PREPARATION OF SOME NEW GERMANIUM(IV) β-DIKETONATES AND A NUCLEAR MAGNETIC RESONANCE STUDY OF LIGAND EXCHANGE REACTIONS FOR SOME TRIS(β-DIKETONATO) TITANIUM(IV) COMPLEXES

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ABSTRACT

PREPARATION OF SOME NEW GERMANIUM(IV) β-DIKETONATES AND A NUCLEAR MAGNETIC RESONANCE STUDY OF LIGAND EXCHANGE REACTIONS FOR SOME TRIS(β-DIKETONATO)TITANIUM(IV) COMPLEXES

By

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Two new dihalobis(β-diketonato)germanium complexes were prepared. They are: cis- and trans-$Ge(dpm)_2Cl_2$, where dpm is dipivaloylmethanate. This is the first trans isomer of the type $M(dik)_2X_2$, where M is titanium(IV), germanium(IV), or tin(IV) and X is a halogen, to be reported. The isomerization of trans-$Ge(dpm)_2Cl_2$ in benzene is first order and reversible:

$$\text{trans-}Ge(dpm)_2Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{cis-}Ge(dpm)_2Cl_2$$

at 44^0 $k_1 = 9.8 \times 10^{-3}$ min^{-1} and $k_2 = 4.2 \times 10^{-4}$ min^{-1}.

Dihalobis(β-diketonato)germanium complexes react with antimony(V) chloride in glacial acetic acid to give tris-(β-diketonato)germanium(IV) hexachloroantimonate(V). Two new complexes were prepared in this manner, $[Ge(dpm)_3][SbCl_6]$, and $[Ge(bzbz)_3][SbCl_6]$, where bzbz is dibenzoylmethanate.

The reaction of cis-$Ge(dpm)_2Cl_2$ with antimony(V) chloride in methylene chloride was found to be slow enough to isolate a reaction intermediate. The spectral

observations and the analysis indicate that this intermediate is the adduct, $[Ge(dpm)_2Cl_2, SbCl_5]$.

Attempts to observe ligand exchange reactions between tris(acetylacetonato)germanium(IV), $[Ge(acac)_3]^+$, and $[Ge(dpm)_3]^+$ or $[Ge(bzbz)_3]^+$ in dichloromethane solution were unsuccessful. However, the three titanium(IV) systems $[Ti(acac)_3]^+$ - $[Ti(dpm)_3]^+$, $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$, and $[Ti(dpm)_3]^+$ - $[Ti(bzbz)_3]^+$ undergo facile ligand exchange reactions in methylene chloride. For the $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$ system, which was studied in greatest detail, equilibrium constants for the formation of each mixed ligand complex from the parent complexes at 25^0 are equal to the values expected for a random statistical distribution of ligands. Enthalpy and entropy changes for the formation of $[Ti(acac)(bzbz)_2]^+$ and $[Ti(acac)_2(bzbz)]^+$ are, respectively, -0.10 ± 0.17 kcal/mole; 1.83 ± 0.46 eu and -0.04 ± 0.19 kcal/mole; 2.04 ± 0.39 eu. A random scrambling of ligands predicts ΔH = 0.0 kcal/mole and ΔS = 2.18 eu for the formation of each mixed ligand complex.

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To Jim and Mary

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I wish to thank Dr. Thomas J. Pinnavaia, who suggested the research reported here, for his guidance and understanding during the course of this work.

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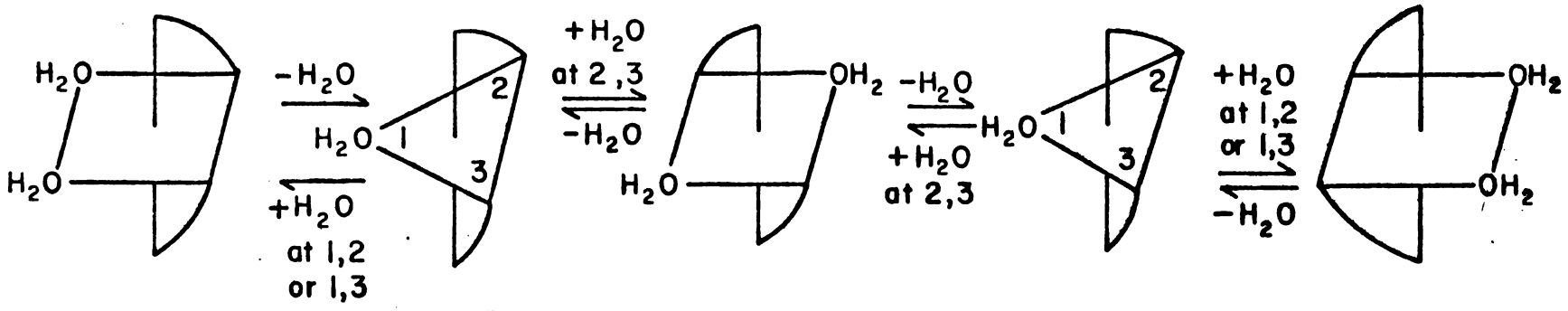
INTRODUCTION

