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Effects of Pressure and Solvent on the Thermal Isomerization of Mercury and Silver Dithizonates

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The thermal isomerizations of mercury and silver dithizonates ($Hg(HD_z)_2$ and $Ag(HD_z)$) were followed spectrophotometrically at high pressures and in various solvents. From the pressure dependence of the rate, the activation volumes for the isomerization of $Hg(HD_z)_2$ in aprotic solvents were estimated to be about 6 $cm^3\,mol^{-1}$, and were compared with those for $Ag(HD_z)$. The observed positive values of the activation volumes have been explained in terms of the increase in the intrinsic volume accompanying the isomerization of dithizone. Based on these results, a possible structure of the transition state for the thermal isomerization of $Hg(HD_z)_2$ in aprotic solvents was proposed. Moreover, we have followed the thermal isomerization of $Hg(HD_z)_2$ in various types of alcohols at low temperatures. The results in alcohols are discussed in terms of solvent hydrogen-bonding ability, and a reaction mechanism is proposed.

It is well-known that dithizone (phenyldiazenecarbothioic acid 2-phenylhydrazide, H_2D_z) forms photo and thermochromic coordination compounds with various kinds of metals. The most important study is that of Meriwether et al.,1) who prepared 24 kinds of metal dithizonates and examined their photochromic behavior in solution. For example, a solution of mercury dithizonate ($Hg(HD_z)_2$) undergoes color changes from orange (O-form) to blue (B-form) upon irradiation with visible light; the orange color returns in the dark. From kinetic and infrared studies, Meriwether et al.1,2) suggested that the photochromic reaction of $Hg(HD_z)_2$ involves a trans-cis isomerization about the C=N bond and a N–to–N hydrogen transfer, as shown in Scheme 1. Later, the detailed reaction mechanism of the photochromic behavior of $Hg(HD_z)_2$ was examined by Mitzner et al.3) and Geosling et al.4) However, mechanistic studies concerning the thermal isomerization (B-form→O-form) do not seem to have been carried out.

In this work we used $Hg(HD_z)_2$ and silver dithizonate ($Ag(HD_z)$), which have slow return rates and allow measurements of the kinetics with our high-pressure apparatus. To obtain further information concerning the structure of the transition state for the thermal isomerization of metal dithizonates in aprotic solvents, we examined the effects of pressure and solvents on the thermal isomerization rate. Meriwether et al.1) added a few drops of ethanol to a toluene solution and found remarkably accelerating effects on the thermal isomerization rates. We have thus been interested in the difference in the reaction mechanisms in alcohols and aprotic solvents, and have examined the isomerization of $Hg(HD_z)_2$ in some alcohols.

Experimental

Mercury and silver dithizonates were prepared according to a reported method,1) and recrystallized from benzene–ethanol and chloroform–hexane, respectively: $Hg(HD_z)_2$, mp 232.5—233.5 °C (lit,1) 228—229 °C); $Ag(HD_z)$, mp 225—226 °C (lit,1) 223 °C). Solvents of reagent grade were stored over molecular sieves and distilled before use.

The instrumentation used for kinetic measurements under high pressures has been described elsewhere.5) A sample solution (about 10^{-4} $mol\,dm^{-3}$) deoxygenated by bubbling nitrogen gas was irradiated with a projection lamp through an interference filter (Toshiba Y-45) to produce the B-form. The photo and thermal isomerizations were quantitatively reproducible. Thermal isomerization from the B-form to the O-form was followed by monitoring the change in the absorption spectra using a Hitachi 139 spectrophotometer.

For kinetic measurements at low temperatures, a handmade cryostat with optical windows was used. The temperature in the cryostat was controlled by a variable-temperature regulator to within ±0.5 °C. After irradiation, the change in the absorbance was followed with a Hitachi 220A spectrophotometer.

Results

The time-dependent spectral change for the thermal return (B→O) of $Hg(HD_z)_2$ was examined. The absorption curves have an isosbestic point at 540 nm, indicating the presence of only two components (the O- and B-forms).

