Mechanism of Racemization of Octahedral Silicon(IV) Complexes with Various β-Diketones in Organic Solvents

Tomoaki INOUE,* Junnosuke FUJITA,** and Kazuo SAITO

Chemistry Department, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980

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Silicon(IV) complexes of 4 kinds of β-diketonate have been resolved and their racemization has been kinetically studied in 1,1,2,2-tetrachloroethane (TCE) and acetonitrile (AN) at 30 to 80 °C. Ultra-violet absorption spectroscopy and isotopic exchange studies with labelled ligands verified intra-molecular mechanism. A similar rate formula to that for the tris(acetylacetonato)silicon(IV)[1] was obtained: $k_0=k_1+k_2$[acid or base]. Increase in basicity of the ligand decreases the rate. Introduction of methyl group on the central carbon of the six-membered chelate ring markedly enhanced the racemization. It seems as if the intermediate species with a unidentate ligand tends to take *trans* form around the C=C axis and retards the recombination, giving rise to bigger k values. Mechanism of acid and base catalysis was also discussed.

In a previous paper we gave the results of kinetics of racemization of tris(acetylacetonato)silicon(IV) [Si(acac)$_3$]$^+$ in 1,1,2,2-tetrachloroethane (TCE) and acetonitrile (AN), and postulated an intra-molecular mechanism through an intermediate with a unidentate ligand.[1] This paper deals with further results of kinetic studies of racemization of some tris(β-diketonato)silicon(IV), with aims of examining the influence of substituents on the chelate rings upon the rate, and of verifying the proposed reaction mechanism.

The ligands are acetylacetone homologues with ethyl and phenyl on α-carbon and methyl on the central carbon. The names and abbreviated symbols are given in Table 1.

Experimental

Materials. *The ligands*: Hdprm, Hdbm and Hmedprm were obtained by the Claisen condensation of the corresponding ketones and esters.[2] Hacac was methylated with methyl iodide in the presence of potassium carbonate and acetone to give Hmeacac.[3] All the products were identified by boiling point measurement, elementary analysis and UV and PMR spectrometry.

The complexes: Dilthey's method was employed for the synthesis of the tris-type complexes. They were obtained in the form of hydrogendichlorides (2 g), which were dissolved in water (30 ml) and converted into perchlorates by adding sodium perchlorate monohydrate (*e.g.* 2 g). The product was dried, dissolved in chloroform (*e.g.* 5 ml) and treated with diethyl ether (60 ml) to precipitate the anhydrous perchlorate, which was filtered off and dried. The conversion yield was *ca.* 80%. The dprm$^-$ and medprm$^-$ complexes are new compounds. Anal. [Si(dprm)$_3$]ClO$_4$: Found: C, 49.6 and H, 6.53; Calcd for $C_{21}H_{33}O_{10}ClSi$, C, 49.6 and H, 6.53%. [Si(medprm)$_3$]ClO$_4$: Found: C, 51.7 and H, 7.07%; Calcd for $C_{24}H_{39}O_{10}ClSi$: C, 52.6 and H, 7.16%.

Resolution: All the tris-type complexes were resolved for the first time. Dibenzoyl-*d*-tartrate used for [Si(acac)$_3$]$^+$[4] is the best agent. The racemic hydrogendichloride (2 g) in a mixture of 80 ml of water and 160 ml of AN was treated with the reagent (0.6 g) in 20 ml of water and 0.1 M soldium hydroxide solution (3.8 ml). Gradual addition of water (200 to 250 ml) gave colorless precipitate of the diastereoisomer (or jelly precipitate for meacac$^-$ and medprm$^-$ complexes). Addition of sodium perchlorate monohydrate (*ca.* 3 g) to the filtrate gave crystalline (+)$_D$-enantiomer of the complex (1 g), which was dissolved in AN (35 ml) and recrystallized by adding diethyl ether (25 ml), to give anhydrous perchlorate.