First order racemizations or configurational rearrangements of octahedral complexes may occur *via* three possible routes, ligand dissociation (intermolecular), bond rupture (intramolecular, chelating ligand), and twists (intramolecular). These three possibilities are discussed in detail by Basolo and Pearson (1). Intermolecular ligand dissociation requires the complete departure of a coordinated ligand and its random mixing with any free ligand in solution. As a result the ligand exchange must be as fast or faster than the configurational changes. An example of an intermolecular ligand dissociation process is the isomerization and subsequent racemization of the *cis*-diaquobis-(ethylenediamine)cobalt(III) cation. This is illustrated in Figure 1. In general, metal complexes containing easily replaceable monodentate ligands appear to change configuration by an intermolecular process, whereas, complexes containing only polydentate ligands usually change configuration by an intramolecular process; either bond rupture or twisting. Intramolecular mechansims require that there be no random mixing of coordinated ligand with free ligand. As a result the ligand exchange must be as slow or slower than the configurational changes. The bond rupture process

Figure 1. Intermolecular ligand dissociation mechanism for the isomerization and racemization of $[(+)\text{-}\underline{cis}\text{-}Co(en)_2(H_2O)_2]^{+3}$.



$\left[(+)\text{-cis-Co(en)}_2(H_2O)_2\right]^{+3}$ $\left[\text{trans-Co(en)}_2(H_2O)_2\right]^{+3}$ $\left[(-)\text{-cis-Co(en)}_2(H_2O)_2\right]^{+3}$

involves an opening-closing mechanism of a chelate ring. It has been shown to be the mechanism for the linkage isomerization which occurs in tris(acetylaceylacetonato)-cobalt(III), Figure 2. This type of linkage isomerization, if accomplished in an intramolecular fashion, can only proceed through bond rupture. The twisting mechanisms require that no bonds be broken during the deformation. Two basic types of twist mechanisms have been proposed, the rhombic and the trigonal twist. The ethylenediaminetetraaceto-cobaltate(III) anion is believed to racemize via a trigonal twist with the participation of solvent water, Figure 3. The rhombic twist has been proposed for the racemization of trichlorotris(biguanidinium)cobalt(III), Figure 4.

The original objective of this research was to test the merits of the various twist mechanisms for the racemization of a mixed β-diketonate complex, M(dik)(dik')(dik"). Previous studies of octahedral metal β-diketonates have shown that an intramolecular path is favored in the isomerization and racemization of metal β-diketonates (2-7). The metal moiety of the complexes studied was aluminum, gallium, indium, cobalt, rhodium, chromium, and titanium. The β-diketonate ligands, represented as $R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}R'$, were both the symmetric variety, R = R', and the unsymmetric variety R ≠ R'. The terminal groups R or R' represented methyl, trifluoromethyl or phenyl groups. All compounds were neutral tris(β-diketonato)metal complexes except for those with titanium as the metal moiety, in which case the complexes

Figure 2. Intramolecular bond rupture mechanism for the linkage isomerization of tris(acetylacetylacetonato)cobalt(III).

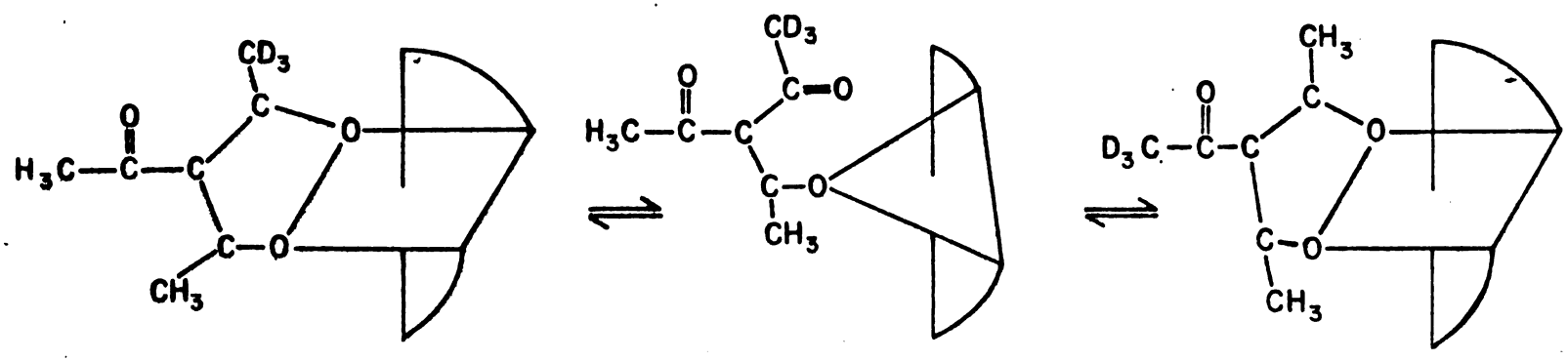

CD3
O
H3C—C—C
C
O
C—O
CH3
CD3
C=O
O
H3C—C—C
C—O
CH3
CH3
O
D3C—C—C
C
O
C—O
CH3

Figure 3. Intramolecular trigonal twist mechanism for the racemization of $[Co(EDTA)]^-$ with the participation of solvent water.

