Ligand Isotopic Exchange of Tris(acetylacetonato)germanium(IV) Perchlorate in Organic Solvents

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The ligand isotopic exchange between tris(acetylacetonato)germanium(IV) perchlorate and acetylacetone[^{14}C] has been studied in 1,1,2,2-tetrachloroethane (TCE), nitromethane (NM), and acetonitrile (AN), at 100—120 °C. In these solvents, the rate formula was $R=k[H_2O][\text{complex}]$; the concentrations of the complex, free ligand, and water in solution were in the ranges from 0.01 to 0.1 mol dm^{-3}. The activation enthalpies and entropies for the k's are 105, 98, and 90 kJ mol^{-1}; and -25, -53, and -69 J K^{-1} mol^{-1}, in TCE, NM, and AN, respectively. Influence of acid and base concentrations, and deuterium isotope effect on the rate in AN suggest that the rate controlling step of the exchange is governed by the ease of the proton transfer between the leaving and the incoming acac$^-$ in an intermediate.

Little information is collected concerning dynamic behavior of octahedral germanium(IV) compounds. We resolved tris(acetylacetonato)germanium(IV) $[Ge(acac)_3]^+$ and postulated an intramolecular mechanism for its racemization involving an intermediate with a unidentate acetylacetonate. The ligand isotopic exchange with free acetylacetone[^{14}C] (Hacac[^{14}C]) was much slower than the racemization, but the kinetics was left unknown.[1] This paper deals with kinetic studies of ligand isotopic exchange between $[Ge(acac)_3]ClO_4$ and Hacac[^{14}C] in dehydrated organic solvents at 100 to 120 °C. The mechanism is discussed with reference to the solvent effect, and compared with those of related reactions including the racemization.

Experimental

Materials. *Tris(acetylacetonato)germanium(IV) Perchlorate*: The complex was prepared by the reported procedure,[1] and recrystallized from acetonitrile (AN) by adding diethyl ether. Found: C, 38.58; H, 4.53%. Calcd for $C_{15}H_{21}O_{10}ClGe$: C, 38.38; H, 4.51%. The pattern of the absorption spectrum and the peak ($\tilde{\nu}$, 34700 cm^{-1}; ε, 35500 dm^2 mol^{-1}) in UV region coincided with those in the reference.

Acetylacetone: Commercially available Hacac was distilled under reduced pressure, dried with anhydrous calcium sulfate, and distilled at *ca.* 15 mmHg at 60 °C. The Hacac[^{14}C] was prepared by the Claisen condensation between acetone[^{14}C] (15 cm^3, 0.25 mCi) and ethyl acetate,[2] and distilled three times to yield $\approx$5 g of Hacac[^{14}C] with a specific activity $\approx$10 μCi g^{-1}. Acetylacetone[*methylene*-$^2H_2$] (Hacac[D]) was prepared by refluxing Hacac with deuterium oxide (D_2O) in dichloromethane, and fractionally distilled twice. The proton NMR spectrum indicated *ca.* 90% deuteration of methylene hydrogens. The purities of these reagents were checked by gas chromatography to be >99.99%.

Solvent for Kinetic Runs: Acetonitrile (AN) was dried by refluxing with diphosphorus pentaoxide (*ca.* 5 g for 1 dm^3) for *ca.* 3 h, and fractionally distilled at 81.6 °C. These procedures were repeated until $\leq$0.003 M (M=mol dm^{-3}) water remained on Karl Fischer titration. Nitromethane (NM) was distilled, frozen under a reduced pressure three times, dried with Molecular Sieve 4A Zeolite, and distilled at $\approx$15 mmHg. The product contained $<10^{-2}$ M water, and $\approx 10^{-5}$ M nitroethane and nitropropanes. 1,1,2,2-Tetrachloroethane (TCE) was washed with concentrated sulfuric acid until the water layer remained colorless, and then with water, fractionally distilled at $\approx$15 mmHg at 60 °C in the dark, and aerated with dry air. 1,2-Dichloroethane (DCE) was washed successively with sodium hydroxide in water, dilute sulfuric acid, and water, and then fractionally distilled in the dark.

Other Reagents: Trichloroacetic acid was sublimed *in vacuo* at 60—70 °C. Trichloroacetic acid[^2H] (CCl_3COOD) was prepared by evaporating D_2O solution of trichloroacetic acid to dryness, and sublimed *in vacuo*. Pyridine was purified by recrystallizing pyridinium perchlorate, treating with solid potassium hydroxide, and distilling at 114—115 °C. Extra pure reagents of 2,6-lutidine and sodium perchlorate were used without further purification. Diethyl ether was dried over calcium chloride overnight, and distilled.

