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Racemization and Isotopic Exchange of Tris(acetylacetonato)silicon(IV) Perchlorate in Organic Solvents

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Racemization of trisacetylacetonatosilicon(IV) ions and their isotopic exchange reaction with acetylacetone-^{14}C (Hacac) have been studied in tetrachloroethane (TCE) and acetonitrile (AN). No solvolysis takes place at least below 60 °C, and the racemization rate R is expressed as follows: $R=$[complex] $(k_1+k_2$[acid]) (in TCE) and $R=$[complex] $(k_3+k_4$[base]) (in AN). The rate constants and activation parameters at 50 °C are as follows: rate constants, 4.79×10^{-6} s^{-1}, 1.35×10^{-4} M^{-1} s^{-1}, 3.87×10^{-5} s^{-1} and 1.19×10^{-1} M^{-1} s^{-1}, activation enthalpy ($\Delta H^{\neq}$/kcal mol^{-1}) 31.6±0.1, 29.3±1.9, 25.7±0.2 and *ca.* 18, and activation entropy ($\Delta S^{\neq}$/cal mol^{-1} K^{-1}) 14.6, 14.2, 0.53, −5.75, respectively, for k_1, k_2 (for trichloroacetic acid), k_3 and k_4 (for 2,6-lutidine). No isotopic exchange is observed within 6 hr at 60 °C in the solvents. The racemization should proceed intra-molecularly and presumably *via* an intermediate of coordination 5 with one of the ligands as unidentate.

Dynamic properties of β-diketonato complexes of metal ions have been studied from various viewpoints. Geometrical isomerization of the complexes with asymmetric β-diketones was studied mainly by measuring their NMR signals.[1] Trisacetylacetonato- and trisbenzoylacetonatocobalt(III) were partly resolved and their racemization and geometrical isomerization discussed in detail.[2] All the work was centered around intra-molecular rearrangement of the complexes. We have conducted kinetic studies of isotopic exchange of some acetylacetonato complexes of typical and transition metal ions, and discussed the intermolecular course of reaction in organic solvents.[3,4] Since these studies have been limited to those of chargeless complex species, we thought it desirable to extend the studies to silicon(IV) which gives univalent cationic complex with three β-diketonato ligands.

Silicon(IV) compounds with tetrahedral structure have been studied extensively, but much less is known about those with co-ordination number six. Phthalocyaninato,[5] tropolonato[6] and β-diketonato[7] complexes were synthesized and their structures discussed. However, reaction kinetics has been studied only with the tris-β-diketonatosilicon(IV) ion.

Dhar, Doron and Kirschner[8] first resolved trisacetylacetonatosilicon(IV) $[\mathrm{Si(acac)_3}]^+$ and studied its hydrolysis, methanolysis and racemization. They concluded that the loss of optical activity is mainly due to solvolysis.[9] Pearson, Edgington and Basolo considered an S_N2 displacement mechanism for the base hydrolysis.[10] From the difference in the rates of loss of optical activity and the hydrolysis, participation of intrinsic racemization was suggested.[9] Muetterties and Wright studied the base hydrolysis of a similar complex with dibenzoylmethane $[\mathrm{Si(dbm)_3}]^+$ in ^{18}O-labelled water, and suggested nucleophilic attack of hydroxide ions on the carbon atom adjacent to the coordinated oxygen.[11]

We found that $[\mathrm{Si(acac)_3}]^+$ undergoes racemization in carefully dehydrated organic solvents without being involved in other reactions such as hydrolysis, and studied the reaction kinetics of the non-catalyzed and acid- or base-catalyzed reaction path in 1,1,2,2-tetrachloroethane (TCE) and acetonitrile (AN). The result has been compared with that of intermolecular isotopic exchange of the complex with ^{14}C-labelled acetylacetone, and the mechanisms of racemization discussed.