All the (+)$_D$-enantiomers gave plus and minus CD peaks from longer to shorter wavelength in the π–π^* transition region and assigned to Λ configuration.[5] The CD peaks are at 306, 400, 324 and 325 nm and the $\Delta\varepsilon$ values of the perchlorates were 30 to 70, 50 to 70, 20 to 30 and 5 to 10, for dprm$^-$, dbm$^-$, meacac$^-$ and medprm$^-$ complexes respectively. The percentage of resolution seems to be *ca.* 10%.

Other reagents: The Hdbm-^{14}C was prepared by Mr. Matsuzawa.[6] Labelled Hmeacac was synthesized from Hacac and methyl iodide-^{14}C similarly to the unlabelled ligand. Acetonitrile (AN) was dehydrated with diphosphoruspentoxide and distilled with potassium carbonate. The water content was *ca.* 3×10^{-3} M. TCE was dehydrated with calcium sulfate and distilled. The water content was 5×10^{-3} M. Mono- and trichloroacetic acid were sublimed *in vacuo*. Pyridine was dehydrated with calcium sulfate and distilled *in vacuo*. The water content was less than 0.01 M.

Procedure for kinetic runs and the measurements are the same as those in Ref. 1.

Results and Discussion

All the complexes are stable in TCE and AN under the given conditions. The absorption spectrum did not change during the measurements, regardless of the concentration of dissolved water and the excessive ligand, and of the presence of acid or base. Hence the change in CD strength or the rotatory power is exclusively due to the racemization of the resolved species. The rate of decrease in rotatory power obeys first order rate law and is expressed by first order rate constant, k_0 which is expressed by Eq. (1)

$$k_0 = 1/2t(\ln[\alpha_0/\alpha_t]) \quad (1)$$

where t is the lapse of time in seconds, and α_0 and α_t are the rotations at Na-D line or 405 nm or CD strength at the plus CD peak in near UV region at time zero and t, respectively. The k_0 values were independent of the complex concentration for 0.001 to 0.02 M in TCE and AN.

The ligand isotopic exchange rate was studied with [Si(dbm)$_3$]$^+$ and Hdbm-^{14}C, and [Si(meacac)$_3$]$^+$ and

* Present address: Chemistry Department, Wayne State University, Detroit, Michigan, U.S.A.

** Present Address: Chemistry Department, Faculty of Science, Nagoya University, Chikusa, Nagoya.

Table 1. The ligands used in this study

Name	R	R′	Abbreviation	pK_a[a]	pK_e[b]
2,4-pentanedione	CH_3	H	Hacac	12.75	8.23
3,5-heptanedione	C_2H_5	H	Hdprm	13.40	8.76
1,3-diphenyl-1,3-propanedione	C_6H_5	H	Hdbm	13.75	[9.1]
3-methyl-2,4-pentanedione	CH_3	CH_3	Hmeacac	—	9.2
4-methyl-3,5-heptanedione	C_2H_5	CH_3	Hmedprm	—	—

a) pK values for the diketone in 75% aqueous dioxane at 30 °C; b) pK values for the enol from of the diketones in water at 20 °C.[7] [The pK_e of Hdbm is an estimated value.]

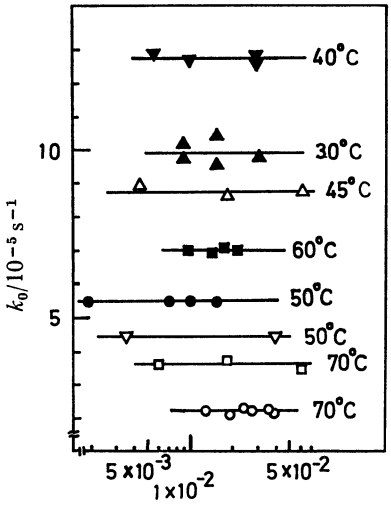

Fig. 1. Relationship between the racemization rate and the concentration of water.
Open marks in TCE, full marks in AN.
□: $[Si(dprm)_3]^+$, ○: $[Si(dbm)_3]^+$,
△: $[Si(meacac)_3]^+$, ▽: $[Si(medprm)_3]^+$.