Kinetic Procedure. *Ligand Isotopic Exchange*: The solution of Hacac[^{14}C] (0.08 to 1 M) in a given solvent was prepared at least 48 h in advance to attain the keto-enol equilibrium. The complex solution ($\approx$0.05 M) in the same solvent was mixed with the ligand solution at room temperature. Whenever required, given amounts of water and/or any other reagents were introduced and the final volume was adjusted to 10 cm^3. Several 1 to 2 cm^3 portions were sealed in Pyrex-glass tubes (10 cm in height and 0.8 cm in diameter) and placed in a thermostatted (±0.2 °C) silicone oil bath at 100—120 °C to let the exchange reaction start.

The ampoules were picked up one by one at proper time intervals and cooled in cold water for 1 min. The content of each ampoule was poured into diethyl ether (30—50 cm^3) and set aside for 30 min at *ca.* 10 °C. The crystallized complex was filtered off, washed with diethyl ether, and dried. It was dissolved in AN (3 to 10 mg in 3 cm^3). A one cm^3 portion was mixed with toluene containing *p*-terphenyl and *p*-bis(5-phenyl-2-oxazolyl)benzene to produce 15 cm^3 solution containing their 0.4 and 0.01%, respectively, and submitted to liquid scintillation counting. Another one cm^3 portion was diluted 100 to 500 fold with AN and the extinction was measured at 288 nm to find the concentration of the original solution in AN. The specific β-activity of the recovered complex, x, was known from these data.

The water content of the reaction mixture was determined by Karl Fischer titration. The UV absorption spectrum of the reaction mixture was recorded to find any change in composition during the kinetic runs.

Calculation of the Exchange Rate: The rate of isotopic exchange was calculated by the McKay formula,

$$R = -[3ab/(3a+b)][\ln(1-F)]/t, \tag{1}$$

where a and b are the concentrations of the complex and the free ligand, respectively, and t and F are the lapse of time and the extent of the reaction at time t, respectively. The F values were given by $(x_0-x_t)/(x_0-x_\infty)$, where the suffix denotes the time lapse from the initiation until the quenching of the exchange reaction.

Acetylacetone is present in tautomeric keto-enol equilibrium in TCE, NM, and AN. The percentages of the enolic form were estimated from the intensities of NMR signals for the enol and keto forms in deuterated solvents ([Hacac] $= 10^{-2}$ M) to be 69, 50, and 58%, respectively at 110 °C. The rate of the keto-enol tautomerization was much greater (*ca.* 10^{-4} s^{-1}) than that of the exchange at >100 °C, and the b was taken as the gross concentration of free Hacac.[13]

Apparatuses. Hitachi 323 Spectrophotometer was used for recording the UV absorption spectra. The β-activity of ^{14}C was recorded with Nuclear Chicago Unilux II-A Liquid Scintillation Counter. Varian A-60 Spectrometer was employed for NMR spectroscopy.

Results

Ligand isotopic exchange was studied in acetonitrile, nitromethane, and TCE. The complex decomposed at >120 °C in TCE, whereas even at 100 °C in DCE.

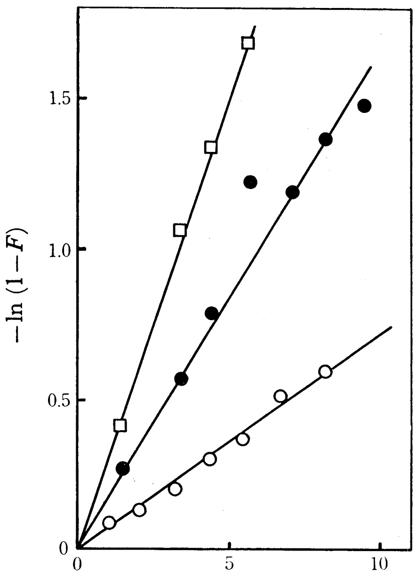

Fig. 1. McKay plot, ln (1−F) *vs.* t. The extent of reaction (F) was calculated from the specific activity of $[Ge(acac)_3]ClO_4$ in acetonitrile at 110.2 °C. Complex, 0.010 M; Hacac[^{14}C], 0.062 M; water, 0.013 M (○), 0.033 M (●), 0.047 M (□).

