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Pressure Effect on the Intramolecular Racemization of Tris(acetylacetonato)germanium(IV) Perchlorate in Organic Solvents

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The volume of activation ($\Delta V^{\ddagger}$) for the intramolecular racemization of tris(acetylacetonato)germanium(IV) perchlorate in 1,1,2,2-tetrachloroethane, propylene carbonate, acetonitrile, and dimethylformamide ranges from +15 to −4 cm^3 mol^{-1} in the pressure region from 0.1 to 284 MPa at 50 and 60 °C. It does not depend on the pressure and temperature. The values are best correlated with the donor number of the solvents and accounted for by the intramolecular mechanism involving an intermediate containing one unidentate acetylacetonate. The $\Delta V^{\ddagger}$ seems to reflect direct participation of the solvent molecule in the transition state rather than the change in the second-sphere coordination around the complex cation. The size of solvent molecules seems to play a less important but appreciable role in determining the $\Delta V^{\ddagger}$ values than the basicity does.

Introduction

The effect of pressure on the rate of various reactions of coordination compounds in the liquid phase has recently attracted growing interest.[1-3] However, the given interpretation of the volume of activation is mostly qualitative. The importance of outer-sphere coordination around complex species has been pointed out. However, the reported data are limited and mostly those in aqueous solution.[4] Racemization of coordination compounds does not involve the change in $\Delta G°$ and permits a detailed discussion on reaction mechanism. The volumes of activation accompanied by the racemization of several tris(bidentate)-type complexes have been measured, but the data represent only those in aqueous solution.[5-7] We found that tris(acetylacetonato)germanium(IV) perchlorate $[Ge(acac)_3]ClO_4$ racemizes at measurable rates at 40–60 °C in various organic solvents and discussed the mechanism in detail.[8] Hence this system suits elucidating how the solvent effect is reflected in $\Delta V^{\ddagger}$ values. We have measured the racemization rate in various organic solvents at 50 and 60 °C under 0.1 to 284 MPa and interpreted the results with reference to the role of solvent molecules.

Experimental Section

Materials. $(-)_{589}$-$[Ge(acac)_3]ClO_4$ was prepared as previously reported,[8] and the purity was examined by elemental analysis, NMR, IR, and UV absorption, and CD spectra. Guaranteed grade 1,1,2,2-tetrachloroethane (TCE) and acetonitrile (AN) were purified by the same method as given in the literature.[8] Guaranteed grade *N*,*N*-dimethylformamide (DMF) and 1,2-propylene carbonate (PC) were dried with the molecular sieve 4A zeolite and fractionally distilled under a reduced pressure.

Measurements. The rate of racemization was measured by the batch method at 50 and 60 °C. The complex solution ($\simeq 10^{-3}$ mol kg^{-1}) in a Teflon cell (3 cm^3) was placed in a thermostated stainless-steel vessel containing low-viscosity silicon oil (Sin-Etsu KF96 10c.s.). Pressure (0.1–284 MPa) was applied immediately with a hand pump and released after an appropriate lapse of time. The solution was promptly cooled and diluted with AN to adjust the concentration to suit UV absorption and CD measurement.

Table I. Rate Constants of the Racemization of $[Ge(acac)_3]^+$ under Pressure for Various Solvents and Temperatures

	$k_p/10^{-5}$ s^{-1}				
	60 °C			50 °C	
pressure/MPa	TCE	PC	AN	AN	DMF
0.1	1.40	10.5	8.85	2.88	14.6
46.6	1.15	9.08			18.6
94.8	0.76	7.78			15.2
143.5	0.63	7.51	8.67	2.79	20.0
190.1	0.38	7.08			22.0
237.6	0.37	6.61	9.15	2.86	20.1
284.0	0.29	5.62	8.65	2.90	22.0

Table II. Activation Parameters of the Racemization of $[Ge(acac)_3]^+$

	activation parameters			properties of the solvents		
solvent	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$/cm^3 mol^{-1}	ϵ_r[b]	DN[c]	$\overline{V}_s°$[d]
TCE	117 ± 3[a]	+16 ± 11[a]	+15.1 ± 0.8	8.20	~0	109.4
PC	102 ± 0	+15 ± 2	+5.4 ± 0.3	70.0	15.1	87.9
AN	102 ± 2[a]	−18 ± 6[a]	0.0 ± 0.2	37.5	14.1	55.7
DMF	100 ± 10[a]	−21 ± 36[a]	−4.1 ± 0.6	36.7	26.6	80.3

[a] Data from ref 8. [b] Dielectric constant at ~20 °C. [c] Gutmann's donor number. [d] Partial molar volume of the solvent (cm^3 mol^{-1}) calculated from the density measurement at 50 °C or at 60 °C.