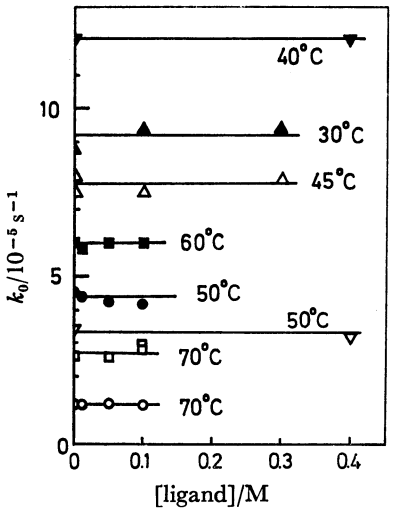

Fig. 2. Influence of the concentration of free ligands on the racemization constants.
Open marks in TCE, full marks in AN.
□: $[Si(dprm)_3]^+$, ○: $[Si(dbm)_3]^+$,
△: $[Si(meacac)_3]^+$, ▽: $[Si(medprm)_3]^+$.

Hmeacac-^{14}C in TCE and AN, both in presence and absence of acid and base. No appreciable isotopic exchange was observed in all the systems within 2—5 half life time of racemization at 70 °C. It is thus concluded that the racemization takes place intramolecularly.

Table 2. Rate constants and activation parameters for the racemization in TCE and AN at 50 °C

Complex	Solvent	k_1 / s^{-1}	$\Delta H^{\neq}$ / kcal·mol^{-1}	$\Delta S^{\neq}$ / cal·mol^{-1} K^{-1}
$[Si(acac)_3]^+$	TCE	4.8×10^{-6}	32±1	15
	AN	3.9×10^{-5}	26±1	0.5
$[Si(dprm)_3]^+$	TCE	1.8×10^{-6}	33±1	16
	AN	2.4×10^{-5}	24±1	−7
$[Si(dbm)_3]^+$	TCE	1.1×10^{-6}	32±1	14
	AN	5.5×10^{-5}	25±1	−1
$[Si(meacac)_3]^+$	TCE	2.0×10^{-4}	34±1	30
	AN	1.8×10^{-3}	28±1	14
$[Si(medprm)_3]^+$	TCE	4.4×10^{-5}	28±1	9
	AN	4.9×10^{-4}	25±1	3

Figs. 1 and 2 show the dependence of the rate constants upon the concentrations of water and free ligand in TCE and AN. It is clear that these concentrations do not affect the rate.

The racemization rate increases in the presence of mono- and trichloroacetic acid in TCE and of pyridine in AN. The influence is exemplified in Figs. 3 and 4. The diagrams are straight lines with intercepts, and k_0 is expressed by Eq. (2).

$$k_0 = k_1 + k_2[\text{acid or base}] \quad (2)$$

The k_1 *path.* Table 2 summerizes the rate constants k_1 and the activation parameters obtained from the experiments at 30 to 80 °C. The basic feature of the kinetics of racemization of the present Si(IV) complexes is very similar to that of previously reported $[Si(acac)_3]^+$ [1]. We postulated an intramolecular mechanism involving an intermediate with a unidentate acetylacetonate ligand and considered the break of the first Si–O bond as the rate-determining step. The present data in Table 2 seem to give support for the proposed mechanism.

If the break of the Si–O bond were the rate-determining step, the k values would decrease and the $\Delta H^{\neq}$ values increase as basicity of the ligand increases. The basicity of the ligands is best indicated by the pK values of their enol forms in the given solvents. However, only limited information is available concerning the pK values of various β-diketones in enol form. These values (pK_e) in water at 20 °C[7] are given in Table 1.