The time dependence of the absorption spectra of $Hg(HD_z)_2$ and $Ag(HD_z)$ was followed in various solvents. First-order kinetics hold, and the observed rate constants agreed to within ±5%. The rate constants for the isomerization of $Hg(HD_z)_2$ at several temperatures and the activation parameters estimated from them are given in Table 1.

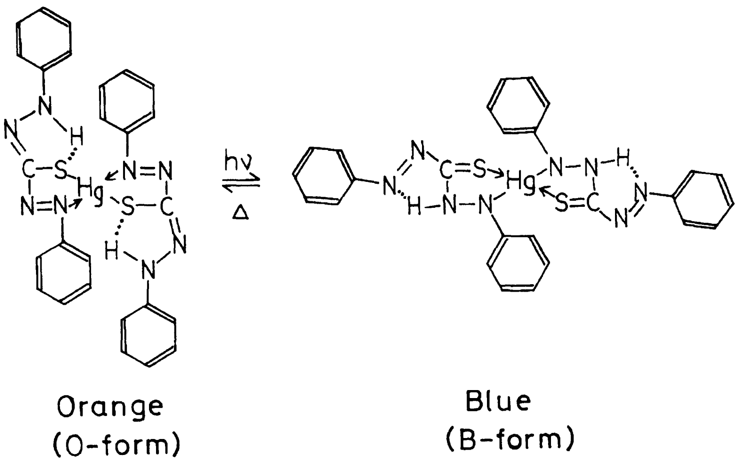
The pressure dependence of the rate constant was approximated by

$$\ln k = ap + b. \tag{1}$$

The activation volume ($\Delta V^{\ddagger}$) at atmospheric pressure was estimated according to

$$\Delta V^{\ddagger} = -RT(\partial \ln k/\partial p)_T = -aRT. \tag{2}$$

The rate constants at various pressures and the activation volumes for the thermal isomerizations of $Hg(HD_z)_2$ and $Ag(HD_z)$ are given in Tables 2 and 3.



Scheme 1.

Table 1. Rate Constants and Activation Parameters for the Thermal Isomerization of $Hg(HD_z)_2$ in Aprotic Solvents (Probable Errors in Parentheses)

Solvent	$10^2\ k^{a)}/s^{-1}$					E_a	$\Delta S_{293}^\ddagger$
	293 K	298	303	308	313	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$
Nitrobenzene	2.04	2.61		4.51	5.44	38.3(0.9)	−155(3)
1,2-Dichloroethane	1.79	2.43	3.11	4.10	5.46	42.0(0.5)	−143(2)
Chlorobenzene	2.19	3.33	4.88	6.67	8.95	53.6(1.2)	−102(4)
Toluene	2.17	3.30	4.72	6.48	8.47	52.0(1.3)	−107(4)
Methylcyclohexane	1.89	2.46	2.84	3.19	3.88	26.0(1.3)	−197(4)

a) Precision within 5%.

Table 2. Rate Constants and Activation Volumes for the Thermal Isomerization of $Hg(HD_z)_2$ in Aprotic Solvents at 293 K (Probable Errors in Parentheses)

Solvent	$10^2\ k^{a)}/s^{-1}$						$\Delta V^\ddagger$
$p/kgf\,cm^{-2\ b)}$	1	100	300	600	900	1200	$cm^3\,mol^{-1}$
Nitrobenzene	2.04		2.08	1.81	$1.76^{c)}$		5.2(1.2)
1,2-Dichloroethane	1.79		1.69	1.57	1.46	1.36	5.7(1.0)
Chlorobenzene	2.19		2.03	1.89	1.80	1.71	$6.6(0.4)^{d)}$
Carbon tetrachloride	1.27	1.22	1.17	1.08	0.970		7.0(0.2)
Toluene	2.17		2.01	1.84	1.68	1.54	7.0(0.1)

a) Precision within 5%. b) 1 $kgf\,cm^{-2}=0.981\times10^5$ Pa. c) at 800 $kgf\,cm^{-2}$.
d) A parabolic equation ($\ln k = ap^2+bp+c$) was used to fit the data.