The pressure device was prepared by the Union Giken Co., Ltd. The pressure was measured with a Bourdon gauge calibrated with Heise's standard gauge. The applied pressure remained unchanged for ca. 100 h within an error of −1%. The temperature was measured with a standard thermometer in a hole of the stainless-steel vessel and found to be constant within an error of ±0.1 °C. The UV absorption and CD spectra were recorded with a Hitachi 323 spectrophotometer and a JASCO J-40 spectropolarimeter, respectively.

Results

The absorption spectra did not change throughout the kinetic runs in all the solvents except DMF. The rate was followed by measuring the decrease in CD strength at 305 nm ($\Delta\epsilon_{305}$) and calculated by eq 1 at a given pressure and temperature, where $\Delta\epsilon_t$ and $\Delta\epsilon_0$ are the CD strengths at time t and 0, respectively, and k_p is the first-order rate constant under pressure p.

$$k_p = [\ln (\Delta\epsilon_0/\Delta\epsilon_t)]/2t \qquad (1)$$

The decrease in CD strength in DMF was accompanied by a slower change of the UV absorption. There must be a

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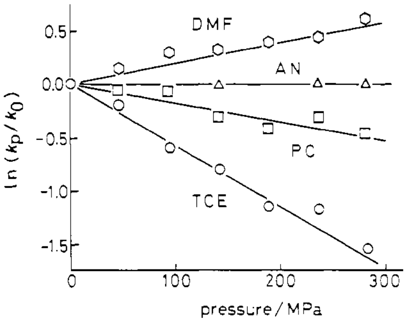

Figure 1. Pressure dependence of the racemization rate constants of $[Ge(acac)_3]^+$ in various organic solvents. k_p and k_0 are rate constants under pressure p and atmospheric pressure, respectively. Solvents are 1,1,2,2-tetrachloroethane (TCE, at 60 °C), propylene carbonate (PC, at 60 °C), acetonitrile (AN, at 60 °C), and *N,N*-dimethylformamide (DMF, at 50 °C).

simultaneous solvolysis in this strongly donating solvent. Since the UV absorption and the CD pattern of the solvolysis product are not known, the k_p values were calculated by using $\Delta\epsilon_{305}/\epsilon_{287}$ in place of $\Delta\epsilon$'s in eq 1 (vide supra), where ϵ_{287} denotes the extinction coefficient at 287 nm.

The k_p values are listed in Table I, and their dependency on the pressure is illustrated in Figure 1. The plots are linear in all the solvents, and the activation volume $\Delta V^{\ddagger}$ is calculated by eq 2. Table II shows the volumes of activation as well as

$$\Delta V^{\ddagger} = -RT[\partial \ln (k_p/k_0)/\partial p] \qquad (2)$$

the enthalpies and entropies of activation given in the literature.[8] The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values in PC were calculated from k_0's at 39.0, 50.0, and 60.0 °C measured in this study.

Conductivity measurement under atmospheric pressure disclosed that the complex salt is in the state of an ion pair in the concentration range from 10^{-3} to 10^{-1} mol kg^{-1} in the solvents.[9] The measurement was not made in PC, in which the ion pair must be dissociated at least partly because of its high ϵ_r ($\simeq$70). The apparent molar volume of the ion pair in all the solvents was estimated to be around 310 cm^3 mol^{-1} on the basis of density measurements.[10] The value is in good accord with that calculated from X-ray crystallographic data, 303 cm^3 mol^{-1}.[11] Hence the structure of the ion pair in the solutions does not seem to differ significantly from that in the crystalline state.

Discussion

The mechanism of the present racemization was discussed in detail.[8] Intermolecular mechanism was clearly excluded by the labeling experiment.[12] An intramolecular mechanism involving one Ge–O bond break was established on the basis of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values and the solvent effect on the rate. The observed $\Delta V^{\ddagger}$ values are not only interpreted by the proposed mechanism but also provide useful support to it.