Experimental

Materials. *Preparation and Resolution of the Complex*: Trisacetylacetonatosilicon(IV) hydrogen dichloride $[\mathrm{Si(acac)_3}]\mathrm{Cl\cdot HCl}$ was prepared by Dilthey's method[12] and resolved by Dhar *et al*'s method[8] with slight modification. Crystals of hydrogen-dibenzoyl-*d*-tartrate salt of this complex $(-)_\mathrm{D}$-$[\mathrm{Si(acac)_3}]$-$(-)_\mathrm{D}$-$\mathrm{C_{18}H_{13}O_8}$ were filtered off from the aqueous solution, and the crystals of $(+)_\mathrm{D}$-$[\mathrm{Si(acac)_3}]\mathrm{ClO_4}$ precipitated with sodium perchlorate from the filtrate. The resolution was partial but the racemization rate was independent of the degree of resolution. $(-)_\mathrm{D}$-$[\mathrm{Si(acac)_3}]\cdot\mathrm{C_{18}H_{13}O_8}$ was converted into $(-)_\mathrm{D}$-$[\mathrm{Si(acac)_3}]\mathrm{ClO_4}$ with the anion exchange resin Dowex 1-X8 by the batch method.

$(+)_\mathrm{D}$-$[\mathrm{Si(acac)_3}]\mathrm{ClO_4}$ was recrystallized from chloroform solution with ether and used for the kinetic runs. This complex is stable for several months in dry air below 15 °C, and for 2 weeks at *ca.* 30 °C. The perchlorate is soluble in nitriles, ketones, carboxylic acids, alcohols, and some haloalkanes, but insoluble in ethers, hydrocarbons and water. The dibenzoyltartrates are very stable, and soluble in carboxylic acids, some alcohols and haloalkanes, but insoluble in ethers, hydrocarbons and water.

$(+)_\mathrm{D}$-Enantiomer of this complex assigned to Λ configuration on the basis of Larsen's treatment.[13] The $\Delta\varepsilon$ of the

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1) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967). J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970); J. R. Hatchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

2) R. C. Fay, A. Y. Girgis and U. Klabunde, *J. Amer. Chem. Soc.*, **92**, 7056 (1970); A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970).

3) K. Saito and K. Masuda, This Bulletin, **41**, 384 (1968).

4) *Idem, ibid*, **43**, 119 (1970).

5) R. D. Joyner and M. E. Kenney, *Inorg. Chem.*, **1**, 236 (1962).

6) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **86**, 5132 (1964).

7) R. M. Pike, *Coord. Chem. Rev.*, **2**, 163 (1967).

8) S. K. Dhar, V. Doron, and S. Kirschner, *J. Amer. Chem. Soc.*, **80**, 753 (1958).

9) *Idem, ibid.*, **81**, 6372 (1959).

10) R. G. Pearson, D. N. Edgington, and F. Basolo, *ibid.*, **84**, 3233 (1962).

11) E. L. Muetterties and C. M. Wright, *J. Amer. Chem. Soc.*, **87**, 21 (1965).

12) W. Dilthey, *Ber.*, **36**, 923 (1903).

circular dichroism (CD) of $\Delta(-)_D$-[Si(acac)$_3$]-$(-)_D$-$C_{18}H_{13}O_8$ and $\Delta(+)_D$-[Si(acac)$_3$]ClO_4 were −162 and +180 at 302 and 304 nm at 25 °C, respectively. The specific rotation was +866° for the Δ-[Si(acac)$_3$]ClO_4 at the D-line at 25 °C.

Solvents: 1,1,2,2-Tetrachloroethane (TCE) was dehydrated with anhydrous calcium sulfate in a dry box and gently distilled. The procedure was repeated three times; the product contained 0.001 M water. Careless procedure gives rise to the increase in water content. Acetonitrile was refluxed with diphosphorus pentoxide and distilled. The procedure was repeated and finally distilled with potassium carbonate. The product contained 0.002 M water. Anhydrous calcium sulfate was also useful for its dehydration. Acetophenone was dehydrated with calcium sulfate and distilled under a reduced pressure. The water content was 0.002 M.