Table 3. Rate Constants and Activation Volumes for the Thermal Isomerization of $Ag(HD_z)$ at 293 K (Probable Errors in Parentheses)

Solvent	$10^2\ k^{a)}/s^{-1}$						$\Delta V^\ddagger$
$p/kgf\,cm^{-2}$	1	300	600	800	900	1200	$cm^3\,mol^{-1}$
Nitrobenzene	1.98	1.81	1.67	1.61			6.4(0.3)
1,2-Dichloroethane	1.42	1.25	1.18		1.07	0.940	7.9(0.4)
Dichloromethane	2.13	1.94	1.84		1.70		5.9(0.3)

a) Precision within 5%.

The rate constants for the isomerization of $Hg(HD_z)_2$ in alcohols at low temperatures are given in Table 4, together with the activation parameters. The thermal isomerization rate in alcohols at room temperature was so fast that the rate could not be followed using our high-pressure apparatus.

Discussion

Thermal Isomerization of $Hg(HD_z)_2$ in Aprotic Solvents. We examined the temperature dependence of the thermal isomerization (B→O) of $Hg(HD_z)_2$ in various aprotic solvents; $\Delta S^\ddagger$ was found to be −100—−200 $J\,K^{-1}\,mol^{-1}$ (Table 1). Mitzner et al.$^{3)}$ also reported similar results. Judging from the large entropy losses, they concluded that the thermal isomerization of $Hg(HD_z)_2$ starts from a nonpolar ground state are proceeds via a dipolar transition state. If the reaction mechanism proposed by Mitzner et al.$^{3)}$ is ac-

Table 4. Rate Constants and Activation Parameters for the Thermal Isomerization of $Hg(HD_z)_2$ in Alcohols (Probable Errors in Parentheses)

Solvent	$10^2\ k^{a)}/s^{-1}$									E_a	$\Delta S_{293}{}^{\ddagger}$
	293 K	283	273	263	253	243	233	223	213	$kJ\,mol^{-1}$	$J\,K^{-1}\,mol^{-1}$
Ethanol	(306)[b)]			93.6	59.2	37.4	20.5	11.6	6.34	25.3(0.2)	−157(1)
1-Propanol			21.6	10.2	4.34	1.72	0.642	0.238	0.0824	45.3(0.3)	−100(1)
1-Butanol	38.0	9.43	6.34	2.07	0.852	0.319				54.5(2.2)	−77.4(8.1)
1-Pentanol	20.6	8.03	3.14	1.03	0.295	0.121	0.0317	0.00763		61.0(0.6)	−58.6(2.2)
2-Propanol	18.0	7.67	2.97	1.12	0.386	0.147	0.0801	0.0464		57.5(0.6)[c)]	−71.4(2.3)[c)]
2-Butanol	18.6	7.11	2.66	1.02	0.315	0.0981	0.0308			60.8(0.5)	−60.3(1.7)
2-Methyl-2-butanol	11.6	6.04	3.25	1.17						48.2(2.2)	−106(7.9)
3-Methyl-3-pentanol	4.34	2.62	1.55	0.910	0.434					35.0(0.6)	−160(3)

a) Precision within 5%. b) The value were calculated by using the Arrhenius equation. c) The activation parameters were calculated using the data obtained above 243 K since the Arrehenius plot showed a upward deviation at low temperatures.

cepted, the solvent polarity dependences of the rate constants and the activation volumes for thermal isomerization (B→O) may be predicted by an electrostatic model. Based on the Kirkwood treatment,[6)] the dielectric influence of solvents on the rate constants is given by

$$\begin{aligned}\ln k &= \ln k_0 + (N/RT)[(\mu_{\ddagger}{}^2/r_{\ddagger}{}^3) - (\mu_B{}^2/r_B{}^3)][(\varepsilon-1)/(2\varepsilon+1)]\\ &= \ln k_0 + (N/RT)[\Delta(\mu^2/r^3)][(\varepsilon-1)/(2\varepsilon+1)]. \qquad (3)\end{aligned}$$

