

the 3s and 3p orbitals will be largely involved in  $\sigma$ -bond formation. However, the extent of 3d orbital mixing into the ring  $\pi$ -system will be unlikely to affect the ordering of  $\pi$ -levels. Certainly in the case of the related  $R_2PS_2N_3$  compounds **7** ab initio Hartree-Fock-Slater calculations indicate that 3d orbitals on phosphorus stabilize the  $\pi$ -system, particularly the upper  $\pi^*$ -levels, but do not change the basic features expected for a pentadienyl-like NSNSN<sup>-</sup> species.<sup>26</sup> By analogy with the spectral assignments reported for the  $R_2PS_2N_3$  system,<sup>26</sup> we propose that the two intense visible absorption bands in  $S_3N_3O_2^-$  correspond to the  $\pi^* \rightarrow \pi^*$  excitations illustrated in Figure 5.

### Summary

The oxidation of the  $S_3N_3^-$  ion by molecular oxygen yields a complex range of products, the identification and characterization of which has been aided by <sup>15</sup>N NMR spectroscopy. The solid-state structures of the  $S_3N_3O^-$  and  $S_3N_3O_2^-$  anions (as the PPN<sup>+</sup> salts) show some structural distortions, but in solution a higher symmetry appears to be achieved (on an

NMR time scale). The origins of the intense visible absorptions exhibited by  $S_3N_3O^-$  and  $S_3N_3O_2^-$  can be understood by considering the expected perturbations on the 10- $\pi$ -electron manifold of  $S_3N_3^-$ . The transitions responsible for the observed absorptions are assigned to  $\pi^* \rightarrow \pi^*$  type excitations.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada, the National Science Foundation EPSCOR program, and the University of Arkansas Research Committee for financial support. We are also grateful to the NSERCC for a University Research Fellowship (to R.T.O.).

**Registry No.** 1, 72884-86-7; 2, 81260-54-0; 3, 86176-90-1; 4, 72884-88-9; 5, 86163-11-3; PPN<sup>+</sup>N<sub>3</sub><sup>-</sup>, 38011-36-8; S<sub>4</sub>N<sub>4</sub>O<sub>2</sub>, 57932-64-6.

**Supplementary Material Available:** Tables of hydrogen atom positions, anisotropic thermal parameters for the non-hydrogen atoms, distances and angles within the two (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup> cations, and structure factor amplitudes for (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sup>-</sup> and (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sub>2</sub><sup>-</sup> (23 pages). Ordering information is given on any current masthead page.

Contribution from the Chemistry Department, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980, Japan

## Kinetics of the Racemization of Tris(tropolonato)silicon(IV) Perchlorate in Organic Solvents<sup>†</sup>

TOMOAKI INOUE\*

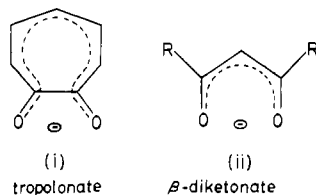
Received August 16, 1982

The racemization of tris(tropolonato)silicon(IV) ion was studied in 1,1,2,2-tetrachloroethane (TCE) and acetonitrile (AN) at 30–70 °C by polarimetry. The reaction is not accompanied by detectable decomposition and ligand substitution of the complex. The following first-order rate constants (s<sup>-1</sup>), activation enthalpies (kcal/mol), and entropies (cal/(K mol)) have been obtained at 50 °C:  $2.0 \times 10^{-5}$ ,  $26.7 \pm 0.7$ ,  $1 \pm 2$  in TCE and  $2.8 \times 10^{-4}$ ,  $25.6 \pm 0.5$ ,  $4 \pm 2$  in AN. The racemization rate is promoted by trichloroacetic acid. The mechanism consistent with the activation parameters and the existence of an acid-catalyzed path is a bond rupture mechanism to give five-coordinate intermediates. An isokinetic plot together with the results of the racemization of tris( $\beta$ -diketonato)silicon(IV) also supports this mechanism.

### Introduction

A bond rupture mechanism to give five-coordinate intermediates has been proposed for intramolecular rearrangement of tris( $\beta$ -diketonato)metal complexes.<sup>1,2</sup> In contrast to this dissociative mechanism, Holm and co-workers<sup>3</sup> proposed a twisting mechanism (with no bond breaking) in the racemization of tris(tropolonato)metal complexes.

We have investigated the racemization kinetics of tris(tropolonato)silicon(IV) ([SiT<sub>3</sub>]<sup>+</sup>)<sup>4</sup> in order to determine the effects of the tropolonato chelate on the activation parameters and mechanism and to provide a comparison with the kinetic behavior of Co(III) and Al(III) tropolonato complexes. As i and ii show, tropolanate is sterically constrained to be a planar



and five-membered chelate ring in contrast to the flexible, six-membered  $\beta$ -diketonate ligand. These differences had also

led us to compare the kinetics of [SiT<sub>3</sub>]<sup>+</sup> with those of [Si( $\beta$ -dik)<sub>3</sub>]<sup>+</sup>.<sup>5</sup>

### Experimental Section

**Reagents.** Tropolone and 3-isopropyltropolone were kindly supplied by Professors Toshio Mukai and Kahei Takase in our department. We prepared tropolone following the literature procedure.<sup>6</sup> The purifications of TCE, An, pyridine, and trichloroacetic acid are described in ref 5.