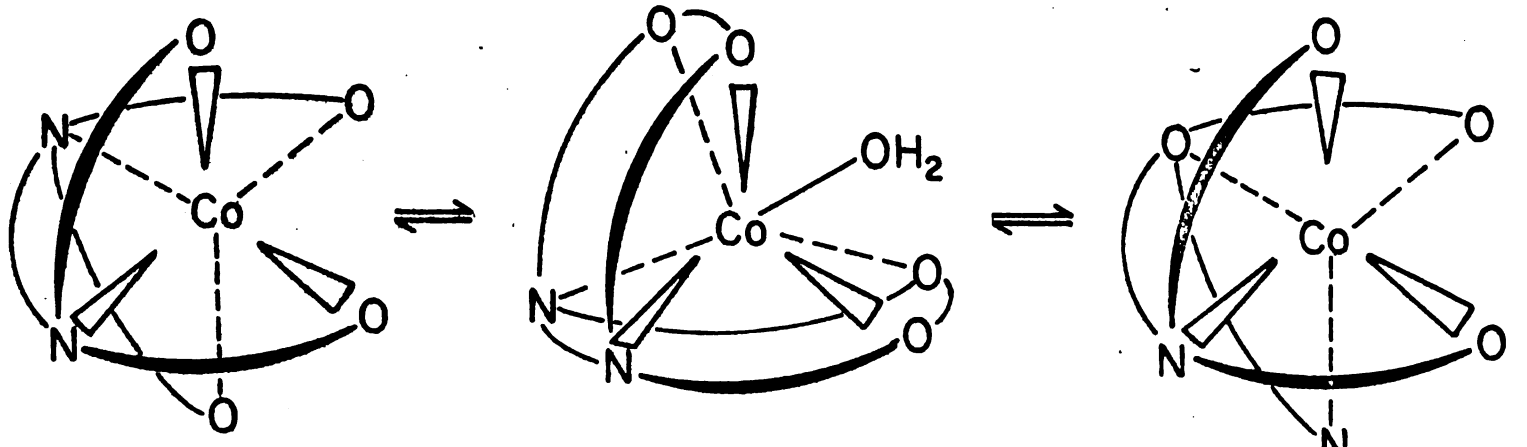
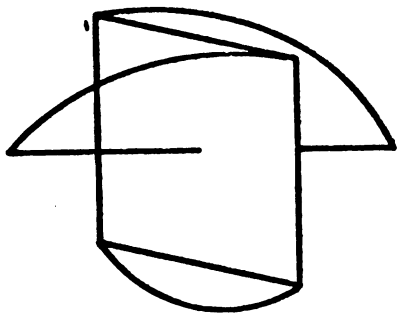
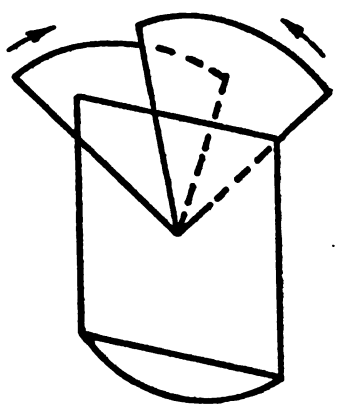
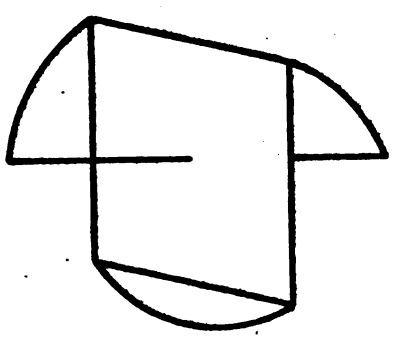

O
O
N
Co
O
N
O
O
dextro
O
O
OH2
Co
N
O
N
O
levo
O
O
O
Co
N
O
N

Figure 4. Intramolecular rhombic twist mechanism for the racemization of $[Co(bigH)_3]^{+3}$.







were dihalobis(β-diketonato)titanium(IV). In these papers nmr spectroscopy has been shown to be an almost ideal method for assignment of geometric configuration of isomers. It can also be used to obtain the equilibrium and rate constants for exchange in these types of β-diketonate complexes. The data in these papers implied that the most probable process for configurational changes in these neutral complexes was intramolecular and proceeded via bond rupture instead of a twist mechanism.

Bond rupture was first proposed by Werner (8). The mechanism involved momentary rupture of one bond to give a five coordinate intermediate with eventual re-formation of the bond to give the isomer of opposite chirality. The required formation of a five coordinate intermediate in the bond rupture mechanism should be more difficult to achieve if the complex initially has a positive charge. Therefore, to enhance the possibility of a twist mechanism and to follow the configurational rearrangements and rates via nmr, the system chosen was a series of cationic tris(β-diketonato)-germanium(IV) complexes. The β-diketones, used as ligands are listed in Table I, together with the abbreviations which will be used. The trivial names are in parentheses.

There are three types of twisting motions, Ray-Dutt (9), Bailar (10), and Springer-Sievers (11), proposed for racemization of octahedral complexes. In the Ray-Dutt or rhombic twist mechanism two chelate rings change position by moving past each other while the third chelate ring remains rigid.

The results are that the R groups on the two rings which have been moved change their environment. The Bailar or trigonal twist mechanism is achieved by twisting the three rings through an angle of 120^0 about one of the C_3 axes of the octahedron. In this case, the environment of all groups on all rings is changed. The Springer-Sievers twist gives the same results as the Bailar twist. In the Bailar twist the oxygen-metal-oxygen bond angle is held constant, whereas, in the Springer-Sievers twist the angle is allowed to expand during deformation. Each twisting mechanism would lead to at least some environmental change of the terminal groups. This is not true for the bond rupture mechanism.