Here, μ and r are the dipole moments and radii, respectively, and subscripts ‡ and B refer to the transition state and the B-form; k_0 is the rate constant in a hypothetical medium of $\varepsilon=1$, and the other symbols have their usual meanings. The second term represents the contribution from the electrostatic solute–solvent interaction. On the other hand, the activation volume is conventionally divided into two terms: the intrinsic terms ($\Delta V_{\rm int}{}^{\ddagger}$) and solvation term ($\Delta V_{\rm sol}{}^{\ddagger}$),

$$\Delta V^{\ddagger} = \Delta V_{\rm int}{}^{\ddagger} + \Delta V_{\rm sol}{}^{\ddagger}. \qquad (4)$$

From Eqs. 2, 3, and 4, $\Delta V_{\rm sol}{}^{\ddagger}$ can be given by

$$\Delta V_{\rm sol}{}^{\ddagger} = -N[\Delta(\mu^2/r^3)]q_p. \qquad (5)$$

Here, $q_p=[3/(2\varepsilon+1)^2](\partial\varepsilon/\partial p)_T$. Using available ε–p data, the q_p values can be estimated.[7)] According to a mechanism reported by Mitzner et al.,[3)] the $\Delta(\mu^2/r^3)$-term of Eq. 3 is expected to be positive. Therefore, a plot of ln k against $(\varepsilon-1)/(2\varepsilon+1)$ should give a linear relationship with a positive slope, and the activation volume is expected to be negative, decreasing linearly with increase in the q_p-values, as has been exemplified by the Menshutkin reaction.[8)] However, when the kinetic data in Table 2 are inspected, systematic solvent effects on the rate of the thermal isomerization are not observed. The rate constants decrease slightly with increasing external pressure, and the estimated activation volumes are about 6 $cm^3\,mol^{-1}$, independent of the solvent polarity. As can be seen in Fig. 1, our results contradict the proposals reported by Mitzner et al.[3)] The above findings suggest that a substantial polarity change upon activation does not occur, and that the observed activation volumes may be ascribed to a change in the intrinsic volume due to a structural change (Eqs. 4 and 5).

For the thermal isomerization of $Hg(HD_z)_2$, the following alternative reaction schemes have been proposed:[4)] One is a stepwise reaction (a), and the other is a simultaneous reaction of the two ligands(b):

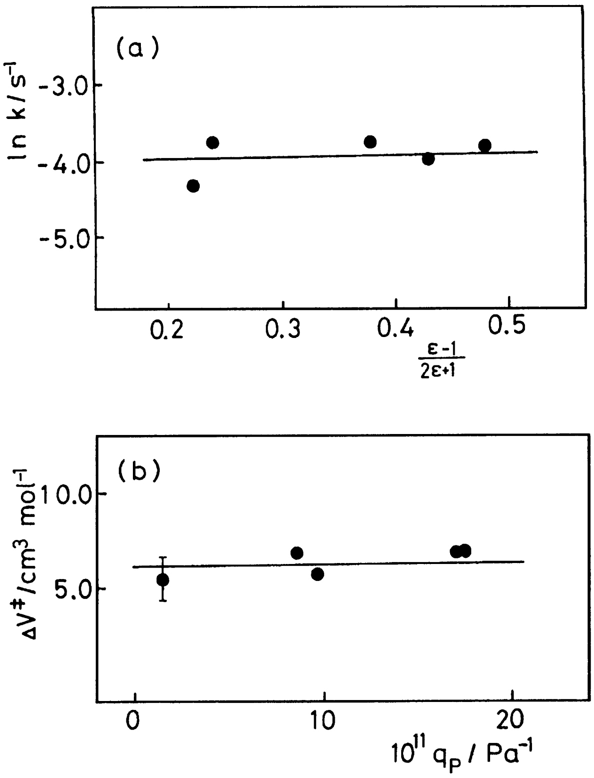


Fig. 1. (a) Relationship between ln k and $(\varepsilon-1)/(2\varepsilon+1)$ for the thermal isomerization of $Hg(HD_z)_2$ in aprotic solvents at 293 K. (b) Relationship between $\Delta V^{\ddagger}$ and q_p-value.