**Partial Resolution.** [SiT<sub>3</sub>]<sup>+</sup> was first resolved by Ito et al.<sup>7</sup>, but the method was not given. We resolved the complex with di-benzoyl-*d*-tartaric acid as follows: The complex chloride (2 g) dissolved in water (340 mL) was cooled in an ice bath. The resolving agent (0.755 g, 1/2 equiv of the complex) in 0.2 M aqueous sodium hydroxide solution (26 mL) was gradually added to the complex solution. The

- (1) J. G. Gordon II and R. H. Holm, *J. Am. Chem. Soc.* **92**, 5319 (1970).
- (2) A. Y. Girgis and R. C. Fay, *J. Am. Chem. Soc.*, **92**, 7061 (1970). S. S. Minor and G. W. Everett, Jr. *Inorg. Chem.*, **15**, 1526 (1976).
- (3) (a) S. S. Eaton, J. R. Hutchison, R. H. Holm, and E. L. Muetterties, *J. Am. Chem. Soc.* **94**, 6411 (1972). (b) S. S. Eaton, G. R. Eaton, R. H. Holm, and E. L. Muetterties, *Ibid.*, **95**, 1116 (1973).
- (4) Abbreviation of ligands: T, tropolonate; 2-C<sub>3</sub>H<sub>5</sub>T, 2-isopropenyltropolonate; 2-C<sub>3</sub>H<sub>7</sub>T, 2-isopropyltropolonate; 2-RT, 2-substituted tropolonate;  $\beta$ -dik,  $\beta$ -diketonates; acac, acetylacetonate; dprm, 3,5-heptanedionate; dbm, 1,3-diphenyl-1,3-propanedionate; Me-dprm, 3-methyl-3,5-heptanedionate; Me-acac, 3-methyl-2,4-pentanedionate; tfac, 1,1,1-trifluoro-2,4-pentanedionate; hfac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; triac, 3-acetyl-2,4-pentanedionate; dibm, 2,6-dimethyl-3,5-heptanedionate.
- (5) (a) T. Inoue and K. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 2417 (1973); (b) T. Inoue, J. Fujita, and K. Saito, *Ibid.*, **48**, 1228 (1975).
- (6) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Sci. Rep. Tohoku Univ. Ser. 1*, **36**, 126 (1952).
- (7) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Inorg. Nucl. Chem. Lett.* **5**, 781 (1969).

\* To whom correspondence should be addressed at Zama High School, Iriya, Zama Kanagawa-ken 228, Japan.

<sup>†</sup> Taken in part from T. Inoue, Ph.D. Thesis, Tohoku University, 1974.

Table I. Rate Constants and Activation Parameters for the Racemization of  $[\text{SiT}_3]^+$  in TCE and AN

temp ( $\pm 0.1$ °C)	solvent			
	TCE		AN	
	$k_1/10^{-6}$ s $^{-1}$	$k_2$ (by $\text{CCl}_3\text{COOH}$ )/ $10^{-5}$ M $^{-1}$ s $^{-1}$	$k_1/10^{-5}$ s $^{-1}$	$k_2$ (by $\text{CCl}_3\text{COOH}$ )/ $10^{-5}$ M $^{-1}$ s $^{-1}$
70	262			
60	66.9	223		
50	17.7	63.5	26.5	24.5
45		33.5	14.8	10.0
40	4.79	19.9	7.75	5.55
35			3.74	2.85
30	1.46	5.15	1.84	1.35
$\Delta H^\ddagger/\text{kcal mol}^{-1}$	$26.2 \pm 0.7$	$24.4 \pm 0.5$	$25.6 \pm 0.5$	$26.8 \pm 2$
$\Delta S^\ddagger/\text{eu}$	$0.9 \pm 2$	2.1	$4.1 \pm 1.7$	7.5
$k$ (interpolated to 50 °C)	$2.01 \times 10^{-5}$	$6.61 \times 10^{-4}$	$2.77 \times 10^{-4}$	$2.22 \times 10^{-4}$

reddish brown precipitate of dibenzoyl-*d*-tartrate,  $(-)_\text{D}$ - $[\text{SiT}_3]$ -*d*- $\text{C}_{18}\text{H}_{13}\text{O}_8$ , was removed by filtration. Sodium perchlorate monohydrate (2 g) was added to the filtrate. The resulting precipitate was filtered and dried. The product was recrystallized from the AN (20 mL)-chloroform (5 mL) mixture solution by an addition of ethyl ether (60 mL). A 0.19-g quantity of  $(+)_\text{D}$  enantiomer,  $(+)_\text{D}$ - $[\text{SiT}_3]\text{ClO}_4$ , was obtained.  $\Delta\epsilon$  at 365 nm was 41. The  $(+)_\text{D}$  enantiomer is assigned to the  $\Lambda$  configuration.<sup>7</sup>

**Kinetics.** The reaction solution in AN was prepared by dissolving 13 mg of  $(+)_\text{D}$ - $[\text{SiT}_3]\text{ClO}_4$  with the necessary amount of water and/or pyridine or trichloroacetic acid and making up to 10 mL in a volumetric flask. The solution was evenly distributed in four small test tubes, which were then sealed with silicon rubber stoppers. All processes mentioned above were carried in a drybox. The tubes placed in a thermostated bath were removed at predetermined time intervals. Upon removal from the bath, the tubes were immediately cooled in a freezing mixture of salt and ice. The optical rotations were determined at 405 nm, and the absorbances at 310 nm were measured after a 1:100 dilution.

For the reaction in TCE, the original solution was prepared by dissolving 15 mg of  $(+)_\text{D}$ - $[\text{SiT}_3]\text{ClO}_4$  in 50 mL of TCE. A 1-mL aliquot of this solution was diluted to 10 mL with TCE and the necessary amount of water and pyridine and/or trichloroacetic acid. The final solution was evenly distributed in four small test tubes and sealed. The reaction took place in a thermostated bath. After the tubes were cooled as above, the CD strengths at 365 nm and the absorbances at 312 nm were measured.

The observed first-order rate constant ( $k_0$ ) for

$$\Lambda \frac{k_0}{k_0} \Delta$$

was calculated from  $k_0 = (1/2t) \ln (\alpha_0/\alpha_t)$  (where  $\alpha_0$  and  $\alpha_t$  are the optical rotations or CD strengths at times zero and  $t$ , respectively).