Table I. Nomenclature for β-diketones used as ligands.

Abbreviation	Name	$R-C(=O)-CH_2-C(=O)-R'$ R = R' =
acac	2,4-pentanedione (acetylacetone)	CH_3
dpm	2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane)	t-C_4H_9
hfac	1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone)	CF_3
bzbz	1,3-diphenyl-1,3-propanedione (dibenzoylmethane)	C_6H_5

With the mixed ligand complex $[Ge(acac)(dpm)(hfac)]^+$ the exchange of each ligand can be observed *via* nmr. These nmr studies distinguish only the symmetry of the transition

state but not the actual path followed by the molecule in reaching the transition state. The symmetry of all transitions states due to twisting mechanisms may be generated by twisting 60^0 about each of the psuedo C_3 axes illustrated in Figure 5. A twisting motion of 60^0 about only one of the psuedo C_3 axes will result in a transition state corresponding to the Bailar or Springer-Sievers twist. Rotation about the other axes give transition states corresponding to a Ray-Dutt twist. Examples of these twists are given in Figure 6. Rotation of 120^0 about axis #1 gives the trigonal twist and the nmr spectrum will show a simultaneous coalescence of all terminal groups. Rotation of 120^0 about axes #2, #3 and #4 give the rhombic twist and the spectrum will show coalescence for all terminal groups except trifluoromethyl, t-butyl, and methyl groups respectively. The merit of twisting about any one of the four axes could be evaluated from the determination of the rate of terminal group interchange via nmr line broadening techniques (12).

If the rate of exchange is determined at various temperatures, the activation energy and the frequency factor of the Arrhenius equation can be determined. Ray and Dutt have found that isomerization which involved the rhombic twist gave a frequency factor of 4.2 sec^{-1}. This low value was attributed to the fact that the activation energy must be redistributed to the specific rotational and vibrational degrees of freedom of the bonds concerned in the twisting

