SHORT PAPER

J. Chem. Research (S),
2000, 193–195

Kinetic and mechanistic studies of the thermal isomerization of bismuth dithizonate[†]

Yoshimi Sueishi* and Yoko Takashima

Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushima Naka, Okayama 700-8530, Japan

The isomerization rates of bismuth dithizonate ($Bi(HD_Z)_3$) having three dithizone ligands have been measured in various kinds of solvents and at high pressures, and the reaction mechanisms in aprotic and protic solvents are discussed.

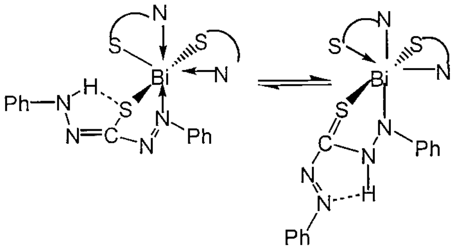
Chromism of metal dithizonate is probably an inherent property and a central metal determines the photochemical stability, rates of the thermal return reaction, and the colour of dithizonate complexes.[1,2] The chromism of bismuth dithizonate ($Bi(HD_Z)_3$) has been recognized as the equilibrium between two coloured forms.[1] A solution of $Bi(HD_Z)_3$ turns from orange (I-form) to violet (II-form) under irradiation conditions, and the orange colour returns in the dark (Scheme 1).[1] The detailed reaction mechanism of the isomerization of $Bi(HD_Z)_3$ with three ligands has not been well established yet: one possibility is the simultaneous reaction and the other is the stepwise reaction for the three ligands.

In this paper, the kinetic pressure and solvent effects on the thermal isomerization rates of $Bi(HD_Z)_3$ are presented and their mechanistic implication is discussed. Moreover, the kinetics for the $Bi(HD_Z)_3$ isomerization in protic solvent are discussed.

Experimental

Bismuth dithizonate ($Bi(HD_Z)_3$) was prepared according to the reported method,[1] and recrystallized from chloroform–hexane mixtures: mp 487–488 K (lit.[1] 492 K). Solvents of reagent grade were stored over molecular sieves and distilled before use.

The instrumentation used for kinetic measurements at low temperature and at high pressure has been described elsewhere.[3,4] A sample solution (~1×10^{-4} mol dm^{-3}), deoxygenated by bubbling nitrogen, was irradiated with a projection lamp through an interference filter (Toshiba Y-45) to produce the II-form. To follow the thermal return, the change in the absorbance was monitored with time by using a Hitachi 220A spectrophotometer. Time-dependence of the absorption spectra of $Bi(HD_Z)_3$ was followed in various kinds of solvents. The return reaction obeys first-order kinetics, and the observed rate was reproducible to within ±5 %.



I (Orange) II (Violet)

Scheme 1

Results and discussion

The isomerization in aprotic solvents: For the thermal isomerization from the II-form to the I-form, two isosbestic points in the range 350–800 nm appeared, which is similar to those of $Hg(HD_Z)_2$.[1] This indicates the absence of reaction intermediates during the thermal isomerization of $Bi(HD_Z)_3$. The rate constants for the thermal isomerization of $Bi(HD_Z)_3$ in various kinds of aprotic solvents are given in Table 1, together with the activation parameters.

As shown in Fig. 1, the activation energy was compensated for by the activation entropy. This finding suggests that a simple interaction mechanism is involved in the thermal isomerization of $Bi(HD_Z)_3$ in various solvents.[5] As may be seen in Table 1, the large loss of activation entropy is observed for the thermal isomerization of $Bi(HD_Z)_3$, which is comparable to that of $Hg(HD_Z)_2$.[4] Judging from the very small activation entropy, the transition state might be highly polar. However, systematic solvent effects are not observed, suggesting that it is not so. In a previous paper,[4] we proposed that the isomerization of dithizone ligands in $Hg(HD_Z)_2$ proceeds by a reaction mechanism involving cyclization upon activation. This accounts for the above large entropy loss upon activation.