$^1\text{H}$  NMR spectroscopy was employed to examine the substitution of  $[\text{SiT}_3]^+$  by 3-isopropyltropolone. The complex perchlorate (10 mg) was dissolved in  $\text{An-d}_3$  (0.9 mL) and 0.97 M trichloroacetic acid in AN (0.2 mL) together with 3-isopropyltropolone (6.5 mg) in a NMR tube. The tube was kept in a thermostat at 50 °C. The  $^1\text{H}$  NMR spectra were recorded at regular intervals. The reaction rate could be calculated from the McKay equation.<sup>8</sup> Owing to the limited complex solubility, the similar  $^1\text{H}$  NMR study in TCE was not possible.

**Apparatus.** A Hitachi 323 spectrometer and Varian A-60-D and HA-100 spectrometers were used for the measurements of electronic absorption and  $^1\text{H}$  NMR spectra, respectively. Other apparatus have been described in ref 5.

## Results and Discussion

The first-order rate plots of the CD strength or the optical rotation were linear in both solvents. However, the absorption at 310 or 312 nm did not change appreciably during the reaction period. Hence, the decrease in CD strength or optical rotation must be owing to the racemization. The linearity of the first-order rate plots implies that the racemization rate is first order for the complex concentration. The observed rate constant,  $k_0$ , was independent of the complex concentration

in the range of  $(2 \times 10^{-5})$ – $(2 \times 10^{-4})$  M in TCE at 60 °C and  $(5 \times 10^{-5})$ – $(5 \times 10^{-3})$  M in AN at 40 °C. Free ligand and water in TCE ( $(0$ – $3) \times 10^{-4}$  M and 0.005–0.05 M) and in AN (0–0.03 M and 0.01–0.04 M) did not affect the reaction rate.

The racemization was catalyzed by trichloroacetic acid in both solvents. Therefore,  $k_0$  may be expressed as  $k_0 = k_1 + k_2[\text{acid}]$ . Pyridine had no influence on  $k_0$  up to 0.5 M in TCE solutions and 11 M in AN solutions. The rate constants and the activation parameters are summarized in Table I.

Because of difficulty in the preparation of labeled tropolone, the isotopic ligand-exchange reaction between  $[\text{SiT}_3]^+$  and labeled tropolone was not examined. Hence, the intermolecular reaction rate of the complex was inferred from the substitution reaction rate between  $[\text{SiT}_3]^+$  and 3-isopropyltropolone.  $^1\text{H}$  NMR spectra of both 3-isopropyltropolone and its tris chelate silicon(IV) complex showed a doublet in the methyl proton region. The chemical shifts of the free ligand were 1.20 and 1.31 ppm, while in the complex<sup>9</sup> they appeared at 1.27 and 1.40 ppm from the tetramethylsilane reference. Therefore, the substitution reaction by 3-propyltropolone is manifested in the spectrum. We found no exchange over the period of 3 half-lives of the racemization reaction. If the racemization of  $[\text{SiT}_3]^+$  were to proceed intermolecularly, the rates of the substitution by 3-propyltropolone should be equal to that of the racemization. The  $\text{p}K_a$  of 3-isopropyltropolone ( $\text{p}K_a = 7.21$ ) is similar to that of tropolone ( $\text{p}K_a = 6.92$ ) and the isopropyl group seems not to interfere with the coordination of the ligand sterically, because it is fairly far from the coordinating oxygens of the ligand. Therefore, in general an intermolecular reaction rate of  $[\text{SiT}_3]^+$  seems to be very slow and the racemization is suggested to proceed intramolecularly. Muetterties and Alegranti<sup>11</sup> examined the intermolecular exchange reaction between 2- or 3-methyltropolone and their tris chelate silicon(IV) complexes in TCE by  $^1\text{H}$  NMR spectroscopy and did not find any exchange at 146 °C. This is further evidence that the intermolecular reactions of Si(IV) complexes of tropolonates are very slow. It is reasonable to presume that the racemization of  $[\text{SiT}_3]^+$  occurs intramolecularly.

Intramolecular reaction may proceed with (bond rupture (BR) mechanism) or without (non-bond-rupture (non-BR) mechanism) rupture of a coordination bond.<sup>12</sup> We believe

(9) The complex should be a mixture of geometrical isomers (facial and meridional). Hence, there are four kinds of isopropyl groups. Since each methyl group is diastereotopic, eight kinds of methyl groups exist. However, only one doublet signal was observed. It must be due to doubling between methyne and methyl protons. The differences of chemical shift between geometrical isomers or/and diastereomers must be very small.

(10) Y. Ikegami, T. Ikegami, and S. Seto, *Kogyo Kagaku Zasshi*, **68**, 1417 (1965).

(11) E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, **91**, 4420 (1969).

(12) J. J. Fortman and R. E. Sievers, *Coord. Chem. Rev.*, **6**, 131 (1971).

(8) H. A. McKay, *Nature (London)* **142**, 997 (1939).

Table II. Rate Constants and Activation Parameters of Racemization of the  $[\text{Si}(\text{O})_6]^+$  Complex at 50 °C