Other Reagents: Pyridine and its derivatives were dehydrated with anhydrous calcium sulfate and distilled. The water content was less than 0.01 M. Trichloroacetic acid was sublimed *in vacuo*. The labelled acetylacetone was prepared by Miss Kazuyo Masuda.[3)]

Experimental Procedure. Racemization: The optically active perchlorate ($\simeq$0.1 g) was dissolved in the solvent (25 ml) in a dried vessel in a dry box. Whenever necessary, a given volume of the acid or the base solution was added to make the concentration 0.001 to 0.1 M. The product was sealed in five small test tubes. They were placed in a thermostat (±0.02 °C) and picked up one by one at proper intervals. They were cooled in a mixture of table salt and ice, and the optical rotation measured at the Na-D line. They were then diluted and the u.v. absorption examined. The runs were carried out in the temperature range 30—60 °C. The rate constant was calculated by the equation

$$k_{\rm obsd} = [\ln(\alpha_0/\alpha_t)]/2t \qquad (1)$$

where α_0 and α_t are the optical rotations at time zero and t, respectively.

Isotopic Exchange Kinetics: The complex (0.04—0.08 g) and acetylacetone-^{14}C (0.01—0.02 g) were dissolved in TCE or AN in a long-necked flask in a dry box and kept in a thermostat (60±0.02 °C). Aliquots were withdrawn at appropriate intervals, and poured into cooled diethylether. The complex precipitated at once free from Hacac, filtered off with a small piece of filter paper, washed with diethylether and dried *in vacuo*. The β-activity of the precipitate (10 mg) on the paper was counted with a 2π gas flow counter with Q-gas.

Apparatus. A JASCO DIP-SL polarimeter and a Hitachi 124 spectrometer were used for the measurement of optical rotation and u.v. absorption spectrum, respectively. JASCO model ORD/UV-5 was used for recording the circular dichroism spectrum. Aloka FC-1E counter was used for the β-activity counting of ^{14}C. The water content was measured by the Karl Fischer method.

Results

The Kinetic Formula in TCE. The change in absorbance at 305 nm and optical rotation at the Na-D line of the reaction mixture are shown in Fig. 1. The constant absorbance indicates the absence of decomposition of the complex. Hence the decrease in optical rotation should be due to racemization of the complex. The dependence of $k_{\rm obsd}$ on the complex concentration is illustrated in Fig. 2. The rate constant remains unchanged in the range 0.005—0.05 M and the racemization rate is given by

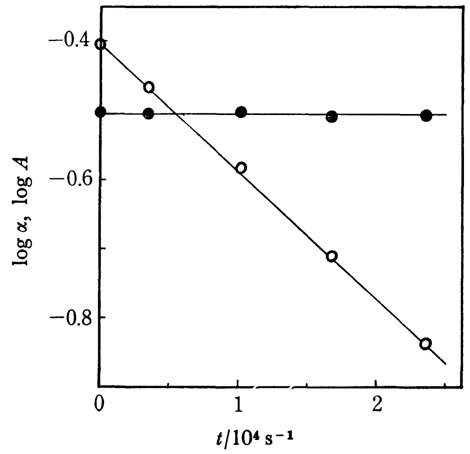

Fig. 1. Change of optical rotation at Na-D line and absorption spectrum at 305 nm in TCE. (● absorption, ○ rotation)

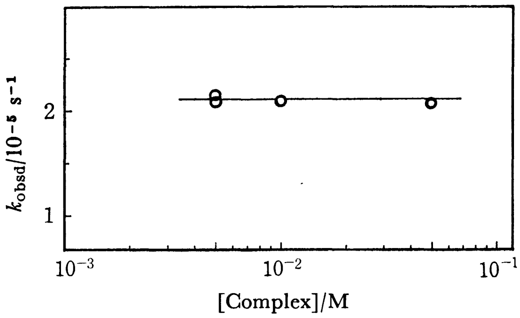

Fig. 2. Influence of the complex concentration upon $k_{\rm obsd}$ in TCE.