So far as the complexes with acac$^-$, dprm$^-$ and dbm$^-$ (hydrogen atom on the R′ position) are concerned, the k_1 values in TCE decrease slightly with increase in pK_e values, and the activation parameters

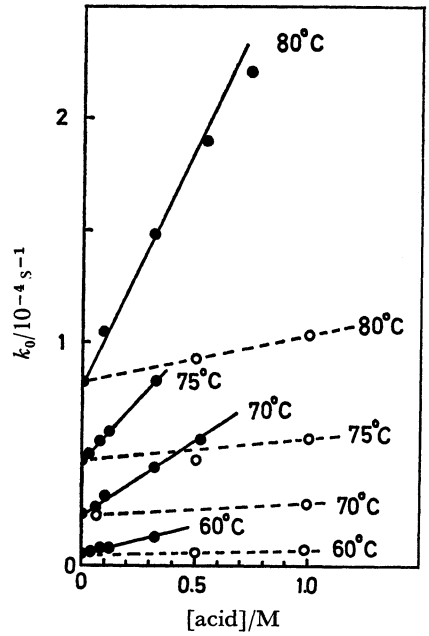

Fig. 3. Influence of acid concentration upon the racemization rate of $[Si(dbm)_3]^+$ in TCE.
Open marks with broken lines, $CH_2ClCOOH$; full marks with solid lines, CCl_3COOH.

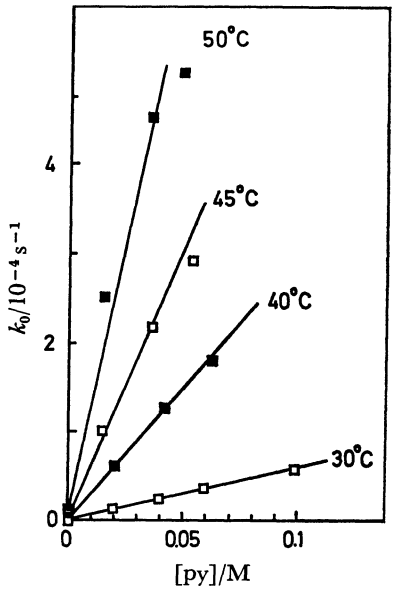

Fig. 4. Influence of concentration of pyridine on the racemization rate of $[Si(dprm)_3]^+$ in AN.

are similar to one another. On the other hand, the complexes with meacac$^-$ and medprm$^-$ (methyl on the R′ position) give much greater k_1 values than the corresponding complexes with hydrogen on R′. The pK_e value of Hmeacac is significantly larger than that of Hacac, and the big k_1 value should be interpreted otherwise.

Whenever alkyl groups are introduced on the R′ position of β-diketones, the keto-enol tautomeric equilibrium is shifted in favor of the keto form,[7] and the enol tautomer tends to take *trans* form around the C=C double bond axis.[8] This fact was also observed by PMR spectroscopy for Hmeacac,[9] and the conversion rate from *cis* to *trans* was reckoned to be very big.[10]

If the β-diketonate anion in the form of unidentate ligand in the intermediate state could be compared to the enol tautomer of the protonated ligand, the unidentate meacac$^-$ and medprm$^-$ ligand would tend to take *trans* form as shown in Fig. 5. Such a rearrangement would decrease the probability of the recombination of the ligand, to facilitate the racemization. When the k_1 value is written as Eq. (3) on the assumption of a stationary state,

$$k_1 = k_a(k_b/[k_{-a}+k_b])(k_c/[k_{-b}+k_c]) \quad (3)$$

the ligands with methyl on R′ would decrease the k_{-a} value to increase k_1. Comparison of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values between Hacac and Hmeacac complexes clearly shows that the labilization comes from the entropy contribution. The latter has bigger $\Delta H^{\neq}$ than the former, reflecting the bigger pK_e value of the ligand. (Comparison between dprm$^-$ and medprm$^-$ complexes is not useful, because pK_e value of the latter ligand is not known.) Thus we conclude that the present data gave concrete support for the reaction mechanism proposed before.