no.	complex	TCE			AN			TCE			ref
		$k_1/10^{-5}$ s <sup>-1</sup>	$\Delta H^\ddagger/\text{kcal}$ mol <sup>-1</sup>	$\Delta S^\ddagger/\text{eu}$	$k_1/10^{-5}$ s <sup>-1</sup>	$\Delta H^\ddagger/\text{kcal}$ mol <sup>-1</sup>	$\Delta S^\ddagger/\text{eu}$	$k_2^a/10^{-5}$ M <sup>-1</sup> s <sup>-1</sup>	$\Delta H^\ddagger/\text{kcal}$ mol <sup>-1</sup>	$\Delta S^\ddagger/\text{eu}$	
1	$[\text{Si}(\text{Me-acac})_3]^+$	20	34.1 ± 1	29.9	181	27.5 ± 1	13.6	192	27.7 ± 1	14.5	5b
2	$[\text{Si}(\text{Me-dprm})_3]^+$	4.4	28.2 ± 1	8.6	49	24.8 ± 1	3.0	25	27.7 ± 1	10.6	5b
3	$[\text{SiT}_3]^+$	2.0	26.2 ± 0.7	0.9	28	25.6 ± 0.5	4.1	66	24.4 ± 0.5	2.1	this work
4	$[\text{Si}(\text{acac})_3]^+$	0.48	31.6 ± 0.1	14.6	3.9	25.7 ± 0.2	0.5	14	29.3 ± 2	14	5a
5	$[\text{Si}(\text{dprm})_3]^+$	0.18	32.7 ± 1	16.2	2.4	23.7 ± 1	-6.7	2.2	25.0 ± 1	-2.8	5b
6	$[\text{Si}(\text{dbm})_3]^+$	0.11	32.4 ± 1	14.3	5.5	25.0 ± 1	-0.8	0.7	25.0 ± 1	-5.1	5b

<sup>a</sup>  $k_2$  is by trichloroacetic acid.

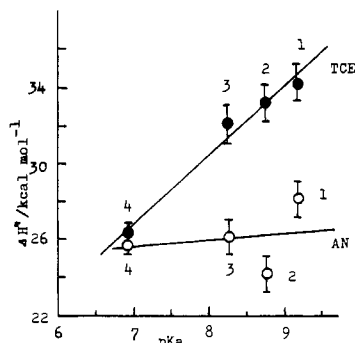


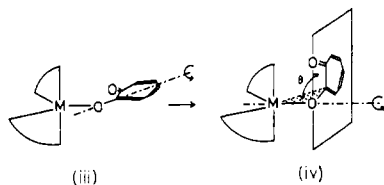
Figure 1. Relationship between  $pK_a$  of enol forms of  $\beta$ -diketones and tropolone and  $\Delta H^\ddagger$  of the racemization of their tris-type complexes of Si(IV): (1)  $[\text{Si}(\text{Me-acac})_3]^+$ ; (2)  $[\text{Si}(\text{dprm})_3]^+$ ; (3)  $[\text{Si}(\text{acac})_3]^+$ ; (4)  $[\text{SiT}_3]^+$ .

that the BR mechanism is more consistent with the observations on the racemization of  $[\text{SiT}_3]^+$  for reasons elaborated below.

The main characteristics of the racemization of  $[\text{SiT}_3]^+$  are (1) a  $k_2$  value relatively larger than those for  $[\text{Si}(\text{Me-dprm})_3]^+$ ,  $[\text{Si}(\text{acac})_3]^+$ ,  $[\text{Si}(\text{dprm})_3]^+$ , and  $[\text{Si}(\text{dbm})_3]^+$  (Table II) and (2) the existence of an acid-catalyzed path even in AN (Table I). An acid-catalyzed path for  $[\text{Si}(\beta\text{-dik})_3]^+$  was not observed in AN. The reason seems to be that the acid is weakened by the solvation by AN.<sup>5</sup> Such a weakened acid in AN catalyzed the racemization of  $[\text{SiT}_3]^+$ . Clearly, trichloroacetic acid in TCE catalyzed strongly the racemization. The large  $k_2$  value could be due to a small value of  $\Delta H^\ddagger$  and the sterically unrestricted approach by the acid to the complex. Such an acid-catalyzed path is in accord with the BR mechanism. As in the case of the racemization of  $[\text{Si}(\beta\text{-dik})_3]^+$ , the proton can attach to the coordinating oxygen of a chelate, weakening the coordination bond. Table I shows a 2 kcal/mol smaller value of  $\Delta H^\ddagger$  for the  $k_2$  path than for the  $k_1$  path in TCE. The proton also interferes with the recombination of the dangling ligand to Si(IV) ion by attaching to the free oxygen atom of the dangling ligand.

The  $k_1$  path also seems to racemize via the BR mechanism. The smaller  $\Delta H^\ddagger$  value for the  $k_1$  path in  $[\text{SiT}_3]^+$  than in  $[\text{Si}(\beta\text{-dik})_3]^+$  in TCE results from the smaller  $pK_a$  of tropolone (Figure 1).

The consideration of molecular models supports the possibility of the BR mechanism for  $[\text{SiT}_3]^+$ : a coordination bond breaks and then the dangling ligand may rotate along the O-C axis (iii); this is followed by the rotation along the M-O axis



(iv) when the dihedral angle reaches about 90°. When a

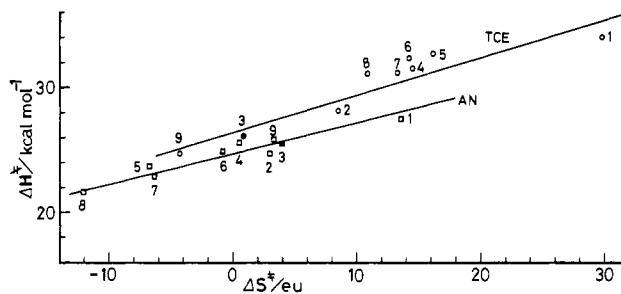
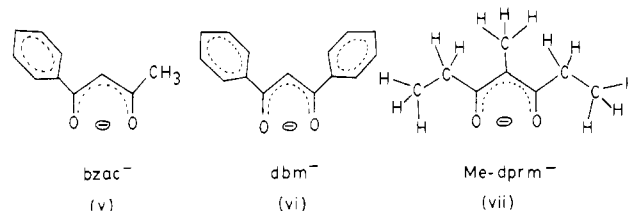


Figure 2. Isokinetic plot for the racemization and isomerization of  $[\text{Si}(\beta\text{-dik})_3]^+$  and  $[\text{SiT}_3]^+$  ( $k_1$  path, at 50 °C; (O) in TCE, (□) in AN): (1-6) numbers as in Table II; (7) racemization of  $fac\text{-}[\text{Si}(\text{bzac})_3]^+$ ; (8) isomerization of  $[\text{Si}(\text{bzac})_3]^+$  ( $fac \rightarrow mer$ ); (9) racemization of  $mer\text{-}[\text{Si}(\text{bzac})_3]^+$ .

coordination bond breaks, the deformation of the M-O-C angle is necessary. The deformation, however, does not preclude the BR mechanism, because a similar deformation is required in the BR mechanism for the racemization of  $[\text{Si}(\beta\text{-dik})_3]^+$ .