The return rates of $Bi(HD_Z)_3$ decrease slightly with increasing external pressures. The activation volumes for the thermal isomerization were estimated from the following equations.

$$\ln k = aP + b \qquad (1)$$

$$RT\,(\partial \ln k/\partial P)_T = -\Delta V^{\ddagger} = aRT \qquad (2)$$

Table 1 Rate constants and activation parameters for the thermal isomerisation of $Bi(HD_Z)_3$ in various kinds of solvents (Probable errors in parentheses)

Solvent	10^2k (s^{-1})							*Ea*	$\Delta S^{\ddagger}_{293\ K}$
	293 K	283	273	263	253	243	233	(kJ mol^{-1})	(J K^{-1} mol^{-1})
Toluene	33.5	14.9	8.75	3.69	1.73	0.974	0.526	39.6(0.2)	−127(2)
Ethylacetate		11.1	6.46	2.83	1.48	0.883		37.3(0.1)	−139(3)
THF	6.15	4.08	1.38	0.449	0.0893	0.0410		59.3(0.2)	−64.7(1.6)
Chlorobenzene		8.25	4.58	2.11	0.775	0.341	0.153	45.1(0.1)	−114(3)
Acetone				17.6	6.05	2.55	1.52	41.6(0.1)	−111(3)

---

* To receive any correspondence. E-mail: ysueishi@cc.okayama-u.ac.jp

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

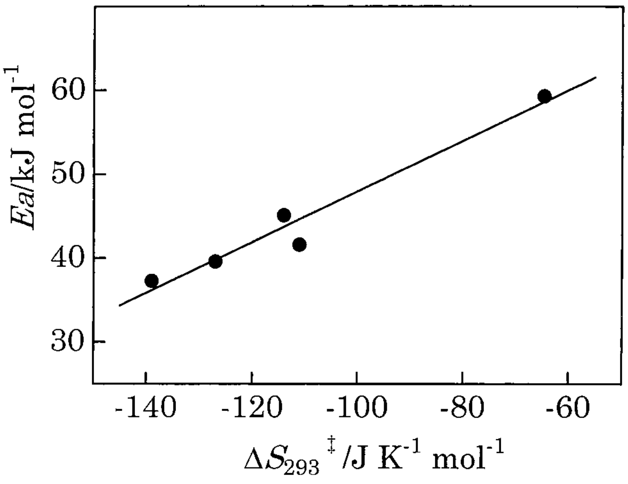
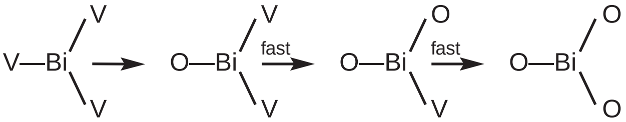


Fig. 1 Relationship between *Ea* and $\Delta S_{293}^{\ddagger}$ for the thermal isomerization of $Bi(HD_Z)_3$.

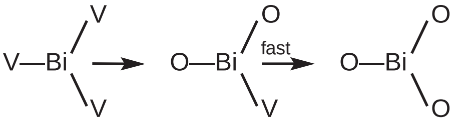
The estimated activation volumes take small positive values (~ 5.5 cm^3 mol^{-1}) regardless of the solvent polarity (Table 2). This indicates that the positive activation volume corresponds to the change in the intrinsic volume accompanying the thermal isomerization of $Bi(HD_Z)_3$. Moreover, the activation volumes for the isomerization of $Bi(HD_Z)_3$ having three ligands are comparable to those observed for silver monodithizonate ($Ag(HD_Z)$: $\Delta V^{\ddagger}$ = ca 7 cm^3 mol^{-1}).[4]

From kinetic studies of some metal dithizonate complexes, Geosling *et al.*[6] suggested that a dithizonate complex with a different conformation is an unstable intermediate. For the thermal isomerization of $Bi(HD_Z)_3$, the following possible reaction mechanisms have been considered: One is a stepwise reaction and the other is a simultaneous reaction of three ligands.