Figure 5. Representation of the psuedo C_3 axes of $[Ge(acac)(dpm)(hfac)]^+$

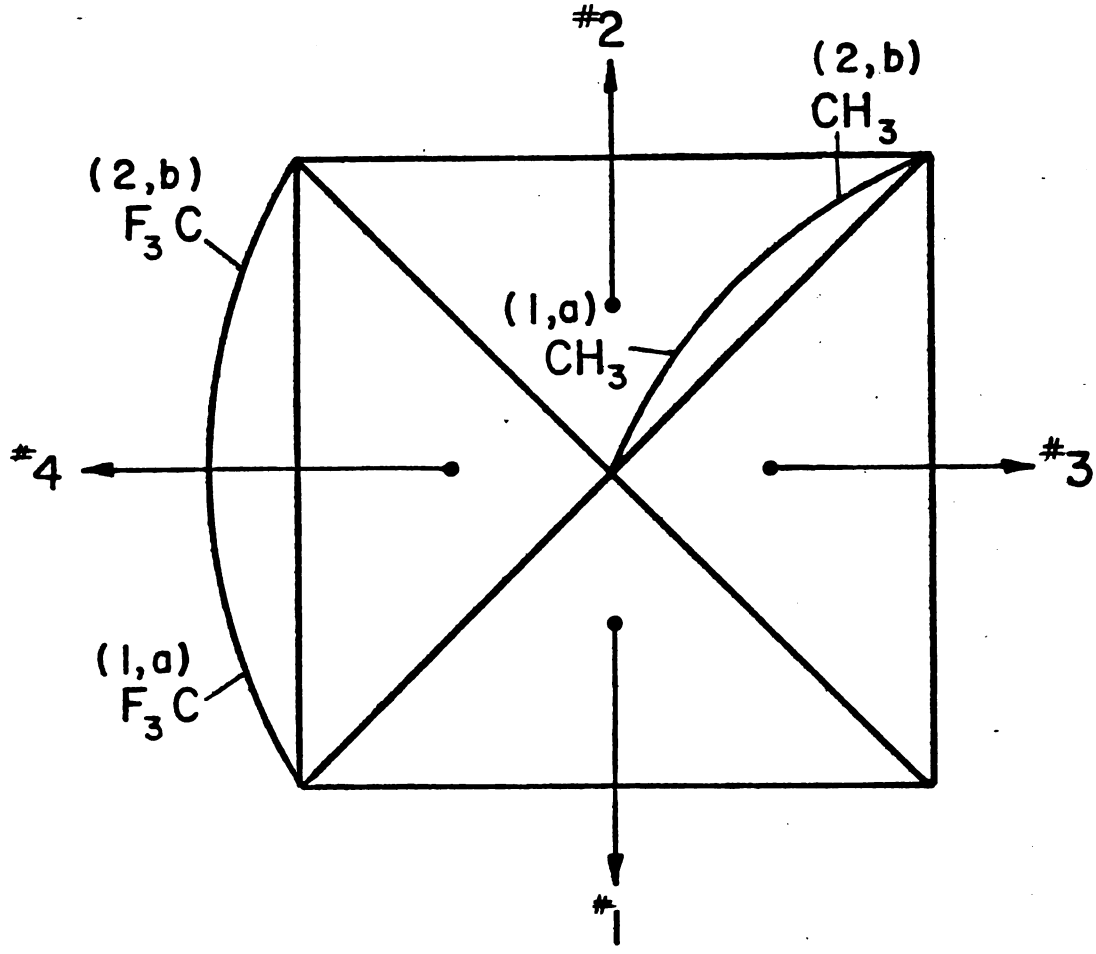
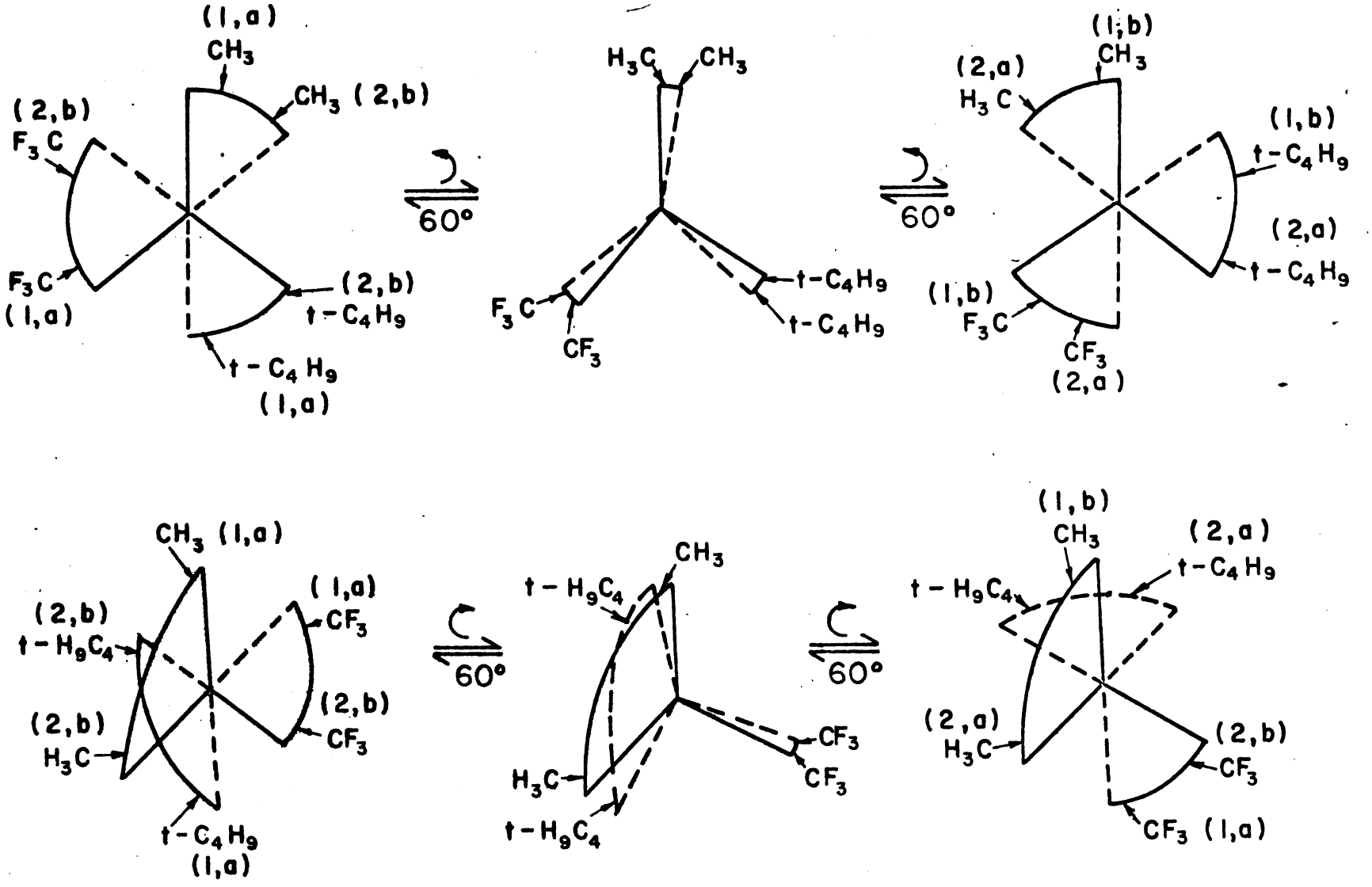

#2
(2,b)
CH3
(2,b)
F3C
(1,a)
CH3
#4
#3
(1,a)
F3C
#1

Figure 6. Examples of rotation about various psuedo C_3 axes of $[Ge(acac)(dpm)(hfac)]^+$.


(1,a)
CH3
CH3 (2,b)
(2,b)
F3C
F3C
(1,a)
(2,b)
t-C4H9
t-C4H9
(1,a)
60°
H3C
CH3
F3C
CF3
t-C4H9
t-C4H9
60°
(1;b)
CH3
(2,a)
H3C
(1,b)
t-C4H9
(2,a)
t-C4H9
(1,b)
F3C
CF3
(2,a)
CH3 (1,a)
(1,a)
CF3
(2,b)
t-H9C4
(2,b)
CF3
(2,b)
H3C
t-C4H9
(1,a)
60°
CH3
t-H9C4
CF3
CF3
H3C
t-H9C4
60°
(1,b)
CH3
(2,a)
t-C4H9
t-H9C4
(2,a)
H3C
(2,b)
CF3
CF3 (1,a)

motion and it is more probable that the energy will be dissipated before this can occur (9). This low frequency factor should hold for twisting mechanisms in general.