From the above discussion, the racemization of  $[\text{SiT}_3]^+$  seems to proceed via the BR mechanism. As Miller et al.<sup>13</sup> pointed out, if some reactions proceed via a common mechanism, the plot of  $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$  gives a linear relation:  $\Delta H^\ddagger = T(\Delta S^\ddagger) + \Delta F^\ddagger$ , where the slope is the so-called "isokinetic temperature". Such an isokinetic plot for  $[\text{SiT}_3]^+$  and  $[\text{Si}(\beta\text{-dik})_3]^+$  was reasonably linear in both solvents (Figure 2). The isokinetic temperatures were 297 and 250 K in TCE and AN, respectively. Therefore, the racemization of  $[\text{SiT}_3]^+$  and  $[\text{Si}(\beta\text{-dik})_3]^+$  may have a common mechanism. This appears to be the BR mechanism, and the rate-determining step is a coordination bond break.

The small  $\Delta S^\ddagger$  for  $[\text{SiT}_3]^+$  seems to be due to the rigid dangling ligand in contrast to the flexible one of the  $\beta$ -diketonates. Base catalysis by pyridine was observed in the case of  $[\text{Si}(\text{bzac})_3]^+$ <sup>14</sup> but not in the case of  $[\text{Si}(\text{dbm})_3]^+$ :



- (13) J. D. Miller and R. H. Prince, *J. Chem. Soc. A*, 1048 (1966); J. E. Leffer and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, 1963, Chapter 9; D. Thusius, *Inorg. Chem.*, **10**, 1106 (1971); T. W. Newton and F. B. Baker, *Adv. Chem. Ser.*, No. 71, 268 (1967).
- (14) T. Inoue, to be submitted for publication.
- (15) B. Jurado and C. S. Springer, Jr., *J. Chem. Soc. D* 85 (1971); M. Pickering, B. Jurado and C. S. Springer, Jr., *J. Am. Chem. Soc.*, **98**, 4503 (1976).
- (16) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).
- (17) R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Am. Chem. Soc.*, **92**, 7056 (1970).

Table III. Rate Constants and Activation Parameters of Rearrangement of Co(III), Al(III), and Ga(III) Complexes