$$R - k_{\rm obsd}[\text{complex}] \qquad (2)$$

Free acetylacetone gave no effect on the rate of racemization (Fig. 3). The racemization is catalyzed by trichloroacetic acid as shown in Fig. 4. The straight lines have intercepts, which coincide with $k_{\rm obsd}$ values obtained in the absence of acid at the given temperature. Weaker acids do not give catalytic action. Hence $k_{\rm obsd}$ is given by

$$k_{\rm obsd} = k_1 + k_2[\text{trichloroacetic acid}] \qquad (3)$$

The results are summarized in Table 1. The catalytic action of trichloroacetic acid is reckoned as acid catalysis for the following reason. When equimolar

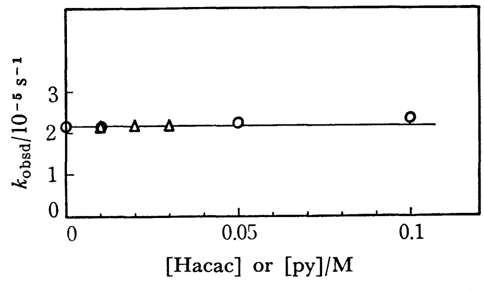

Fig. 3. Influence of concentration of free Hacac and pyridine in TCE. (△ Hacac, ○ pyridine)

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13) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

Table 1. Rate constants and activation parameters

t	TCE		AN		Acetophenone
°C	k_1/s^{-1}	$k_2/M^{-1}\,s^{-1}$	k_3/s^{-1}	$k_4/M^{-1}\,s^{-1}$ a)	k_5/s^{-1}
30b)			2.63×10^{-6}	1.66×10^{-2}	
40	9.50×10^{-7}	3.55×10^{-5}	1.08×10^{-5}		7.20×10^{-6}
50	4.79×10^{-6}	1.35×10^{-4}	3.87×10^{-5}	1.19×10^{-1}	2.85×10^{-5}
60	2.12×10^{-5}	6.23×10^{-4}	1.37×10^{-4}		1.19×10^{-4}
$\Delta H^{\ddagger}$ c)	31.6 ± 0.1	29.3 ± 1.9	25.7 ± 0.2	18.5	28.7
$\Delta S^{\ddagger}$ d)	14.6	14.2	0.53	−5.75	8.93

a) k_4 for 2,6-lutidine, b) ±0.05 °C, c) kcal mol^{-1} at 50 °C, d) cal mol^{-1} K^{-1} at 50 °C.

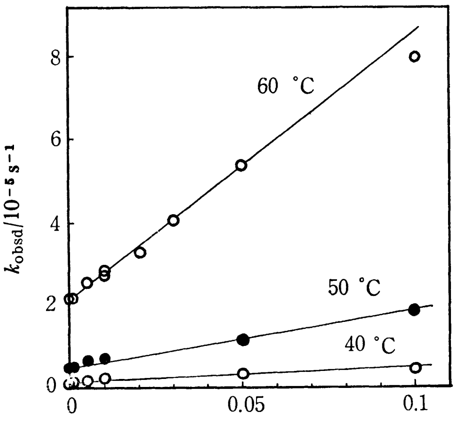

Fig. 4. Influence of concentration of trichloroacetic acid in TCE.

amounts of trichloroacetic acid and pyridine were added to the TCE solution, the k_{obsd} decreased as compared with that in the presence of trichloroacetic acid alone. On the other hand, the electric conductivity of the equimolar mixture was greater than those of pure solutions of trichloroacetic acid and pyridine in TCE. This fact shows that the dissociation of trichloroacetic acid was facilitated by the addition of pyridine. If the trichloroacetate anion had been the catalyzing species, the equimolar mixture should have exhibited greater catalytic activity. Hence, the proton seems to be the catalyzing species.

The fact that pyridine shows catalytic activity in AN (see below) but not in TCE can be interpreted by considering that pyridine is capable of forming hydrogen bonding with TCE[14] and does not behave as a base in this solvent.

