of the photochromism via (ET)[5] is shown in Fig.2. It has been widely recognized that high pressure kinetic field yields valuable information on the mechanism of liquid-phase reactions [6]. Transition state theory describes effects of high pressure on the reaction rate in term of a volume of activation, AV', related to the pressure derivative of observed rate constant, kales, by [Eq. 3];

$$\left(\frac{\partial \ln k_{\text{obs}}}{\partial P}\right)_{T} = -\frac{1}{PT} \left(\frac{\partial MS}{\partial P}\right)_{S} = -\frac{\Delta V}{RS} = --------3$$

AV defied as a difference between the partial molar volumes of reactants and activated complex, AV'' gives important information on the structural changes that occur in the reaction system as well as on the involvement of solvent molecules in the reaction. In other words, data of high pressure kinetic faithfully reflects solvational changes during the activation step, it is not surprising that quit a few measurements have been preformed on (ET) processes between metal complexes [6]. We attempted to measure pressure dependence of rate. (ET) between two neutral species. Because of the charge separation, solvation increases in such a princess and the system would be provided us information on extent of solvent reorganization in transition state.

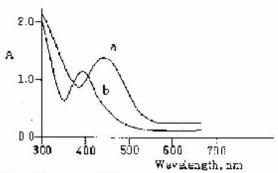


Fig. 1. The UV/V spectrum of the 1-ethyl-4-(methoxycarbonyl) pyridinium indiale in methyl acctato(a) and acetonitrile(b).

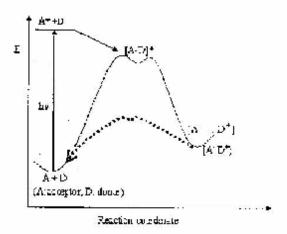


Fig. 2. The photochromism via electron transfer. Results and discussion

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

The pyridinyl radion! 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 λ_{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 1ethyl-4-(methoxycarbonyl)pyridinium indide in acetonitile before and after irradiation which explains formation of the radical 1 within about a second and the decay of I 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 1-6 illustrate pressure dependence of first order rate constant k_i in acctonitrile, 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, ΔV^2 , were estimated to be about (zero± 1 cm².mol⁻¹) at 25°C in all solvents, la contrast of the preceding thermal (E1) 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 activation $(\Delta V^a = -57 \text{ cm}^a, \text{mol}^{-1})$ at 25°G acctonitrile[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.

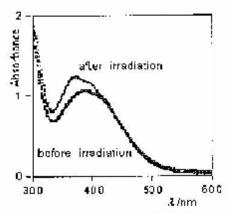


Fig.3. Absorption spectra of 2 before and after irradiation in authorityile

Table 1. First-Order Rate Constants ($k(s^*)$) for the Electron Transfer in 1 in Various solvents with standard deviation ≤ 1.6 .

P/MPa	MeCN		AcOEt				EOH			
	5°C 1	5°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	6.2 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	43	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	<u>ئ</u>	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	.11	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	4.3	5.3	4.6 5	.2	4.2	5.0	5.0	4.6	5.0
100	5.1 5	CI 3.5	5.7	4.8 3	.9	4.8	4.7	3.9	4,7	4.8

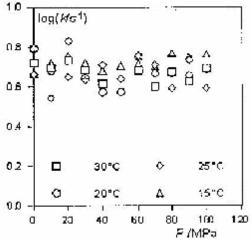


Fig. 5. Plots of log k against pressure in ethylogetale for thermal (ET) I.

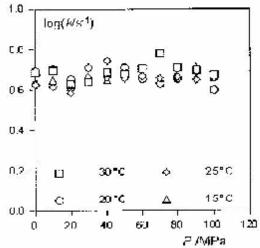


Fig. 6. Plots of log kagenest pressure in ethanol for thermal (ET) 1

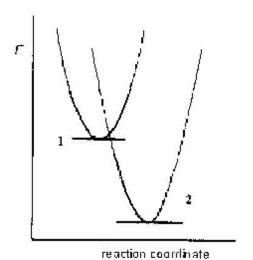


Fig. 7. A schematic illustration of a possible energy profile for the (ET) reaction in subside 2.

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

I-ethyl-4-(methoxycarbonyl) pyridinium icxlide 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. Highpressure 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 preformed by a computer. The fading 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°-1.10°M) in all solvents were degassed by using thaw cycles with a high vacuum рштр.

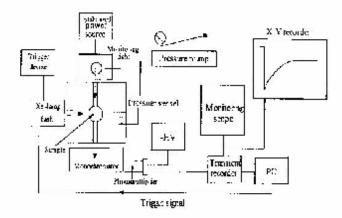


Fig. 8. Block diagram of high pressure flash photolysis equipment.

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