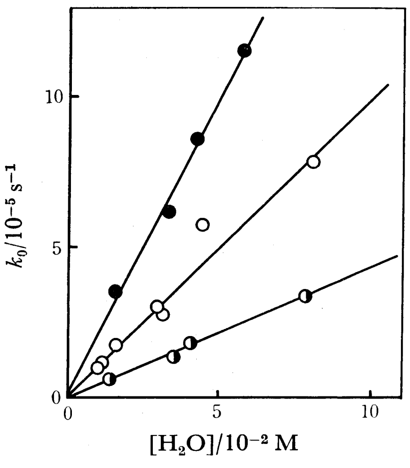

Fig. 2. Exchange rate constant k_0 *vs.* water content in acetonitrile, at 100.3 °C (◑), 110.2 °C (○), and 119.3 °C (●); [Hacac] ≈ 0.06 M, [complex] $= 0.01$ M.

General Aspect. McKay's R remained constant until F reached 0.7 (see Fig. 1) at 100—120 °C, and the UV absorption of the reaction mixture remained unchanged during these periods. Hence the following ligand exchange between the complex and the free ligand should take place exclusively.

$$[Ge(acac)_3]^+ + Hacac^* \rightleftharpoons [Ge(acac)_3{}^*]^+ + Hacac \quad (2)$$

The rate R was proportional to the complex concentration from 0.005 to 0.015 M, and the observed rate constant k_0 was calculated by the following equation:

$$R = k_0 \text{ [complex]}, \quad (3)$$

while the free ligand concentration (0.03 to 0.09 M) gave very little influence, the plot of k_0 against water concentration (0.01 to 0.1 M) is linear as exemplified in Fig. 2 in AN, and the k_0 is expressed by

$$k_0 = k_x[H_2O]. \quad (4)$$

The k_x values in various solvents are given in Table 1. Ionic strength in acetonitrile solution (≤ 0.109 M, $NaClO_4$) gave very little influence on the rate at 110 °C.

Acid and Base Catalysis. Trichloroacetic acid enhanced the exchange in acetonitrile; also the separation-induced exchange became appreciable. The effect approached saturation when the acid concentration reached that of water (0.015 M) in the reaction mixture.

Pyridine and 2,6-lutidine caused change in UV absorption spectra of the reaction mixture in acetonitrile and gave precipitate after *ca.* 100 min at 110 °C even at a concentration lower than 0.01 M. A side reaction may have taken place. However, the original complex was partly recovered without decomposition to enable approximate measurement of its specific activity. The rate of exchange appeared to be smaller than in the absence of pyridine base.

Deuterium Isotope Effect. The rate of proton exchange between Hacac[^{14}C] and water is much greater than the ligand isotopic exchange rate of the complex. Hence the deuterium isotope effect should be reckoned as the gross influence of these protic species. Three kinetic runs were performed in solutions containing 0.010 M complex, 0.060 M Hacac, and 0.0060, 0.024, and 0.058 M water, the gross [H]/[D] ratios being 0.48, 0.60, and 0.71, respectively. The observed k_x's were smaller than those in the absence of excessive deuterium. Since the influence of proton and deuteron should be additive, the result was extrapolated to the purely deuterated system to find $k_{x(D)}$ 0.73 M^{-1} s^{-1} at 110 °C. The gross $k_{x(H)}/k_{x(D)}$ ratio is therefore 1.4. Deuterated trichloroacetic acid also gave smaller rate than the ordinary trichloroacetic acid did.

Discussion

A plausible mechanism of the ligand exchange of $[Ge(acac)_3]^+$ is visualized in Fig. 3.

Catalytic Action of Water and Acid. If the solvent had contained no water, no ligand isotopic exchange

TABLE 1. RATE CONSTANTS OF LIGAND ISOTOPIC EXCHANGE OF $[Ge(acac)_3]ClO_4$[a)]