Either Si–O or C–O bond can be broken at the rate-determining step. Pinnavaia, Collins and Howe studied the NMR spectra of various alkyldimethylsilyl ether of Hacac in enol form and found a very rapid intramolecular rearrangement in *cis*-$R(CH_3)_2Si(acac)$, which interchanges the allylic and acetyl methyl groups on the acac moiety.[11] The Arrhenius activation energy for the interchange was measured at -36 to $+38$ °C to be 13.8 ± 0.5 kcal per mol. These are tetrahedral silicon(IV) compounds and the results may reflect the ease of homolytic cleavage of Si–O bond. Hence they should not be directly applied to our octahedral silicon(IV). Nevertheless we tend to consider that Si–O bond would be broken at the rate-determining step, although nothing decisive could be stated at the present stage.

In AN the racemization is faster than in TCE, and

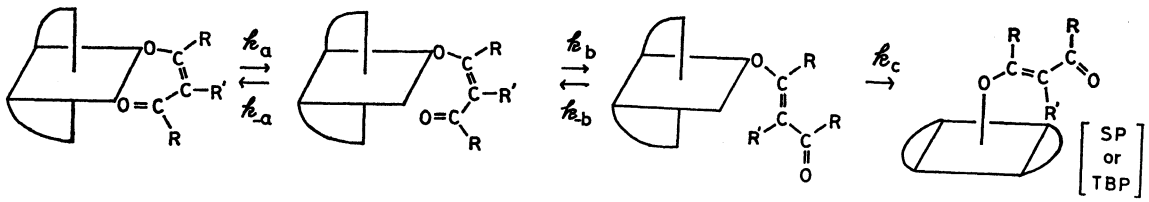

Fig. 5. Plausible racemization mechanism.

TABLE 3. SECOND ORDER RATE CONSTANT AND ACTIVATION PARAMETERS FOR THE RACEMIZATION IN THE PRESENCE OF ACID AND BASE AT 50 °C

Complex	Acid (Base)	k_2 / $M^{-1}\,s^{-1}$	$\Delta H^{\neq}$ / kcal·mol^{-1}	$\Delta S^{\neq}$ / cal·mol^{-1} K^{-1}
Acid catalysis in TCE				
[Si(acac)$_3$]$^+$	CCl_3COOH	1.4×10^{-4}	30±2	14
[Si(dprm)$_3$]$^+$	CCl_3COOH	2.2×10^{-5}	25±1	−3
	$CH_2ClCOOH$	2.0×10^{-6}	22±1	−17
[Si(dbm)$_3$]$^+$	CCl_3COOH	7.1×10^{-6}	25±1	−5
	$CH_2ClCOOH$	5.0×10^{-7}	27±2	−4
[Si(meacac)$_3$]$^+$	CCl_3COOH	2.0×10^{-3}	28±1	−5
[Si(medprm)$_3$]$^+$	CCl_3COOH	2.5×10^{-4}	28±1	11
	$CH_2ClCOOH$	1.5×10^{-5}	28±2	6
Base catalysis in AN				
[Si(acac)$_3$]$^+$	pyridine	1.5×10^{-1}	26±2	11
[Si(dprm)$_3$]$^+$	pyridine	1.3×10^{-1}	29±1	21
[Si(meacac)$_3$]$^+$	pyridine	3.0×10^{-2}	27±1	19
[Si(medprm)$_3$]$^+$	pyridine	3.7×10^{-2}	27±1	19