$$\text{(a) B–M–B} \longrightarrow \text{O–M–B} \xrightarrow{\text{fast}} \text{O–M–O}$$

and

$$\text{(b) B–M–B} \longrightarrow \text{O–M–O.}$$

Here, B and O represent the configurations of the ligand in the B- and O-forms, respectively. Geosling et al.[4] tentatively concluded that both ligands of $Hg(HD_z)_2$ isomerize simultaneously. However, since the thermal isomerizations for the above two reaction routes (a and b) obey first-order kinetics, the reaction routes are spectroscopically and kinetically indistinguishable from each other.

The concept of volume is more straightforward than that of entropy, and the activation volume gives useful information concerning the reaction mechanism. The activation volumes for the above two reaction routes can be expressed as follows:

$$\text{(a)}\quad \Delta V^{\ddagger} = \Delta V_{\mathrm{B}\rightarrow\mathrm{O}}^{\ddagger}$$

and

$$\text{(b)}\quad \Delta V^{\ddagger} = 2\Delta V_{\mathrm{B}\rightarrow\mathrm{O}}^{\ddagger},$$

where $\Delta V_{\mathrm{B}\rightarrow\mathrm{O}}^{\ddagger}$ represents the activation volume arising from isomerization of one dithizone molecule. Therefore, in order to discuss the reaction mechanism, it is instructive to compare the pressure effect on the isomerization of mercury bisdithizonate with that of silver monodithizonate.

Isomerization of $Ag(HD_z)$. It is recognized that $Ag(HD_z)$ undergoes a color change (yellow⇌violet), which is induced by visible light; this color change is reversed in the dark.[1] $Ag(HD_z)$ shows a similar behavior to that of bisdithizonate of mercury, and a common mechanism has been proposed.[1,2] In fact, it was found that the thermal return obeys first-order kinetics; the rate constants in a few solvents are given in Table 3. The return rates are independent of the solvent polarity, and are slightly retarded as the external pressure increases. The estimated activation volumes take positive values (=about 7 $cm^3\,mol^{-1}$) regardless of the solvent polarity. These findings indicate that the activation volume observed for $Ag(HD_z)$ corresponds to the change in the intrinsic volume accompanying the isomerization of one dithizone molecule.

Reaction Mechanism. As suggested above, the activation volumes for the thermal isomerization of $Hg(HD_z)_2$ are comparable to those of $Ag(HD_z)$. We have thus concluded that a stepwise mechanism is favorable for $Hg(HD_z)_2$. As a transition state for the reaction in which the solvent effects are not observed and the large entropy losses occur upon activation, the following cyclic structure is tentatively proposed (Scheme 2). If the above cyclic transition state is assumed for the reaction, a negative activation entropy is expected. In this connection, for the thermal isomerizations of triphenylformazans involving cyclization upon activation, we have reported the activation entropies to be −150—−300 $J\,K^{-1}\,mol^{-1}$.[5] Though the loss of entropy for the isomerization of $Hg(HD_z)_2$ is not as large as that for triphenylformazans, this supports the idea presented above. The observed positive activation volumes may be related to an increment in the volume due to an expansion of the ring.