No isotopic exchange was observed within 6 hr at 60 °C regardless of the presence or the absence of trichloroacetic acid.

In Acetonitrile. Plots of the rotation and the absorbance *vs.* time disclosed that racemization is not involved in decomposition of the complex. Independence of the rate constant of the concentrations of the complex and of free acetylacetone indicates that a relationship similar to Eq. (2) also holds in this solvent. Water in the concentration range 0.002—0.01 M and trichloroacetic acid gave no influence upon the rate of racemization. The racemization is catalyzed by bases such as strychnine, 2,6-lutidine, γ-picoline, pyridine and pyridine *N*-oxide, the extent decreasing in this order. The catalytic activity of pyridine was quenched by the addition of an equimolar amount of trichloroacetic acid, and the acceleration seems to be due to the base catalysis. The plot of k_{obsd} values *vs.* the concentrations of these bases gave straight lines with intercepts, which coincide with the k_{obsd} values in the absence of the bases (Fig. 5). Thus the rate constant is given by

$$\text{Rate} = k_{obsd}[\text{complex}] = [\text{complex}](k_3+k_4[\text{base}]) \quad (4)$$

The data are listed in Tables 1 and 2. The k_4 values are not sufficiently reproducible and the plots gave different gradients according to the batch of a given base, although the intercepts were always equal. It

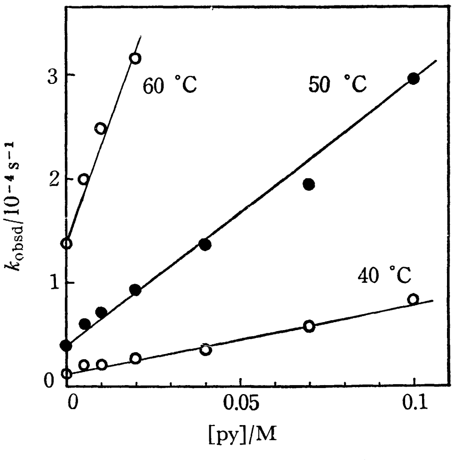

Fig. 5. Influence of pyridine concentration upon k_{obsd} in AN.

Table 2. Approximate k_4 values for some bases at 30 °C

Base	pK_a a)	$k_4/M^{-1}\,s^{-1}$
Strychnine	8.0	2×10
2,6-Lutidine	6.58	2×10^{-2}
γ-Picoline	6.02	2×10^{-3}
Pyridine	5.17	1.5×10^{-4}
Pyridine *N*-oxide	0.56b)	2×10^{-4} c)
4-Cyanopyridine	1.86	0

a) at 25 °C, b) at 23 °C, c) at 50 °C.

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[14] H. Götz, E. Heilbronner, A. R. Katritzky, and R. A. Jones, *Helv. Chim. Acta.*, **44**, 387 (1961); G. R. Wiley and S. I. Mitler, *J. Amer. Chem. Soc.*, **94**, 3287 (1972).

appears as if some unidentified compounds in the pyridine bases give catalytic action on top of that of the bases themselves. Hence only approximate values of k_4 are listed in Table 2. Nevertheless, they increase with increase in basicity of the bases. There was no influence of water and trichloroacetic acid upon the rate.

No appreciable isotopic exchange was observed within 20 hr at 60 °C both in the absence and the presence of bases.

In Acetophenone. The results are given in Table 1. No influence was observed in the presence of different amounts of water and free acetylacetone.

Discussion

All experimental results are summarized in Table 1. The absence of isotopic exchange clearly indicates that the racemization takes place *via* an intramolecular mechanism. Since no net chemical reaction is involved during the course of racemization, some kind of twisting mechanism should be operating.

Intra-molecular racemization can proceed either with or without break of one of the metal-oxygen bonds between silicon(IV) and acetylacetonate. The latter mechanism maintaining coordination number 6 was interpreted by Ray and Dutt[15] and by Bailar[16] in slightly different ways. However, racemization of [Si(acac)$_3$]$^+$ is subject to acid catalysis in TCE and to base catalysis in AN. Such catalytic actions are more easily understood by considering an intermediate with coordination number 5, because twist mechanism without bond break will be less sensitive towards acid and base catalysis.