The first step of this research was to prepare $[Ge(acac)(dpm)(hfac)]^+$. Mixed ligand complexes are often made by combining solutions of the tris compounds in the ratio of ligand-mix desired in the mixed ligand complex. A large variety of these mixed β-diketonato complexes have been prepared (13-15) in this manner. It was hoped that equilibration of a solution which contained equal molar ratios of $[Ge(acac)_3]^+$, $[Ge(dpm)_3]^+$, and $[Ge(hfac)_3]^+$ would give the desired $[Ge(acac)(dpm)(hfac)]^+$ complex. Fortman and Sievers have prepared the analogous aluminum complex (16).

Unfortunately, $[Ge(hfac)_3]^+$ could not be prepared and as a result the desired mixed ligand complex could not be made. An equimolar solution of $[Ge(acac)_3]^+$ and $[Ge(dpm)_3]^+$ in methylene chloride was allowed to remain at room temperature for ten hours. No mixed ligand complexes were formed. An equimolar mixture of $[Ge(acac)_3]^+$ - $[Ge(bzbz)_3]^+$ in methylene chloride was heated at 210^0 in a sealed tube for eight hours. No mixed ligand complexes were formed. Experiments using the analogous titanium complexes showed formation of mixed ligand complexes but their spectra were unsuitable for kinetic studies. However, the pair $[Ti(acac)_3]^+$-$[Ti(bzbz)_3]^+$ in methylene chloride did give spectra which could be used for thermodynamic studies, and this was done.

Although no thermodynamic or kinetic data could be obtained for a germanium mixed ligand complex some new compounds were made, and some interesting observations on the chemistry of the various germanium complexes were noted. The literature has few papers concerning the chemistry of β-diketonate complexes of germanium (17-21). It appears from our observations that the compounds are, in general, sluggish or inert as compared to their titanium and Group IIIa analogs. The reaction time required for the preparation of the dichlorobis(β-diketonato)germanium(IV) complexes is comparatively longer and they are less sensitive to air than their titanium and tin analogs. Also the tris complexes do not undergo the usual exchange reactions. A possible adduct was discovered which may give a clue to the mechanism which converts the dihalobis(β-diketonato)metal(IV) complexes to the tris(β-diketonato)metal(IV) hexachloroantimonate(V) complexes. In addition, the first solid <u>trans</u> dihalobis-(β-diketonato)metal complex has been prepared and its rate of isomerization has been studied.

II. EXPERIMENTAL

A. Reagents and General Techniques

Germanium(IV) chloride was obtained from several sources. One sample was prepared from arsenic-free germanium dioxide and hydrochloric acid as described by L. S. Forster et al. (22). A yield of 91% was obtained, reported yield, 94%. The compound was also prepared from the elements as described by G. Brauer (23). The yield was only 9.9% because the system was flushed with nitrogen during distillation. Like many metal chlorides, germanium tetrachloride is very volatile and was swept out of the system with the nitrogen. Commercially prepared germanium tetrachloride was used soon after delivery without further purification.

Commercially prepared 1,3-diphenyl-1,3-propanedione and 2,2,6,6-tetramethyl-3,5-heptanedione were used without purification. Acetylacetone was fractionally distilled. The dihydrate of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was mixed with phosphorus pentoxide, allowed to stand overnight, and then the β-diketone was distilled from the mixture.

All glassware was dried in a glass oven at 175^0 and cooled when possible in a desiccator containing calcium

sulfate. Glassware for distillations and reactions had standard tapered joints. The required glassware and techniques used for filtration and recrystallization of these air-sensitive compounds have been described fully by Fay and Pinnavaia (24).

Since both germanium and titanium compounds are susceptible to hydrolysis, all solvents were dried and used freshly distilled when possible.

Chloroform, used primarily in the preparation of the dichlorobis(β-diketonato)germanium(IV) complexes, was dried as follows. A slurry of chromatographic grade aluminum oxide and reagent grade chloroform was made, allowed to sit for thirty minutes, and then decanted. This procedure was repeated twice to ensure dryness and removal of the ethanol, which was present as a stabilizer. The dry chloroform was stored over aluminum oxide and was decanted off as needed. Ethanol-free chloroform was discarded after a week due to the possibility of phosgene formation.

Reagent grade anhydrous diethyl ether was allowed to stand in contact with calcium hydride for four hours, then decanted into a distillation system fitted with a long vigreaux column. The system was swept with nitrogen, and the ether was refluxed for several hours over lithium aluminum hydride. Ether was distilled as needed into oven-dried glassware that was swept with nitrogen. The ether was subsequently handled in a nitrogen atmosphere.

Methylene chloride was used as the solvent in nmr studies and in the preparation of the tris complexes. Reagent grade methylene chloride was allowed to reflux over calcium hydride for approximately twelve hours. The solvent was kept in an inert atmosphere as much as possible.