Solvent	Temp	[Ge]	[Hacac]	$[H_2O]$	k_x [b)]	Notes
	°C	10^{-2} M	10^{-2} M	10^{-2} M	10^{-3} M^{-1} s^{-1}	
CH_3CN (AN)	100.3	1.00	5.97	1.4—7.8	0.45±0.03	4 runs
	110.2	1.05	3.12	0.91	1.03	
		1.05	3.04	0.96	1.00	Aged Hacac[c)]
		1.00—1.05	6.24	1.0—8.2	0.99±0.10	7 runs
		1.00	6.24	1.1—3.2	1.00±0.03	$[NaClO_4] \leq 0.099$ M, 4 runs
		1.00	6.24	1.7—1.9	1.61±0.03	$[CCl_3COOH]$ = (0.0059—0.035 M), 4 runs
		1.00	6.24	1.1	0.34	$[C_5H_5N]$ = 0.0051 M
		1.05	9.36	1.2	0.97	
	119.3	1.00	5.97	1.6—5.8	1.94±0.23	4 runs
CH_3NO_2 (NM)	100.3	0.997	2.91—9.65	2.2—10	0.24±0.06	9 runs
	110.2	0.997	5.81—9.65	3.7—9.3	0.51±0.06	4 runs
	119.3	0.997	5.81	2.6—7.1	1.18±0.09	4 runs
$CHCl_2CHCl_2$ (TCE)	100.3	1.01	5.97	2.4—7.7	0.51±0.06	4 runs
	110.2	1.01	2.89—8.68	1.7—6.3	1.26±0.16	4 runs

a) Rate law: $R = k_x[Ge][H_2O]$. b) Figures without error ranges represent those obtained by one kinetic run each. c) Used after aging as a solution in AN for 1000 min at 110 °C.

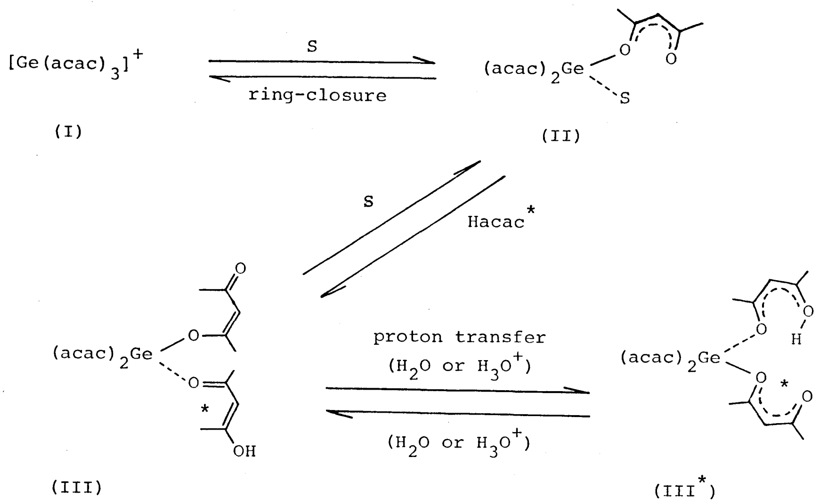

Fig. 3. Plausible mechanism of ligand isotopic exchange of $[Ge(acac)_3]ClO_4$ in organic solvents.[4)] S: Solvent molecule. Asterisks indicate labelling with ^{14}C.

would have occured below 120 °C. Water in organic solvents can act as either a nucleophile or a proton donor of a moderate strength. It can also bring about indirect influence including change of permittivity of the bulk environment, and that of the degree of intermolecular association of the complex (*e.g.*, ion-pair formation with perchlorate). Since the ionic strength in acetonitrile gave very little effect on the exchange rate under the experimental conditions, intermolecular association should not give a dominant effect. Permittivity of the solvent can change with increase in water content, but neither this effect is important, because no exchange takes place in the absence of water in the given temperature range. Proton transfer from free Hacac to coordinated acac⁻ is essential for the ligand exchange to take place, and proton donors such as protic acid and water can directly assist such a transfer. Acid as well as water accelerated the exchange, but bases did not. Catalytic activity of a protic acid seemed to saturate when the acid concentration reached a certain level. These observations as well as the deuterium isotope effect suggest that the water molecule serves as proton carrier, and that the proton transfer participates in the rate limiting step.[5)]

Reaction Mechanism. We postulated a plausible mechanism of racemization of $[Ge(acac)_3]^+$[1)]; *i.e.*, one of the Ge–O bonds of the original Δ-complex is broken with the aid of nucleophilic action of the solvent molecule to give an intermediate (II in Fig. 3, with a unidentate acac⁻), which successively undergoes inversion to give Λ-isomer. The solvent-assisted break of Ge–O bond was reckoned as the rate limiting step.