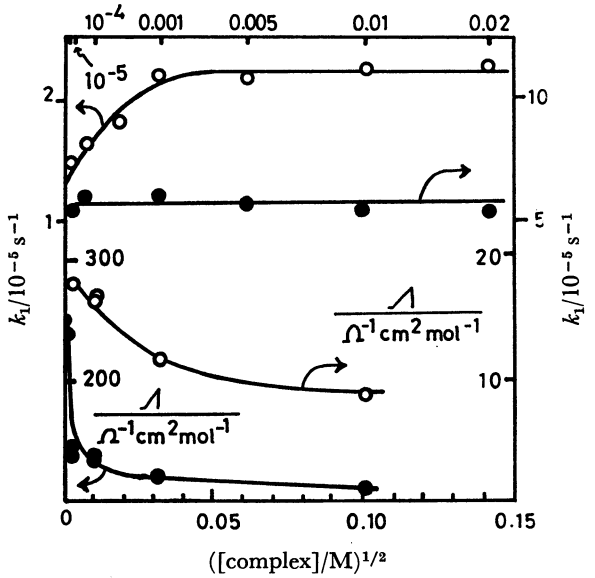

Fig. 6. Dependence of the molar conductivity and the racemization rate constant on the complex concentration of [Si(dbm)$_3$]ClO_4.
Upper: Rate constant k_1 in TCE(○) at 70° and in AN(●) at 50 °C. Lower: conductivity in TCE(○) and in AN(●) at 20 °C.

the $\Delta H^{\neq}$ values are smaller by *ca.* 6 kcal per mole. This fact indicates that the break of Si–O bond is facilitated in AN with dielectric constant 37.5. In a similar racemization of [Ge(acac)$_3$]$^+$ in various organic solvents,[12] we have proposed solvent-assisted dissociation of Ge–O bond, on the basis of a good correlation between Gutmann's donor number and the rate constant. Such a contribution cannot be excluded in the present racemization. However, silicon(IV) has a smaller octahedral ionic radius (0.47 Å) than germanium(IV) (0.53 Å), and the approach of a solvent molecule to Si(IV) would be more difficult than to Ge(IV). Hence solvent-assisted bond break seems less feasible for the present silicon(IV) complexes. Increase in racemization rate accompanied by the introduction of methyl on R′ could be similarly interpreted to that in TCE.

When the complex concentration was less than 0.001 M, the k_1 value decreased with decrease in concentration, as exemplified in Fig. 6. The decrease in molar conductivity with increase in complex concentration in TCE and AN is also illustrated in Fig. 6. The complexes seem to be present almost perfectly as ion pairs in more than 10^{-4} and 10^{-3} M solution in TCE and AN, respectively. The change in k_1 must reflect the state of the complexes. The constant values in more than 10^{-3} M solutions must be those of ion pairs. (The data in Tables 2 and 3 are so, too.) The racemization must proceed mostly in the form of ion pairs.

The k_2 *path.* The second order rate constants and activation parameters are shown in Table 3. Increase in racemization rate in the presence of acid was seen only in TCE. This effect must be due to the proton catalysis.[1] The absence of acid catalysis in AN may be due to hydrogen bond formation between the acid and AN.[13] Difference in $\Delta H^{\neq}$ values between k_1 and k_2 path is larger in most complexes in Table 2 than that in [Si(acac)$_3$]$^+$. We postulated in our previous paper that the protons are attached to the coordinated oxygen atom and facilitate the break of Si–O bond at the rate-determining step.[1] Ligands of the complexes in Table 2 are more basic than acac$^-$ and are subject to proton catalysis more remarkably. The stronger acid, trichloroacetic gives bigger influence than the weaker acid monochloroacetic does. Introduction of methyl on R′ increases the rate, and this fact can be interpreted by Eq. (3). Since the complexes are almost entirely in the form of ion pairs in the solutions used for the present study, interaction of protons with the complexes is not electrostatically implausible.

Base catalysis is only seen in AN. The absence of such an effect in TCE would be due to the hydrogen bond formation between pyridine and TCE.[14] The dbm$^-$ complex did not give k_2 path up to 0.05 M pyridine for 0.001 to 0.02 M complex. Pyridine can

attack the Si(IV) ion as well as the ligand as a nucleophile. However, the $\Delta H^{\neq}$ values for the k_1 and k_2 paths in AN do not differ much. Hence pyridine seems to occupy the vacant coordination site of the intermediate with a unidentate ligand, to decrease the k_{-a} of Eq. (3). The dbm^- ligand is bulky and may hinder the approach of pyridine to the vacant site.

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