Interpretation of $\Delta V^{\ddagger}$. Intramolecular racemization of tris(bidentate) complexes of transition-metal ions without bond breaking (twist mechanism) is believed to have very small $\Delta V^{\ddagger}$ values so far as the spin state remains unchanged.[4,5] Our $\Delta V^{\ddagger}$ values range from −4 to +15 cm^3 mol^{-1}. They are much larger than those expected for the twist mechanism, indicating the participation of bond breaking in the rate-determining step.

The break of the Ge–O bond to give an intermediate with a unidentate ligand can take place with either an associative or dissociative rate-determining step. The sign of $\Delta V^{\ddagger}$ values is often used as a useful criterion for discerning the participation of an associative or a dissociative rate-determining step. The values in Table II include both positive and negative signs and may indicate that the mechanism of racemization differs remarkably in the given solvents. However, the observed $\Delta V^{\ddagger}$ values can be consistently interpreted in the following manner.

The $\Delta V^{\ddagger}$ values can reflect either the change in the state of the second coordination sphere accompanied by the formation of the transition state or the change in volume of the substrate itself. The break of one Ge–O bond will leave the negative charge of that particular ligand at the remaining Ge–O bond, and the local charge of the free end of acac$^-$ would not be large enough to cause the electrostatic contraction of the solvent. The extent of electrostatic contraction of the second sphere can be estimated by Heydmann's equation.[13] If the bond break had brought about charge separation, the $\Delta V^{\ddagger}$ would have been largely affected by the dielectric constant of the medium, the absolute value decreasing in proportion to $[3/(2\epsilon_r + 1)^2](\partial\epsilon_r/\partial p)_T$. Table II indicates that the observed $\Delta V^{\ddagger}$ values are independent of the dielectric constant, and the contribution of this factor should not be significant. Hence the $\Delta V^{\ddagger}$ values should be accounted for in connection with the change in volume of the complex itself.

Reaction in TCE. The $\Delta V^{\ddagger}$ value is largely positive in TCE, and we think this fact is correlated to the absence of nucleophilicity of TCE. So far as the TCE molecules in the second coordination sphere neither contract nor coordinate to the vacant site made by the break of a Ge–O bond, the molar volume of the complex will increase rather than decrease. The observed positive $\Delta V^{\ddagger}$ must reflect such an increase in the molar volume of the complex.[14]

Solvent Effect. The change in $\Delta V^{\ddagger}$ value seems to be correlated with the donor number (DN) of the solvents. There is an overall trend towards more negative $\Delta V^{\ddagger}$ values with increase in DN. If the rate-determining step of the present racemization were in the solvent-assisted bond break to form an intermediate containing one unidentate acac$^-$ as suggested previously,[8] the smaller $\Delta V^{\ddagger}$ value in the donating solvents than that in TCE could be interpreted by considering the participation of the solvent molecules in the first coordination sphere to different extents. The magnitude of such a participation must be ruled by both electronic and steric factors. A more basic molecule interacts with Ge^{IV} more intimately to increase the k_0 and to decrease the $\Delta V^{\ddagger}$ in the sequence TCE, AN, and DMF. Propylene carbonate (PC) with a DN similar to that of AN, however, gives a significantly larger $\Delta V^{\ddagger}$ than AN does. This must be due to a steric factor. The PC molecule is larger, and its electric dipole is more blunt than AN. Hence it cannot squeeze deeply into the first coordination sphere, and the overall volume of the transition state would not decrease to such an extent as might be expected from the high DN.

Another implication can be encountered, however, by considering dissociation of the ion pair $[Ge(acac)_3]^+,ClO_4^-$ on pressure application. It was demonstrated that free $[Ge(acac)_3]^+$ racemizes more slowly than the ion pair by a factor of 1.2 to 2 depending on the solvent.[8,9] An enhanced disso-

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(14) If the break of the Ge–O bond is immediately followed by rapid cis-trans change of the unidentate ligand,[15] the acetyl moiety will protrude from the original complex. This change will bring about an increase of molar volume by 15–18 cm^3 mol^{-1}.[16] The contraction of the complex itself accompanied by the tentative formation of a species with coordination number 5 should not overcompensate the increase caused by the protrusion.

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ciation of the ion pair will result in an apparent decrease of $\Delta V^{\ddagger}$. Such an effect is significant in those solvents with larger dielectric constants, e.g., PC. No information is available, however, concerning the pressure effect on the ion pair formation in organic solvents.