The rate laws and the activation parameters of the present exchange differ considerably from those of the racemization(see Table 2). The racemization rate is insensitive to the water concentration, largely affected by the donor number[6)] of the solvent, and not

TABLE 2. RATE CONSTANTS AND ACTIVATION PARAMETERS OF RACEMIZATION AND LIGAND ISOTOPIC EXCHANGE OF $[Ge(acac)_3]ClO_4$ IN ORGANIC SOLVENTS

Solvents	ε[a)]	DN[b)]	Racemization			Ligand isotopic exchange		
			k_r [c)]	ΔH^*	ΔS^*	k_x [d)]	ΔH^*	ΔS^*
			$10^{-5}\ s^{-1}$	$kJ\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$	$10^{-4}\ M^{-1}\ s^{-1}$	$kJ\ mol^{-1}$	$J\ K^{-1}\ mol^{-1}$
$CHCl_2CHCl_2$ (TCE)	8.2	$(\simeq 0)$	0.58	117 ± 4	$+16\pm 12$	5.1	105 ± 20	-20 ± 50
CH_3NO_2 (NM)	36	2.7	0.42	111 ± 4	-5 ± 14	2.4	98 ± 15	-53 ± 40
CH_3CN (AN)	38	14.1	2.9	102 ± 2	-18 ± 6	4.5	90 ± 12	-69 ± 32
$(CH_3)_2NCHO$ (DMF)	37	26.6	10	97 ± 11	-21 ± 36			
C_5H_5N (pyridine)	12	33.1	$27\ M^{-1}$ [e)]	99 ± 12	-7 ± 42			

a) Relative permittivity at *ca.* 20 °C. b) Donor number in ref. 6. c) Rate $= k_r$[complex], where [complex] $\approx 10^{-3}$ M at 50 °C. d) Rate $= k_x[H_2O]$[complex], at 100 °C. e) k_2 in *rate* $= (k_1 + k_2[\text{pyridine}])$[complex], in acetonitrile at 50 °C.

changed in the presence and the absence of excessive Hacac, while the exchange rate is sensitive to the water content, and the solvent effect is small as compared with that in the racemization. All these facts support that the ligand isotopic exchange has a different feature from that of the racemization.

The racemization equilibrium must have been readily reached at >100 °C where the isotopic exchange was observed. The solvent molecule in the sixth coordination site of intermediate II may be replaced by the free ligand, Hacac[^{14}C], to give intermediate III. Since the concentration of free Hacac overwhelms that of II, change in Hacac concentration would not affect the concentration of III. The solvent molecules, especially nitromethane and acetonitrile, can give stable second sphere coordination towards III, to make III more stable than II. Whenever originally coordinated $acac^-$ in III undergoes ring-closure to give I, no ligand exchange takes place. On the other hand, when proton is transferred from the incoming Hacac [^{14}C] to the originally coordinated $acac^-$, this is protonated and leaves the coordination site to result in ligand exchange; the deprotonated $(acac[^{14}C])^-$ undergoes ring-closure to restore $[Ge(acac[^{14}C])_3]^+$. The observed proton catalysis should operate in the proton transfer stage. The aprotic solvents used in this work can hardly assist the proton transfer, and the exchange is very slow in the absence of water or trichloroacetic acid, which assists the transfer. [Autoprotolysis constants (pK_i at 25 °C) of nitromethane and acetonitrile are 19.5 and 28.5, respectively.]

The activation enthalpies decrease and the activation entropies become more negative in the sequence 1,1,2,2-tetrachloroethane < nitromethane < acetonitrile, although the experimental errors remain rather large. The nucleophilicity of the solvent molecules (*e.g.*, Donor number) is well correlated with this sequence, which seems to reflect the ease with which the intermediate II is formed.

The large minus ΔS^* values (which are responsible for making the isotopic exchange slow) seem to reflect the steric difficulty with which the two unidentate moieties in III have their mutual orientations favorable for proton transfer. Especially in nitromethane and acetonitrile, these molecules in the second coordination sphere would prevent the tenure of favorable orientations to make ΔS^* values more negative.

The differences in ΔH^*, ≈ 10 kJ mol^{-1} regardless of the solvents, between the racemization and the isotopic exchange are significant beyond the experimental errors, and ΔH^*'s of the isotopic exchange are smaller than those of the racemization. This observation suggests that the activation enthalpies in a given solvent consist mostly of those for the formation of the intermediates II and III, *i.e.*, that for the break of one Ge–O bond. The smaller ΔH^*'s for isotopic exchange than those for racemization are explained by the larger stability of III than II, because Hacac is more nucleophilic than acetonitrile, nitromethane, and 1,1,2,2-tetrachloroethane,[7)] to give stronger interaction at the sixth coordination site of the intermediate. The extent of the stabilization of III brought about by the substitution of Hacac for the solvent molecules in II's is smaller to one another for the three kinds of solvent. The differences in nucleophilicities between Hacac and the solvent molecules may be partly compensated by the stabilization coming from the second sphere coordination of the solvent molecules.