no.	compd	process	solvent	$k/s^{-1}$ (temp/°C)	$\Delta H^\ddagger/kcal$ mol <sup>-1</sup>	$\Delta S^\ddagger/eu$	ref
1	Co(tfac) <sub>3</sub>	isom <sup>a</sup>	CHCl <sub>3</sub>	$(5.20 \pm 0.16) \times 10^{-4}$ (90)	$30.1 \pm 0.6$	$8.6 \pm 1.7$	16
2	Co(acac) <sub>3</sub>	racem <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> Cl	$4 \times 10^{-5}$ (90)	$34.2 \pm 0.6$	$14 \pm 2$	17
3	Co(acac) <sub>2</sub> (triac)	racem	C <sub>6</sub> H <sub>5</sub> Cl	$2.1 \times 10^{-4}$ (90)	$33.0 \pm 0.5$	$13 \pm 1$	18
4	Co(triac) <sub>3</sub>	racem	C <sub>6</sub> H <sub>5</sub> Cl	$4.7 \times 10^{-4}$ (90)	$30.4 \pm 1.3$	$9 \pm 1$	18
5	Co(mhd) <sub>3</sub>	isom ( <i>fac</i> → <i>mer</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$(5.75 \pm 1.70) \times 10^{-5}$ (90)	$32.9 \pm 1.1$	$8.7 \pm 2.9$	1
6		isom ( <i>mer</i> → <i>fac</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$(2.75 \pm 0.80) \times 10^{-5}$ (90)	$32.6 \pm 1.4$	$6.3 \pm 3.9$	1
7		racem ( <i>fac</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$(1.00 \pm 0.07) \times 10^{-4}$ (90)	$29.9 \pm 0.6$	$1.5 \pm 1.6$	1
8		racem ( <i>mer</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$(1.50 \pm 0.10) \times 10^{-4}$ (90)	$31.6 \pm 0.7$	$6.8 \pm 1.8$	1
9	Co(bzac) <sub>3</sub>	isom ( <i>fac</i> → <i>mer</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$(8.89 \pm 0.6) \times 10^{-5}$ (90)	$32.0 \pm 0.5$	$11.0 \pm 1.3$	2
10		isom ( <i>mer</i> → <i>fac</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$2.94 \times 10^{-5}$ (90)	$32.0 \pm 0.6$	$8.8 \pm 1.8$	2
11		racem ( <i>fac</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$1.09 \times 10^{-4}$ (90)	$32.2 \pm 0.7$	$11.9 \pm 2.0$	2
12		racem ( <i>mer</i> )	C <sub>6</sub> H <sub>5</sub> Cl	$9.33 \times 10^{-5}$ (90)	$31.6 \pm 0.9$	$10.0 \pm 2.6$	2
13	Co(2-C <sub>3</sub> H <sub>7</sub> T) <sub>3</sub> <sup>g</sup>	racem ( <i>fac</i> )	CHCl <sub>3</sub>	$1.25 \times 10^4$ (90)	$13.7 \pm 1.1$	$-2.1 \pm 3.5$	3a
14		racem ( <i>mer</i> )	CHCl <sub>3</sub>	$4.09 \times 10^4$ (90)	$15.6 \pm 1.4$	$4.8 \pm 3.9$	3a
15		isom ( <i>fac</i> → <i>mer</i> )	CHCl <sub>3</sub>	$4.5 \times 10^2$ (90)	$15.0 \pm 1.3$	$-5.1 \pm 4.2$	3a
16	Co(2-C <sub>3</sub> H <sub>5</sub> T) <sub>3</sub> <sup>g</sup>	racem ( <i>mer</i> )	CDCl <sub>3</sub>	$2.34 \times 10^4$ (90)	$16.2 \pm 1.1$	$5.4 \pm 3.9$	3a
17		isom ( <i>fac</i> → <i>mer</i> )	CDCl <sub>3</sub>	$5.9 \times 10^2$ (90)	$14.9 \pm 1.2$	$-5.3 \pm 3.7$	3a
1	Al(tfac) <sub>3</sub>	isom	CHCl <sub>3</sub>	$3.4 \times 10$ (103)	$22.8 \pm 1.8$	8.5	16
2	Al(acac) <sub>2</sub> (hfac)	site ex <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	$8.0 \times 10$ (25)	$17.8 \pm 0.7$	$10.0 \pm 2.4$	19
3	Al(acac) <sub>2</sub> (dbm)	site ex	<i>o</i> -C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	$2.2 \times 10^{-3}$ (25)	$21.4 \pm 0.6$	$0.9 \pm 1.5$	19
4	Al(acac)(hfac) <sub>2</sub>	site ex	C <sub>6</sub> H <sub>6</sub>	$8.5 \times 10^{-1}$ (25)	$18.4 \pm 1.3$	$2.9 \pm 4.2$	19
5		site ex	CH <sub>2</sub> Cl <sub>2</sub>	$8.6 \times 10^{-1}$ (25)	$20.7 \pm 0.7$	$10.7 \pm 2.2$	19
6		site ex	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	1.5 (25)	$18.9 \pm 0.6$	$5.7 \pm 1.9$	19
7	Al(pmhd) <sub>3</sub>	<i>d, e</i>	C <sub>6</sub> H <sub>5</sub> Cl		$29.4 \pm 1.4$	$19.5 \pm 3.5$	20
8		<i>d, f</i>	C <sub>6</sub> H <sub>5</sub> Cl		$28.8 \pm 1.4$	$17.6 \pm 3.5$	20
9	Al(dibm) <sub>3</sub>	racem	C <sub>6</sub> H <sub>5</sub> Cl	$2.9 \times 10^{-3}$ (25)	$18.3 \pm 1$	$-8.6 \pm 1.5$	15
10	Al(dibm)(hfac) <sub>2</sub>	racem ( <sup>1</sup> H NMR)	CCl <sub>4</sub>	$6.9 \times 10^{-1}$ (25)	$20.7 \pm 1$	$10.3 \pm 3$	15
11		site ex ( <sup>19</sup> F NMR)	C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	$6.0 \times 10^{-1}$ (25)	$21.5 \pm 1$	$12.9 \pm 4$	15
12		racem ( <sup>1</sup> H NMR)	C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub>	$7.1 \times 10^{-1}$ (25)	$20.8 \pm 1.5$	$10.7 \pm 5$	15
13		racem ( <sup>1</sup> H NMR)	C <sub>6</sub> H <sub>5</sub> CF <sub>3</sub> (55 mol %), CH <sub>2</sub> Cl <sub>2</sub> (45 mol %)	1.0 (25)	$21.5 \pm 2$	$13.7 \pm 6.5$	15
14	Al(2-C <sub>3</sub> H <sub>7</sub> T) <sub>3</sub>	racem ( <i>fac</i> )	CHCl <sub>2</sub> CHCl <sub>2</sub>	$1.2 \times 10^2$ (25)	$10.0 \pm 3.6$	$-16 \pm 12$	3a
15		racem ( <i>mer</i> )	CHCl <sub>2</sub> CHCl <sub>2</sub>	$7.5 \times 10$ (25)	$11.7 \pm 2.0$	$-11 \pm 7$	3a
16		isom ( <i>fac</i> → <i>mer</i> )	CHCl <sub>2</sub> CHCl <sub>2</sub>	$4 \times 10^{-2}$ (25)	$25.1 \pm 4.0$	$21 \pm 12$	3a
17	Al(2-C <sub>3</sub> H <sub>5</sub> T) <sub>3</sub>	isom	CHCl <sub>2</sub> CHCl <sub>2</sub>	1.0 (25)	$16.2 \pm 1.0$	$-4.3 \pm 3.2$	3a
18		racem ( <i>fac</i> )	CH <sub>2</sub> Cl <sub>2</sub>	$8.0 \times 10$ (25)	$12.6 \pm 1.4$	$-7.4 \pm 4.8$	5a
1	Ga(tfac) <sub>3</sub>	isom	CHCl <sub>3</sub>	$3.8 \times 10$ (61.5)	$20.1 \pm 1.6$	8.6	16
2	Ga(acac) <sub>2</sub> (hfac)	site ex	CH <sub>2</sub> Cl <sub>2</sub>	$7.7 \times 10^2$ (25)	$14.7 \pm 1.2$	$3.9 \pm 4.6$	19
3	Ga(acac) <sub>2</sub> (dbm)	site ex	C <sub>6</sub> H <sub>6</sub>	$7.7 \times 10^{-2}$ (25)	$19.6 \pm 3.2$	$2.2 \pm 9.3$	19
4	Ga(pmhd) <sub>3</sub>	<i>d, f</i>	C <sub>6</sub> H <sub>5</sub> Cl		$19.7 \pm 1.2$	$3.6 \pm 3.4$	20

<sup>a</sup> Isomerization. <sup>b</sup> Racemization. <sup>c</sup> Site exchange. <sup>d</sup> Mixture of racemization and isomerization. <sup>e</sup> Trigonal-bipyramidal mechanism. <sup>f</sup> Square-pyramidal mechanism. <sup>g</sup> Extrapolated value from the data of ref 3a.

