JOURNAL OF PHOTOCATALYSIS SCIENCE

JPS 3(1), June 2012, pp. 35-40

Research paper

# Dynamic Solvent Effects on the Photo-induced Chromism of Silver Dithizonate

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*Abstract:* The pressure dependence of the rate constant for photochromism of silver dithizonate (Ag(HDz)) was measured in highly viscous solvent, glycerol triacetate (GTA), as well as in their chemically similar nonviscous solvent, methyl acetate (AcOMe). In AcOMe, the reaction was slightly retarded upon external pressures. On the other hand, in GTA, the reaction was strongly retarded by an increase in external pressures suggesting the slow thermal fluctuation of the solvent molecules at high pressures in highly viscous systems. These retardations were concluded as a manifestation of a failure of transition state theory at high viscosities and the results were rationalized on the basis of a two-dimensional reaction-coordinate model. The dynamic results also provide evidence in support of stepwise mechanism for the photochromic reaction of metal dithizonates.

*Keywords:* photochromism; pressure effect; activation volume; dynamic solvent effect; transition state theory

# 1. Introduction

Dithizone ( $H_2Dz$ ) is a well-known chelating ligand to form photochromic complexes with various metals. The photochromism of metal dithizonates have been studied extensively by Meriwether *et al.* and it has been suggested that the photochromic reaction involves a *trans-cis* isomerization about the C = N bond and a N to N hydrogen transfer (Figure 1) [1]. This chromism has been recognized as the equilibrium between two colored forms. A solution of metal dithizonate turns from **1a** to **1b** under irradiation conditions, and **1b** 

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thermally returns to **1a** in the dark[1]. Sueishi *et al.* investigated the effects of pressure and solvents on the thermal isomerization of metal dithizonates and proposed the plausible mechanism based on these statistic effects [2-4].

The dynamic solvent effects may also play an important role to control the reaction rates in condensed phase[5]. Previously, we reported the effects of pressure on the thermal Z/E isomerizations of substituted azobenzenes, *N*-benzylideneanilines [6–8], and carbocyanines [9], and the ring closure reactions of merocyanines [10] and hexadienones [11] in their electronic ground



Figure 1: Photo and thermal isomerization of metal dithizonates

state in highly viscous conditions realized by a combination of high pressure and a viscous solvent. When the reactions were studied in common solvents such as ethanol, methyl acetate (AcOMe), and methylcyclohexane, normal pressure effects, were observed in the whole range of pressure studied (P < 800MPa). Under the transition state theory (TST) valid condition, pressure effect on the reaction could be rationalized on the basis of the partial molar volume difference between the reactant and the activation complex ( $\Delta V^{*}$ ):

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T} = -\frac{\Delta V^{*}}{RT} \tag{1}$$

However, unusual pressure-induced retardations were observed at high pressures when highly viscous solvents at higher pressures such as 2-methylpentane-2,4-diol, glycerol triacetate (GTA) and 2,4dicyclohexyl-2-methylpentane were used. The activation energies of these reactions were 50 kJ mol<sup>-1</sup> or higher and TST seemed to be applicable to these reactions in low viscosity solvents [12, 13]. Since the retardations of the reactions were observed at viscosities higher than 10 Pa s, they were taken to indicate the failure of TST caused by slow solvent fluctuations. Such viscosity dependences of rate constant were successfully interpreted in terms of two-dimensional reaction coordinate model first proposed by Agmon and Hopfield [14, 15]. In this model, the reaction system and the solvent are described by two independent coordinates, and, if the solvent thermal fluctuations are not fast enough, the solvent reorganization process itself becomes the rate-limiting step and the dynamic effect of the rate of the solvent thermal fluctuations on the reaction rate is observed. The overall process is approximated to a two-step reaction mechanism [16] and is examined by the direct comparison of the observed rate constant  $k_{obs}$  with TST rate constant  $k_{TST}$  [16–18]:

$$\frac{1}{k_{obs}} = \frac{1}{k_{TST}} + \frac{1}{k_f}$$
 (2)

where  $k_{\rm f}$  is the rate constant for the fluctuationlimited solvent rearrangement.

Previously, we firstly reported that the high-pressure experiments using high-viscous solvents demonstrated the larger dynamic solvent effects to the thermal isomerization of zinc dithizonate  $(Zn(HDz)_2)$  even at moderate viscosities [19]. In the present work, we examined the pressure effect on the thermal isomerization of metal dithizonate with monovalent metal ion, silver dithizonate (Ag(HDz), Figure 2), in highly viscous solvent at higher pressures and compared the dynamic behavior of Ag(HDz) with that of  $Zn(HDz)_2$ .

#### 2. Experimental Procedure

Ag(HDz) was prepared according to the reported method and recrystalized from chloroform: mp 222-225 °C (lit. 223 °C) [1]. Reagent grade solvents were used. A sample solution (~ 1 x 10<sup>-5</sup> mol dm<sup>-3</sup>), deoxygenated by bubbling nitrogen gas, was employed for the photochemical reaction. The photochemical conversion of thermally stable 2a to 2b was carried out by irradiation with visible light and then the thermal return was spectrophotometrically followed bv monitoring the time-dependent absorbance at  $\lambda_{max}$  of the **2a** (470 nm). The experimental



Figure 2: Photo and thermal isomerization of Ag(HDz)

details for high-pressure measurements were described elsewhere [20]. To study the nonequilibrium effects of viscous solvents at higher pressures, we used GTA. In order to measure the equilibrium pressure effects, similar experiments were carried out in nonviscous solvents, AcOMe. The return reaction obeys first-order kinetics at all conditions studied and the observed rate was reproducible within ±5%.