DMF with the largest DN gives a negative $\Delta V^{\ddagger}$. The molecule is not as large as PC and can go deep into the coordination sphere to overcompensate the increase in volume at the transition state caused by the break of one end of the ligands. The complex undergoes solvolysis in this solvent. However, since the solvolysis proceeds more slowly than the decrease in CD strength by a factor of more than 10, the encountered experimental error will remain less than ca. 10%. If one of the acac$^-$ ligands leaves the coordination sphere to give bis(acetylacetonato)bis(dimethylformamide)germanium(IV) ion on solvolysis, the product can be of either cis or trans isomerism. If the trans isomer were formed, it cannot be optically active and the experimental error comes only from the apparent molar extinction coefficient ϵ, whenever the ratio $\Delta\epsilon_{305}/\epsilon_{287}$ is used in place of the CD strength itself for the first-order kinetic plot. If *cis*-$[Ge(acac)_2(DMF)_2]^+$ were formed with retention of the configuration, the product could contribute to the CD strength at 305 nm. However, bis(β-diketonato) complexes of metal ions have UV absorption maxima due to the exciton band at a lower wavenumber region than the tris-type complexes do.[17] The CD strength at the negative exciton peak of this bis(β-diketonato) complex should shift to the lower wavenumber region for the present Δ isomer, which has a negative CD peak at a lower wavenumber side. The $\Delta\epsilon$ decreases more steeply than the molar extinction coefficient does at the higher wavenumber side of the peaks. Therefore, the contribution of *cis*-$[Ge(acac)_2(DMF)_2]^+$ to the $\Delta\epsilon_{305}/\epsilon_{287}$ ratio cannot be large. The ln $(\Delta\epsilon_{305}/\epsilon_{287})$ vs. time plots, in fact, remained linear until 70% of the initial $[Ge(acac)_3]^+$ racemized. This fact supports indirectly the legitimacy of our kinetic treatment.

Conformity of the racemization mechanism in donating and less donating solvents was also discussed on the basis of the rather continuous change of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.[8] The present results support that the racemization proceeds via an intermediate with one unidentate ligand that was formed by a solvent-assisted bond break. However, a less donating solvent assists the bond break to only a very small extent.

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Cyclic Voltammetry Studies of Metalloflavin Complexes in Aqueous Solution

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Electrochemical studies of stable tetraammineruthenium(II) complexes of 10-methylisoalloxazine, 3,10-dimethylisoalloxazine, and riboflavin are reported. While approximating metal-stabilized flavosemiquinones in some of their properties, these complexes are best formulated as Ru^{II}-Fl_{ox} rather than Ru^{III}-Fl·. The reduction of the flavin ligand is shown to proceed through two successive single-electron steps rather than by the apparent two-electron process exhibited by the free flavins under similar conditions. This appears to be largely due to destabilization of the fully reduced flavin. Measurements of the pK_a values were determined spectrophotometrically and are used to extrapolate from experimental reduction potential data as a function of pH. Coordination of the metal to the N-5 and O-4 positions of the isoalloxazine ring modulates the acid-base behavior of the flavin so that distinct pH regions emerge where electron transfer occurs without simultaneous proton transfer. A minimum separation between the two one-electron flavin reduction potentials occurs when the flavosemiquinone complex is 50% protonated at the N-1 position. An unusually high oxidation potential for the Ru(II) indicates substantial donation of electron density from the metal onto the isoalloxazine ring. Several types of absorption phenomena are present owing to time-dependent adsorptions of the complex and interactions of the free flavin following dissociation of the reduced complex. Such processes are identified and discerned form bulk solution redox couples. The results are discussed in terms of possible mechanisms for protein control of flavin redox behavior.

Introduction

Flavin coenzymes occur in a variety of oxidoreductase proteins to interface between organic oxidations (and reductions) occurring by two-electron processes and electron transfer to (or from) metal centers requiring single electrons.[1-3] Only molybdenum, which occurs relatively rarely in biological systems, also performs this interface function. In addition to being able to operate by one- or two-electron steps, flavins exhibit electrochemical potentials which are modulated over a range of 600 mV by the effects of protein binding.[3]

Since flavins engage in electron transfer with a variety of metal centers in proteins, it has long been speculated that metal coordination of these coenzymes may take place.[1,2 4-6] However, only in one case have flavin and metal sites been shown to be in a proximity close enough to allow a strong interaction evident in EPR spectra.[7] For this reason a lower limit of 10-15 Å is usually placed on the distance between flavin and metal sites in proteins. While separations of this

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