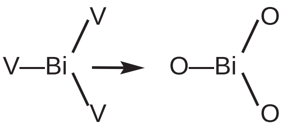
Mechanism (1): The ligand isomerizes consecutively.



Mechanism (2): The two ligands isomerize simultaneously in the rate-determining step.



Mechanism (3): The three ligands isomerize simultaneously in the rate-determining step.



Here, O and V represent the configuration of the ligand in the I and II forms, respectively. Since the thermal isomerizations for the above three reaction routes obey first-order kinetics, the reaction routes are spectroscopically and kinetically indistinguishable. As suggested by Whalley,[7] the volume is easier to understand on an elementary level than thermodynamic quantities since the nuclear positions tell one a good deal about the volume. The activation volumes for the above three reaction routes can be expressed as: (1) $\Delta V^{\ddagger} = \Delta V_{V\to O}^{\ddagger}$, (2) $\Delta V^{\ddagger} = 2\Delta V_{V\to O}^{\ddagger}$, and (3) $\Delta V^{\ddagger} = 3\Delta V_{V\to O}^{\ddagger}$, where $\Delta V_{V\to O}^{\ddagger}$ represents the activation volume arising from the isomerization of one dithizone molecule. As discussed above, the pressure effects on the $Bi(HD_Z)_3$ isomerization suggest that one dithizone ligand isomerizes in the rate-determining step. Accordingly, the above findings argue in favour of the stepwise mechanism (mechanism (1)).

The isomerization in protic solvent: Figure 2 shows the return rates (k_{obs}) in 1-butanol-toluene mixtures: k_0=1.73×10^{-2} s^{-1} in toluene at 253 K. The rate constant of the thermal isomerization increases remarkably with increasing the concentration of 1-butanol. Previously, we have pointed out that alcohols participate in the reaction as hydrogen transfer agents within a hydrogen-bonded aggregate of mercury dithizonate ($Hg(HD_Z)_2$) and alcohols, resulting in the accelerated effects.[4] In analogy with $Hg(HD_Z)_2$ in alcoholic solution, the dithizone ligand in $Bi(HD_Z)_3$ forms hydrogen bonds with alcohols. Therefore, the apparent isomerization rate (k_{obs}) of $Bi(HD_Z)_3$ in alcoholic solution can be expressed as follows.

$$k_{obs} = \frac{[Bi(HD_Z)_3(II)]}{[Bi(HD_Z)_3(II)]_{Total}} k_o + \frac{[Bi(HD_Z)_3(II)\ldots ROH]}{[Bi(HD_Z)_3(II)]_{Total}} k_H \qquad (3)$$

where, k_0 and k_H represent the rate constants for the isomerization of free $Bi(HD_Z)_3(II)$ and hydrogen-bonded $Bi(HD_Z)_3(II)$ of the conformation II, respectively. $Bi(HD_Z)_3(II)\ldots ROH$ denotes the complex between $Bi(HD_Z)_3(II)$ and alcohols. $[Bi(HD_Z)_3(II)]_{Total} = [Bi(HD_Z)_3(II)]+[Bi(HD_Z)_3(II)\ldots ROH]$. The equilibrium constant *K* between $Bi(HD_Z)_3(II)$ and alcohols can be given by

$$Bi(HD_Z)_3(II) + ROH \rightleftharpoons Bi(HD_Z)_3(II)\ldots ROH$$

$$K = \frac{[Bi(HD_Z)^3(II)\ldots ROH]}{[Bi(HD_Z)_3(II)][ROH]} = \frac{[Bi(HD_Z)_3(II)\ldots ROH]}{([Bi(HD_Z)_3(II)]_{Total} - [Bi(HD_Z)_3(II)\ldots ROH][ROH]} \qquad (4)$$