#### 3. Results and Discussion

Pressure dependence of the rate constant in AcOMe and GTA are plotted in Figure 3. In AcOMe, the rate constants slightly decreased with increasing pressures. The pressure dependence of  $k_{obs}$  was approximated by equation (3), where  $k_p$  and  $k_{0.1}$  are the observed rate constant at pressure *P* and 0.1 MPa, respectively [19]. The activation volume at 0 MPa was estimated from equation (4) which is obtained from equation (3) according to equation (1).

$$\ln\left(\frac{k_P}{k_{0.1}}\right) = aP^2 + bP + c \tag{3}$$

$$\Delta V_0^{\neq} = -bRT \tag{4}$$

The positive activation volume  $(\Delta V_0^{1} = +7.8 \text{ cm}^3 \text{ mol}^{-1} \text{ at } 308 \text{ K})$  is in accordance with the behavior for the isomerization of other metal dithizonates in various non-viscous



Figure 3: Pressure Dependence of the isomerization rate constant of Ag(HDz) in AcOMe and GTA

solvents (+5 ~ +7 cm<sup>3</sup> mol<sup>-1</sup>)[2-4] and is ascribed to the difference in the intrinsic volume due to the structural change. The activation parameters at 0.1 MPa are listed in Table 1. The negatively large activation entropy was observed for Zn(HDz)<sub>2</sub> and Ag(HDz), which was as large as that of Hg(HDz)<sub>2</sub> and Pd(HDz)<sub>2</sub> [2, 3], which may suggest the dipolar transition state.

Table 1Activation Parameters for the Isomerisation ofAg(HDz) and  $Zn(HDz)_2$  in AcOMe at 0.1 MPa.

	Ea/kJ mol <sup>-1</sup>	DH <sup>1</sup> /kJ mol <sup>-1</sup>	∆S'/J mol <sup>-1</sup> K <sup>-1</sup>
Ag(HDz)	61.9	59.3	-56.3
$Zn(HDz)_2$	48.4	45.9	-93.3

The rate constants measured in GTA decreased rapidly with increasing pressures from the beginning. Because of high viscosity of solvent, the photo-isomerization of **2a** to

2b could not occur in spite of long irradiation above 200 MPa. The larger pressure-induced retardations in GTA than expected from small activation volume in AcOMe are ascribed to the solvation changes and the reaction rate is limited by the rate of solvent thermal fluctuations. In other words, dynamic solvent effects were observed and TST is invalid in GTA even at ambient pressures. Thus, the  $k_{TST}$ for the valid TST could not be estimated by linear extrapolations of the lower-pressure data [6]. The results obtained in AcOMe for the valid TST were adapted instead in order to discuss the dynamic solvent effect observed in GTA. The fluctuation-limited rate constant  $k_c$  for solvent GTA were then estimated from equation (2) and the results obtained at 308 K are plotted against pressure comparing with those for  $k_{\text{TST}}$  and  $k_{\text{obs}}$  as shown in Figure 4. It was found that  $k_{\rm f}$  were close to  $k_{\rm obs}$  even at lower pressures, which suggested that the solvent reorganization process itself becomes the rate-limiting step and hence the dynamic solvent effects were observed from the beginning of the external pressures. The validity of the two-dimensional reaction coordinate model can be further tested by examining the viscosity dependence of  $k_{\mu}$ represented by equation (5). The pressure dependencies of viscosity for the solvent GTA were estimated according to equation (3). The  $k_{i}$  values were then plotted against the viscosities according to equation (5) and are shown in Figure 5.

$$k_f \propto \eta^{-p}$$
 where  $0 \le \beta \le 1$  (5)

The plots are linear and their  $\beta$  values (0.47 ~ 0.75) are smaller than 1 as expected for the viscosity dependent of the fluctuationlimited rate process [6-11]. These results thus seem to confirm the validity of twodimensional reaction coordinate model for the present reaction system. The  $\beta$  values for Ag(HDz) are almost the same as those for Zn(HDz), in GTA (0.46 ~ 0.53)[19]. These



**Figure 4:** Pressure Dependence of the Fluctuationlimited Rate Constant  $k_i$  in the isomerization of Ag(HDz) in GTA at 308 K with a comparision to  $k_{abs}$  and  $k_{TST}$ 



**Figure 5:** Viscosity Dependence of the Fluctuationlimited Rate Constant  $k_i$  in the Isomerization of Ag(HDz) in GTA at Various Temperatures. The Values in Parentheses Corresponds to the Slope for each Plot

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results indicate that the dynamic route of reactions for Ag(HDz) and Zn(HDz), is almost the same. Sueishi et al. studied the kinetic and mechanistic studies of isomerization of bismuth dithizonate (Bi(HDz)<sub>2</sub>) having three dithizone ligands and concluded that the isomerizations of each ligand occur independently and the first one dithizone ligand isomerizes in the rate determining step [4]. Meriwether et al. also assumed the photochromic process in metal dithizonates is unaffected by the presence of second or third dithizone ligand attached to the same central metal [1]. Our dynamic results provide evidence in support of stepwise mechanism for the photochromic reaction of metal dithizonates.

## 4. Conclusions

The high-pressure experiments by using the combination of highly viscous solvent and high pressures demonstrate the dynamic solvent effects on thermal isomerisation of Ag(HDz) even at moderate pressures. The results are rationalized on the basis of two-dimensional reaction coordinate model which are treated the solvent and the chemical coordinate as two independent coordinate and provide evidence in support of stepwise mechanism for the photochromic reaction of metal dithizonates.

#### Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (C) (No 18550040) from Japan Society for the Promotion of Science.

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