Benzene, hexane, and dichloroethane were also treated with calcium hydride as described above and used shortly after distillation. Other solvents used were pruified and dried with the procedures described by Weissberger (25). Commercially prepurified nitrogen was used without further drying.

B. Preparations

The standard sequence of reactions involved in the preparation of tris(β-diketonato)germanium(IV) hexachloroantimonates was as follows:

a. $GeCl_4 + 2H(dik)_2Cl_2 \longrightarrow Ge(dik)_2Cl_2 + 2HCl\ (g)$.

b. $3Ge(dik)_2Cl_2 + 2SbCl_5 \longrightarrow 2[Ge(dik)_3][SbCl_6] + GeCl_4$.

Most reactions were found to give more than one crop of crystals and the chemical analyses of products were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

All the bis β-diketonates were prepared *via* reaction "a" and employed analogous techniques. A side arm flask equipped with a reflux condenser and a phosphorus pentoxide drying tube was placed on a hot plate-magnetic stirrer.

Nitrogen was passed through the side arm of the reaction flask containing the previously purified chloroform and the germanium(IV) chloride was added. The solution was stirred, and then the appropriate ligand was added. The resulting solution was refluxed and stirred until hydrion paper indicated that hydrogen chloride gas was no longer being evolved. The reaction was usually refluxed for an additional half hour. Crystallizations and filtrations were performed in an inert atmosphere and all products were dried *in vacuo* at room temperature.

The tris complexes were made *via* reaction "b". Antimony pentachloride was added directly to a side arm flask which contained the bis complex and solvent. Mixing and refluxing when required were accomplished with a hot plate-magnetic stirrer. Glass systems were swept with nitrogen during the reaction. Crystallization and subsequent handling were done in a nitrogen atmosphere to prevent hydrolysis. All samples were dried *in vacuo* for two hours at room temperature.

1. *cis*-Dichlorobis(2,4-pentanedionato)germanium(IV).

This compound was prepared in the manner described by Ong and Prince (20). Germanium tetrachloride (3.9 ml, 34.5 mmoles) was added to 25 ml of chloroform. Acetylacetone (18.0 ml, 18.0 mmoles) was then added to the germanium(IV) chloride solution at room temperature. The mixture was refluxed for three hours and was subsequently cooled in a

dry ice-acetone bath for 0.5 hour. The white crystalline product was filtered under nitrogen, washed with ten ml of cold hexane and dried. The yield was 74%, and the melting point was 228-232°, lit. 236-40° (20) and 238-244° (26). The compound was used in the preparation of the tris complex without further purification.

2. cis-Dichlorobis(2,2,6,6-tetramethylheptanedionato)-germanium(IV).

Dipivaloylmethane (11.0 ml, 56.6 mmoles) was added to a solution of germanium tetrachloride (3.2 ml, 28.3 mmoles) in thirty ml of chloroform. The resulting solution was refluxed for 119 hours. The reaction vessel was periodically swept with nitrogen gas. The compound was found to be very soluble in most solvents. The product was recovered when the volume of chloroform was reduced to half, then hexane was added until a slight turbidity in the warm solution was noted. The flask was then placed in a dry ice-acetone bath for 1.5 hours, after which the fine white crystals were filtered and dried. The yield was 40.2% and the melting point was 135.8-137.8°.

Anal. Calcd. for $Ge(C_{11}H_{19}O_2)_2Cl_2$: C, 51.79; H, 7.52; Cl, 13.90; Ge, 14.23. Found: C, 51.71, H, 7.73; Cl, 14.49; Ge, 14.65.

3. trans-Dichlorobis(2,2,6,6-tetramethylheptanedionato)-germanium(IV).

The trans isomer of $Ge(dpm)_2Cl_2$ was recovered from the reaction mixture after slow crystallization of the cis isomer from methylene chloride-hexane or benzene-hexane solutions. This isomer was also obtained by digestion of the cis isomer in methylene chloride-hexane or benzene-hexane at room temperature. The melting point was 139-140°.

4. cis-Dichlorobis(1,3-diphenyl-1,3-propanedionato)-germanium(IV)

Dibenzoylmethane (13.3 g, 59.2 mmoles) was dissolved in 100 ml of benzene, and then germanium(IV) chloride (3.4 ml, 29.6 mmoles) was added. The solution was refluxed for 110 hours and the system was periodically flushed with nitrogen. The volume was reduced to one-third by passage of nitrogen over the warm solution, at which point a precipitate was formed. The crude product weighed 9.6 g (55% yield) and had a melting point of 259-269°. Recrystallization was attempted from methylene chloride, but after the product was heated in 220 ml of solvent much of the solid remained. The undissolved yellow powder was filtered and then dried. It weighed 5.78 g (33.3% yield) and had a melting point of 274-278°.

Osipov (21) has prepared this compound in a similar manner. Carbon tetrachloride was used as the reaction solvent and the reaction time was about 40 hours. The reported

melting point was 258° which corresponded to the lower limit of the melting point of the crude product described above.

Anal. Calcd. for $Ge(C_{15}H_{11}O_2)_2Cl_2$: C, 60.07; H, 3.30. Found: C, 59.68; H, 3.54.