Table 2 Rate constants and activation volumes for the thermal isomerization of $Bi(HD_Z)_3$ at 283K (probable errors in parentheses)

Solvent		10^2k (s^{-1})					$\Delta V^{\ddagger}$
	P/kgf cm^{-2}	1	300	600	900	1200	(cm^3 mol^{-1})
Toluene		14.9	13.9	13.1	12.0	11.4	5.4 (0.6)
Chlorobenzene		8.25	7.58	7.08	6.47	6.13	5.8 (0.5)

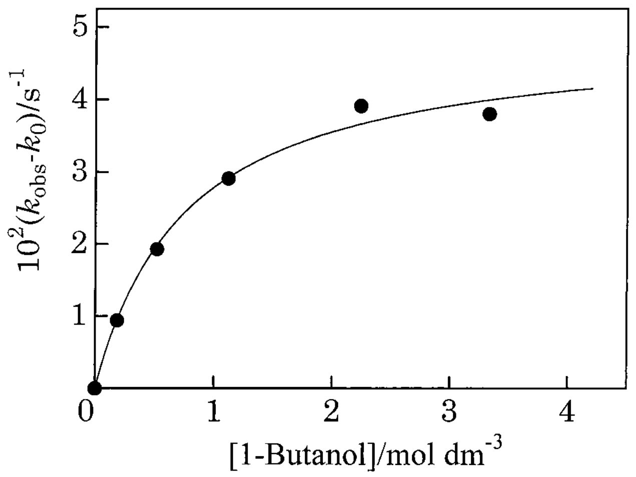


Fig. 2 The plots of $k_{obs}–k_0$ against the concentration of 1-butanol for the Bi(HD$_Z$)$_3$ isomerization at 253 K. Solid line represents $k_{obs}–k_0$ values calculated from equation 5.

Using equations 3 and 4, equation 3 can be rewritten as

$$k_{obs}–k_0 = \frac{K(k_H–k_0)[\mathrm{ROH}]}{1+K[\mathrm{ROH}]} \qquad (5)$$

From fitting the experimental data (Fig. 1) to eqn 5, $k_H–k_0$ and K values can be determined. From the fitting results and k_0 values (=1.73×10^{-2} s^{-1}), we have estimated to be K =1.33 mol^{-1} dm^3 and k_H=6.61×10^{-2} s^{-1} for the Bi(HD$_Z$)$_3$ isomerization in toluene-1-butanol at 253 K. Using the estimated parameters and eqn 5, the return rates of Bi(HD$_Z$)$_3$ were calculated. As can be shown by the solid line in Fig. 2, the experimental data can be reproduced well by taking into account the accelerated effect due to hydrogen bonding.

The thermal isomerization of Bi(HD$_Z$)$_3$ is in harmony with the stepwise reaction mechanism, and the kinetics for the thermal isomerization of Bi(HD$_Z$)$_3$ in alcoholic solution has been established.

Received 26 December 1999; accepted 22 March 2000
Paper 99/60

References

1 L. S. Meriwether, E. C. Breiptner, and C. L. Sloan, *J. Am. Chem. Soc.*, 1965, **87**, 4441.
2 L. S. Meriwether, E. C. Breiptner, and N. B. Colthup, *J. Am. Chem. Soc.*, 1965, **87**, 4448.
3 Y. Sueishi and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 2598.
4 Y. Sueishi, T. Mukai, K. Matsumoto, S. Yamamoto, and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 3153 .
5 J. E. Leffler, *J. Org. Chem.*, 1966, **31**, 533.
6 C. Geosling, A. W. Adamson, and A. R. Gutierrez, *Inorg. Chim. Acta*, 1978, **29**, 279.
7 E. Whalley, *Advances in Physical Organic Chemistry*, , p.93 V. Gold, (ed.) Academic Press, London, (1964).