An intermediate with coordination number 5 can be either trigonal bipyramid or square pyramid but should have a plane of symmetry with the unidentate ligand at the apical position. When one of the bonds of a ligand is broken, a trigonal bipyramidal intermediate seems to be easily formed without involving drastic intra-molecular rearrangement. (Fig. 6) On the other hand, if a square pyramidal intermediate were to be formed, the intra-molecular rearrangement would be more substantial and require bigger enthalpy of activation. Stability of trigonal bipyramidal and square pyramidal structure was compared both theoretically and experimentally by several authors.[17] It seems that former is energetically more favorable although the energy difference does not appear very big. This does not necessarily imply that the energy barrier to be overcome is also small; however, we are inclined to presume the trigonal bipyramidal intermediate to be more feasible.

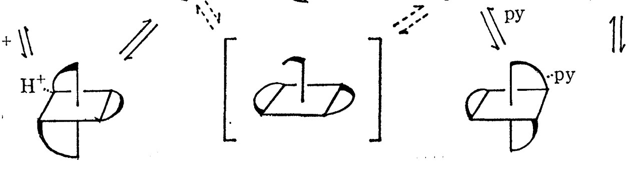

Fig. 6. Plausible mechanism of racemization.

Two possible rate-determining steps can be encountered whenever an intermediate with coordination number 5 is involved. One is to assume that the bond breaks to give the intermediate as rate-determining step and the intra-molecular rearrangement proceeds fast. An alternative is to regard that one of the bonds of a given ligand breaks and forms quickly and the intra-molecular rearrangement to be the rate-determining step. So far as the intermediate has trigonal bipyramidal structure, the intra-molecular rearrangement will not require big enthalpy, and we can presume that the break of the first bond of one of the ligands will be the rate-determining step. From kinetic studies in ^{18}O-labelled water, Muetterties and Wright[11] suggested that the rate-determining step for the aquation of [Si(dbm)$_3$]$^+$ is the break of one of the ligands facilitated by the attack of water upon the carbonyl carbon. This is in line with our result, although the reaction environment differs.

If the break of one of the bonds of a ligand were the rate-determining step, the acid and base catalysis should be understood in such a way that acid or base will affect the metal ligand bond to facilitate its break. Such an action will give lower $\Delta H^{\ddagger}$ values as compared with those in the absence of catalysis. The $\Delta H^{\ddagger}$ values for k_1 and k_2 path are 31.6±0.1 and 29.3±1.9 kcal per mole, respectively. Although the difference is only slightly bigger than the experimental error, acid catalysis can be understood as to facilitate the bond break at the rate-determining step. The difference in $\Delta H^{\ddagger}$ values in the presence and the absence of base catalysis is more marked, although the experimental error must be bigger. Primary and secondary amines change the absorption spectrum of the reaction mixture and seem to bring about net chemical reaction. As Table 2 shows, there is an overall trend that the greater the basicity of a given pyridine base, the greater the catalytic activity with smaller $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values. This may suggest that the base catalysis operates bimolecularly. The possible attack can take place on either the central silicon or the ligand. Bulky molecules such as *l*-strychnine and 2,6-lutidine give remarkable catalytic action, and the attack upon silicon is less likely. Optically active *l*-strychnine catalyzed both Δ- and Λ-complex equally.

In the absence of catalytic action, the racemization proceeds faster in AN(and acetophenone) than in TCE. Such a solvent effect could be understood by considering that AN, as a weak base, gives more marked solvation than TCE, and facilitates the break of the Si–O bond in the rate-determining step.

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[15] P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[16] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958).

[17] R. J. Gillespie, *J. Chem. Soc.*, **1963**, 4672; J. Zemann, *Z. Anorg. Allgem. Chem.*, **324**, 241 (1963); L. Sacconi, *Pure Appl. Chem.*, **17**, 95 (1968).