Thermal Isomerization of $Hg(HD_z)_2$ in Alcohols. Since the isomerization rate in alcohols is very fast at room temperature, we examined the return rates at low temperatures. The obtained rate constants are given in Table 4. Using the activation parameters and the Arrhenius equation, the rate constant in ethanol at 293 K was calculated to be 3.06 s^{-1}, which is remarkably large compared with those in aprotic solvents at 293 K. As a whole, the rate constants in alcohols decrease in the order primary>secondary>tertiary. This may be due to an increase in the steric hindrance around the hydroxy group. Hinckley et al.[9] have also obtained a similar trend for the equilibrium of Rhodamine B in alcohols. Rhodamine B exists as an equilibrium mixture of zwitterion (Z) and lactone (L) forms. The position of the equilibrium depends on the ability of the solvent to stabilize the Z-form; the equilibrium constant (=[Z]/[L]) in alcohols decreases in the order primary > secondary > tertiary. Hinckley et al.[9] have discussed the factors which affect the equilibrium position. They have suggested that the ability of the solvent hydroxy group to form hydrogen bonds to the Z-form is reduced in secondary and tertiary alcohols, and is an important factor.

In various kinds of primary alcohols there is no large difference in the steric hindrance about the hydroxy group. Figure 2 shows Kirkwood plots for the isomerization of $Hg(HD_z)_2$ in primary alcohols. Linear plots with a positive slope were obtained; this is different from those in aprotic solvents. The solvent effect on the isomerization rate in primary alcohols can be explained in terms of an electrostatic model, suggesting that the transition state is more polar than that of the B-form.

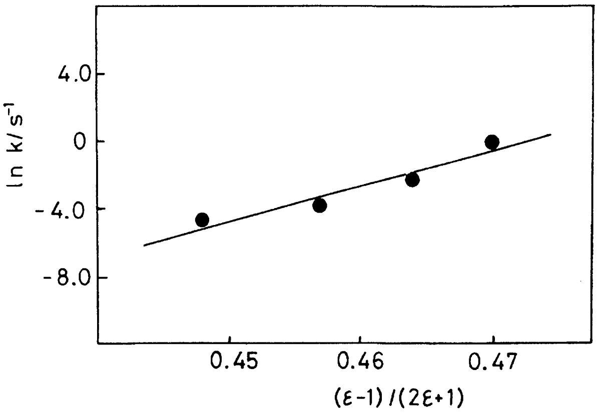
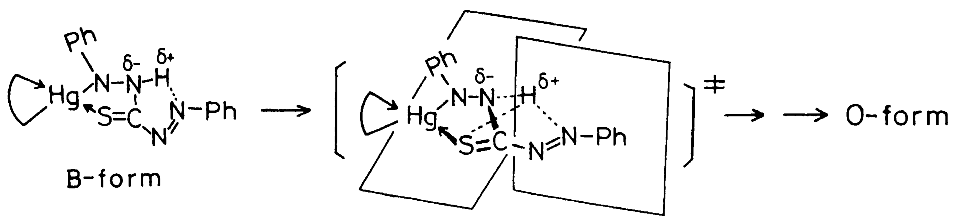
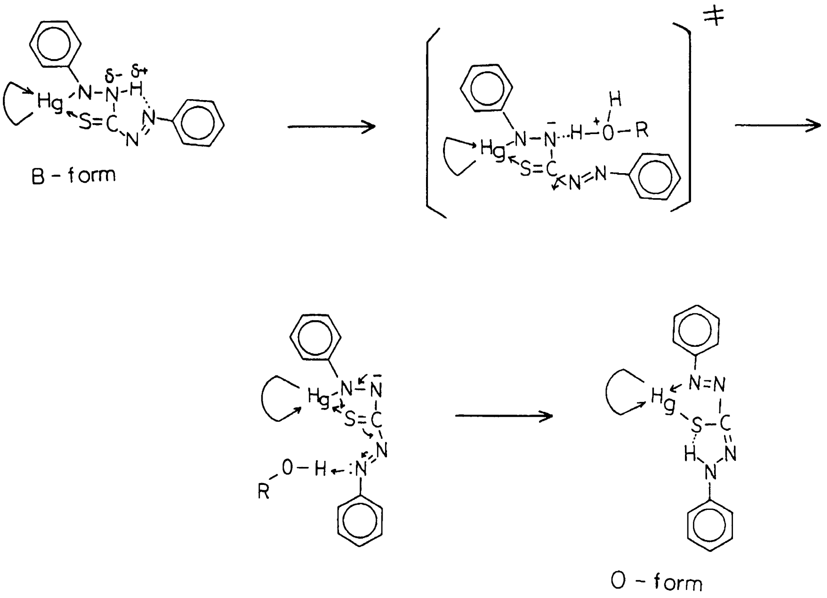