The donor number of water (18) is larger than those of the solvents (<14), and comparable with that of Hacac. The concentration of water is much lower than those of the sovents by a factor $\approx 10^2$, and water may be unable to assist the formation of intermediate II. However, the activity of water should be large enough in the vicinity of III, to assist the proton transfer. β-Diketones have large affinity with water; even crystalline hydrates are known with hexafluoroacetylacetone. Water can have loose association with free Hacac in these solvents. Hence, water molecules can be present in the neighborhood of III when free Hacac interacts with II to give III, and facilitate the proton transfer between two unidentate $acac^-$ ligands.

Comparison with Related Compounds. Silicon(IV), tin(IV), and titanium(IV), the other members of Family IV of the periodic table also give octahedral complexes of the type $[M(\beta\text{-dik})_3]^+$ and *cis*-[M(β-

dik$)_2X_2$] with various β-diketones in enolate form. Since no ligand field effect can be expected for these d^0 and d^{10} ions, the contribution of the ionic radius should be important in interpreting the different kinetic behavior of these complexes. Silicon(IV)[8] and germanium(IV)[1] complexes of the type $[M(\beta\text{-dik})_3]^+$ are inert towards ligand exchange and hydrolysis. Their racemization was measured in the temperature range 30 to 70 °C, and the mechanism was claimed to be intramolecular involving a unidentate β-diketonate. Their ligand isotopic exchange is measurable at ≥ 100 °C, and the unidentate ligand must resist against break of the remaining bond. The central metal ion possesses a high charge, $+4$, and the partial charge separation caused by break of one M–O bond on unidentate formation will increase the effective charge of M(IV) further to make the remaining bond stronger.

Corresponding tin(IV)[9] and titanium(IV)[10] complexes are much more labile and their ligand isotopic exchange was measured only below -10 °C. In both cases water seems to play an important part in the rate determining step, presumably as a nucleophile. Particularly the tin(IV) complex gave a partially hydrated product $[Sn(OH)(H_2O)(acac)_2]ClO_4$, which was reckoned as a common intermediate for the hydrolysis and the isotopic exchange. Tin(IV) with a large ionic radius must be more readily subject to the nucleophilic attack of water even at a low temperature to result in rapid substitutions. Water acts as a proton carrier for germanium(IV) with a smaller ionic radius, (*loc. cit.*); overwhelming amount of donor solvent molecules can assist the break of one Ge–O bond only at a high temperature. Similar consideration was applied to octahedral complexes of aluminium, gallium, and indium, $[M(\beta\text{-dik})_3]^0$.[11]

Intramolecular site exchange process was observed by dynamic NMR technique in *cis*-$[M(\beta\text{-dik})_2X_2]^0$ complexes of Family IV metal ions.[12] There seems to be remarkable difference in the rate and in the activation parameters among these complexes. In the complexes of titanium(IV),[13] these values are centered around in the following ranges: rate constant k at 25 °C, 10^1—10^3 s^{-1}; Arrhenius activation energy E_A, 25—60 kJ mol^{-1}; activation entropy ΔS^*, -10—-150 J K^{-1} mol^{-1}. The tin(IV) complexes have the values: k, 10^{-1}—10^1 s^{-1}; E_A, 50—70 kJ mol^{-1}; ΔS^*, -40—-60 J K^{-1} mol^{-1}.[14] On the other hand the germanium(IV) complex $[Ge(dpm)_2X_2]$ (dpm=2,2,6,6-tetramethyl-3,5-heptanedionate, X=Cl, Br, and I) rearranges intramolecularly with $k \approx 10^{-6}$ s^{-1}, $E_A \approx 105$ kJ mol^{-1} and $\Delta S^* \approx 0$ J K^{-1} mol^{-1}.[15] These observations are very similar to those in the intermolecular ligand exchange and hydrolysis of $[M(\beta\text{-dik})_3]^+$ (although the total charges of the complexes are different) suggesting significant influence of the radius of the central ion.

The present octahedral germanium(IV) complex is as inert as cobalt(III) and chromium(III) complexes, and should be included in the group of "inert complex." The source of such an inertness seems to consist in, at least partly, the stability of the Ge–O bond between germanium(IV) and unidentate acac$^-$.

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