As the electrical difference such as the  $pK_a$  values of  $bzac^+$  and  $dbm^+$  is not large, the steric difference between the methyl group and phenyl group might be related to the catalytic action of pyridine. In spite of the fact that the space along the  $C_3$  axis of  $[SiT_3]^+$  is wide open, the base catalysis was not observed. In contrast, in the case of  $[Si(Me-dpm)_3]^+$ , in spite of the fact that ethyl groups in the ligands block the space along the  $C_3$  axis, the base catalysis was observed. Hence, pyridine seems not to interact with the central  $Si^{4+}$  ion from the space along the  $C_3$  axis. On the other hand, if pyridine interacts from the other spaces, it should also catalyze the racemizations of  $[SiT_3]^+$  and  $[Si(dbm)_3]^+$ . From the above discussion, the catalytic action cannot be explained in terms of the interaction of pyridine with the complex at a ground state.

Since the noncatalyzed path ( $k_1$ ) and the case-catalyzed path ( $k_2$ ) in the racemization of  $[Si(\beta-dik)_3]^+$  in AN have closely similar values for their activation enthalpies and the  $k_2$  path has a positive activation entropy (about 18 cal/(mol K)), the base might interact on the vacant coordination site of five-coordinate intermediates after the rate-determining step.

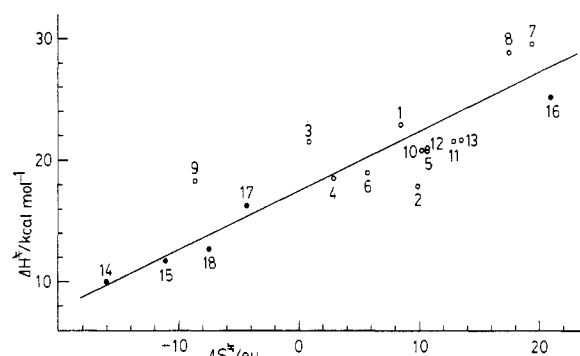


Figure 3. Isokinetic plot for the intramolecular rearrangement of Al( $\beta$ -dik)<sub>3</sub> (O) and Al(2-RT)<sub>3</sub> (●) complexes. Numbers and conditions are the same as in Table III.

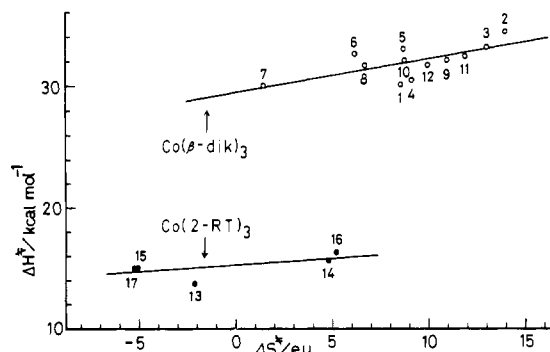
If this is true, in the cases of  $[SiT_3]^+$  and  $[Si(dbm)_3]^+$ , pyridine might be unable to approach the intermediates for a certain steric reason. The reason cannot be discussed any more from this study.

Table III shows rate constants and activation parameters of the racemization and the isomerization of Co(2-C<sub>3</sub>H<sub>5</sub>T)<sub>3</sub>, Co(2-C<sub>3</sub>H<sub>7</sub>T)<sub>3</sub>, Al(2-C<sub>3</sub>H<sub>5</sub>T)<sub>3</sub>, and Al(2-C<sub>3</sub>H<sub>7</sub>T)<sub>3</sub>.<sup>3</sup> The differences in the kinetic parameters between the  $[SiT_3]^+$  complex and Co(III) and Al(III) complexes are extremely large. The rates and the activation enthalpies of the latter are  $10^8$ – $10^{10}$  times and  $1/3$ – $1/2$  times those of the former, re-

(18) U. Klabunde and R. C. Fay, "Abstracts of Papers", 156th National Meeting of the American Chemical Society, Atlantic City, NJ, Sept 1968, No. INOR 37.

(19) D. A. Case and T. J. Pinnavaia, *Inorg. Chem.*, **10**, 482 (1971).

(20) J. R. Hutchison, J. G. Gordon, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).



**Figure 4.** Isokinetic plot for the intramolecular rearrangement of  $\text{Co}(\beta\text{-dik})_3$  (○) and  $\text{Co}(2\text{-RT})_3$  (●) complexes. Numbers and conditions are the same as in Table III.

spectively. An exception occurs for the isomerization of  $\text{Al}(2\text{-C}_3\text{H}_7\text{T})_3$ . The differences suggest there might be some differences in mechanisms. If the isomerization of  $\text{Al}(2\text{-C}_3\text{-H}_7\text{T})_3$  occurs by means of the BR mechanism,<sup>3a</sup> the similarity in  $\Delta H^\ddagger$  in the cases of both  $\text{Al}(2\text{-C}_3\text{H}_7\text{T})_3$  and  $[\text{SiT}_3]^+$  suggests that the racemization of  $[\text{SiT}_3]^+$  also occurs by means of the BR mechanism.

We can compare mechanisms of tropolonato and  $\beta$ -diketonato complexes for only the three cases of Si(IV), Al(III), and Co(III). In the case of Si(IV) complexes, the racemizations of both tris(tropolonato) and tris( $\beta$ -diketonato) complexes proceed via the BR mechanism as discussed above. For Al(III) complexes, the linearity (isokinetic temperature 500

K) of the isokinetic plot (Figure 3) suggests that the common mechanism of both racemizations is the BR mechanism. In contrast, Co(III) complexes show huge differences between  $\text{Co}(2\text{-RT})_3$  and  $\text{Co}(\beta\text{-dik})_3$ . The value of  $\Delta H^\ddagger$  for  $\text{Co}(2\text{-RT})_3$  is half that of  $\text{Co}(\beta\text{-dik})_3$ , and the rate is around  $10^{11}$  times that of the latter. The isokinetic plot (figure 4) places the tropolonato and  $\beta$ -diketonato complexes in different mechanistic groups. The isokinetic temperatures for  $\text{Co}(2\text{-RT})_3$  and  $\text{Co}(\beta\text{-dik})_3$  were 110 and 267 K. This evidence suggests there are different mechanisms in the case of Co(III) complexes. Since it is reasonable for  $\text{Co}(\beta\text{-dik})_3$  to racemize via the BR mechanism,<sup>1,2</sup>  $\text{Co}(2\text{-RT})_3$  may racemize via the non-BR mechanism.