Fig. 2. Relationship between $\ln k$ and $(\varepsilon-1)/(2\varepsilon+1)$ for the thermal isomerization of $Hg(HD_z)_2$ in primary alcohols at 263 K.



Scheme 2.



Scheme 3.

In order to discuss the reaction mechanism in alcohols, we examined the relationships between the activation energy and entropy (Fig. 3). From the figure, the following points can be seen: (1) The plots for the isomerizations in primary alcohols and aprotic solvents give two straight lines. (2) With an increase in the steric hindrance around the hydroxy group, the points for secondary and tertiary alcohols are observed to approach a straight line for isomerization in aprotic solvents. According to Leffler,[10] a linear activation energy–entropy relation suggests that a simple interaction mechanism is involved in the reaction. For the shift of the activation energy–entropy plots (Fig. 3), we have observed a similar behavior in the isomerization of *N*,*N*′-diacylindigos.[11] We have explained that the shift is not due to a mechanism change, but, rather, to a free-energy change for the process of thermal isomerization. In the present case, as has been reported by Meriwether et al.,[2] the effect of added water and ethanol on the return rate suggests that hydrogen-bond formation is an important factor in determining the isomerization rate. On the other hand, the N–H of the $Hg(HD_z)_2$ complex is easily deuterated by shaking a benzene solution with D_2O.[2] Taking into account these results, a plausible reaction mechanism for isomerization in alcohols would be as follows (Scheme 3). Alcohols may participate in the reaction as hydrogen transfer agents within a hydrogen-bonded aggregate of the complex and alcohols. The rate constants and the activation parameters in 3-methyl-3-pentanol are compared with those in aprotic solvents. In tertiary alcohols, the steric hindrance around the hydroxy group will become more severe, which is responsible for reducing the ability to form hydrogen bonds.[9] In the present study, the steric hindrance around the hydroxy group of 3-methyl-3-pentanol is the most se-

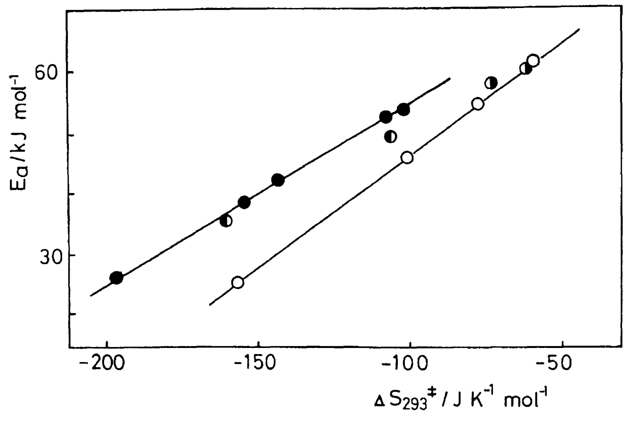


Fig. 3. Relationship between E_a and $\Delta S_{293}{}^{\ddagger}$ for the thermal isomerization of $Hg(HD_z)_2$; (○) in primary alcohols, (◑) in secondary alcohols, (◐) in tertiary alcohols, (●) in aprotic solvents.

vere, and thus, the thermal isomerization may proceed by a similar reaction mechanism as that for isomerization in aprotic solvents. This idea is supported by the activation energy–entropy relationship.

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