As the variations of the rate constants and activation parameters of Ga(III) and Al(III) complexes are similar, we propose that  $\beta$ -diketonato complexes of both main-group and transition metals and tropolonato complexes of main-group metals racemize via the BR mechanism, intramolecularly, but that the tropolonato complexes of transition metals racemize via the non-BR mechanism, intramolecularly.

**Acknowledgment.** The author expresses thanks to Professors Toshio Mukai and Kahei Takase for their kind supply of tropolone, to Professors Junnosuke Fujita and Kazuo Saito and Drs. Hiroaki Kido, Motoyasu Saito, and Kazuko Takahashi and to Professor John F. Endicott (Department of Chemistry, Wayne State University, Detroit, MI) for their useful discussions, and the Ministry of Education of Japan for a grant in aid.

**Registry No.**  $[\text{SiT}_3]\text{ClO}_4$ , 86308-23-8; trichloroacetic acid, 76-03-9.

Contribution from the Department of Chemistry,  
University of Pittsburgh, Pittsburgh, Pennsylvania 15260

## Metal-to-Ligand Charge-Transfer Spectra of Pentacyanoruthenate(II) Complexes of Aromatic Nitrogen Heterocycles

CRAIG R. JOHNSON and REX E. SHEPHERD\*

Received October 21, 1982

The MLCT transitions of  $(\text{CN})_5\text{Ru}^{3+}$ ,  $(\text{CN})_5\text{Fe}^{3+}$ , and  $(\text{NH}_3)_5\text{Ru}^{2+}$  complexes of aromatic nitrogen heterocycles (L) correlate linearly with the reduction potentials of these ligands and the Hammett substituent constants,  $\sigma_p$ . The  $(\text{CN})_5\text{FeL}^{3+}$  complexes are most sensitive to the nature of L. Comparisons are also made to the  $\text{W}(\text{CO})_5\text{L}$  and  $(\text{NH}_3)_5\text{OsL}^{2+}$  complexes where the  $\text{W}(0)$  complex follows trends established by the parent series but the Os(II) complexes do not. A simple MO description of these complexes is given to account for the trends of the MLCT transitions for metal centers vs. metal centers and for a given metal center with altering the "spectator ligand" set. Back-bonding capabilities of the  $(\text{CN})_5\text{Fe}^{3+}$ ,  $(\text{CN})_5\text{Ru}^{3+}$ , and  $(\text{CO})_5\text{W}$  moieties are found to be about the same (<10% mixing); these may be classed as "hard" centers toward L. The results for the  $(\text{NH}_3)_5\text{OsL}^{2+}$  series show that orbital mixing is sufficient to best describe the observed transitions as ligand-to-metal based, with  $(\text{NH}_3)_5\text{Os}^{2+}$  as a "soft" center toward L. The hardening influence of  $\text{CN}^-$  toward Fe(II) or Ru(II) is opposite its known softening effect toward Co(III).  $\text{CN}^-$  operates as a  $\sigma - \pi$  donor toward Fe(II) and Ru(II) while only as a  $\sigma$  donor toward Co(III).

### Introduction

Extensive studies have been made on  $(\text{NH}_3)_5\text{RuL}^{2+}$  and  $(\text{CN})_5\text{FeL}^{3+}$  complexes,<sup>1,2</sup> where L represents an aromatic nitrogen heterocycle such as pyridine (py) or pyrazine (pz). These compounds have been well characterized, and their thermal<sup>3</sup> and photochemical<sup>4</sup> reactivities have been investigated. Metal-to-ligand back-bonding has been shown to make

an important contribution to the properties of these complexes. The low-spin  $d^6$  configuration of both series of complexes provides filled orbitals of the proper symmetry to interact with relatively low-energy, unoccupied  $\pi^*$  orbitals on the ligand (L). A notable feature of the UV-visible spectra of these complexes is a strong absorption attributable to a metal-to-ligand charge-transfer (MLCT) transition,  $\pi^* \leftarrow t_{2g}$ .<sup>2,5</sup> The energy of this transition varies with the identity of L in a manner consistent with the ability of the ligand to act as a  $\pi$  acceptor. Studies of complexes where L is a substituted pyridine have shown that electron-releasing substituents increase the energy of the transition while electron-withdrawing substituents decrease the energy.<sup>1a,2b</sup> This is the expected order for a charge

- (1) (a) Ford, P. C. *Coord. Chem. Rev.* **1970**, *5*, 75-99. (b) Taube, H. "Survey of Progress in Chemistry"; Scott, A. F., Ed.; Academic Press: New York, 1973; Vol. 6, Chapter 1.
- (2) (a) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *12*, 1039-1045. (b) Hrepic, N. V.; Malin, J. M. *Ibid.* **1979**, *18*, 409-413.
- (3) (a) Shepherd, R. E.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392-1401. (b) Toma, H. E.; Malin, J. M. *Ibid.* **1973**, *12*, 2080-2083.
- (4) (a) Malouf, G.; Ford, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 601-603; **1977**, *99*, 7213-7221. (b) Figard, J. E.; Peterson, J. D. *Inorg. Chem.* **1978**, *17*, 1059-1063.

- (5) Ford, P.; Rudd, D. F. P.; Gaunder, R.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 1187-1194.