5. Attempted Preparation of Dichlorobis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)germanium(IV).

All attempts to make $Ge(hfac)_2Cl_2$ were unsuccessful. Neither the method of preparation used for the other bis complexes nor the addition of germanium tetrachloride to 1,1,1,5,5,5-hexafluoro-2,4-pentanedione in the absence of solvent gave a discernible reaction after 120 hours.

Fernelius and Bryant (27) have made several β-diketonate complexes by reaction of the metal chloride with the sodium salt of the desired ligand:

$$2Na + 2H(dik) \longrightarrow 2Na(dik) + H_2(g).$$

$$MCl_4 + 2Na(dik) \longrightarrow M(dik)_2Cl_2 + 2NaCl.$$

Germanium tetrachloride (3.2 ml, 27.2 mmoles) was added to sodium hexafluoroacetylacetonate (12.4 g, 54.4 mmoles) in dioxane and the turbidity of the solution increased. After twelve hours the supernatant was decanted. Crystallization was attempted from dioxane without success. The solvent was then pumped off and a gritty brown and white residue remained. This residue was taken up in 40 ml of methylene chloride and gave a clear dark brown solution. Upon addition of 95 ml of hexane the solution became cloudy. After

the flask cooled in the freezer overnight, the off-white precipitate was filtered and dried in vacuo. The light red-brown mother liquor was evaporated to dryness under vacuum to yield a very small amount of an off-white residue. The two residues were combined and placed in a vacuum sublimer. Sublimation at 80^0 gave a brown oily sublimate and a brown clay-like residue. Examination of the liquid nitrogen trap showed a light yellow oil had frozen out at the top of the trap and a colorless liquid was present in the bottom of the trap. Since none of the four components were sensitive to air, it was concluded that none of them were $Ge(hfac)_2Cl_2$. Of the three methods tried the most promising was the addition of germanium tetrachloride to sodium hexafluoroacetylacetonate.

6. Tris(2,4-propanedionato)germanium(IV)hexachloroantimonate(V).

This compound was first prepared by Cox, Lewis, and Nyholm (19). The reaction solvent was changed from chloroform to methylene chloride. $Ge(acac)_2Cl_2$ (3.6 g, 10.5 mmoles) was added to 120 ml of methylene chloride, and then antimony pentachloride (1.9 ml, 10.5 mmoles) was added. The $Ge(acac)_2Cl_2$ disappeared immediately and the yellow solution was reduced to twenty ml by passing nitrogen over the surface of the solution at room temperature. Crystallization was accomplished by addition of an equal volume of ether to the solution, which was subsequently cooled in a

dry ice-acetone bath. The product was washed with 10 ml of hexane and recrystallized once. A 50% yield with a melting point of 165-167° was obtained, reported; 34%, 165-167° (28).

7. Mixed Complex of Dichlorobis(2,2,6,6-tetramethylheptanedionato)germanium(IV) with Antimony Pentachloride.

$Ge(dpm)_2Cl_2$ (1.43 g, 2.82 mmoles) was dissolved in 100 ml of methylene chloride. Then antimony pentachloride (0.36 ml, 2.82 mmoles) was added to the solution at room temperature. The orange solution was evaporated to 15 ml under a stream of nitrogen then 25 ml of ether was added. After 0.5 hour the white needle crystals were collected and washed with 5 ml of hexane. The crystals were dried in the vacuum line for two hours, and then in an Abderhalden apparatus for four hours, at 80°. The yield was 80.5% and the melting point was 232-234°.

Anal. Calcd. for $Ge(C_{11}H_{19}O_2)_2Cl_2 \cdot SbCl_5$: C, 32.65; H, 4.74; Cl, 30.67. Found: C, 32.85; H, 4.95; Cl, 28.40.

The preparation was repeated and sent for analyses.

Anal. Found: C, 32.36; H, 5.17; Cl, 27.53.

Unfortunately, Galbraith was not notified that the compound was air sensitive. It is felt that this contributed to the poor correlation of calculated versus actual composition.

8. Tris(2,2,6,6-tetramethylheptanedionato)germanium(IV) hexachloroantimonate(V).

$[Ge(dpm)_3][SbCl_6]$ was obtained by reaction of $Ge(dpm)_2Cl_2$ and antimony(V) chloride in glacial acetic acid. $Ge(dpm)_2Cl_2$ (2.8 g, 5.5 mmoles) was dissolved in 40 ml of glacial acetic acid, then antimony pentachloride (0.71 ml, 5.50 mmoles) dissolved in ten ml of glacial acetic acid was added. A fine white precipitate was formed almost immediately. The mixture was refluxed for two hours, then filtered and dried. Recrystallization was accomplished by dissolution of the product in the minimum amount of methylene chloride and addition of hot hexane. The flask was then cooled in the freezer overnight and the yellow, needlelike crystals were filtered and dried. The yield was 46% and the melting point was 275.5-277.5^0(d).

Anal. Calcd. for $[Ge(C_{11}H_{19}O_2)_3][SbCl_6]$: C, 41.41; H, 6.02; Cl, 22.23. Found: C, 45.49; H, 6.66; Cl, 20.25.

9. Tris(1,3-diphenyl-1,3-propanedionato)germanium(IV) hexachloroantimonate(V).

$Ge(bzbz)_2Cl_2$ (5.1 g, 8.7 mmoles) was dissolved in 200 ml of glacial acetic acid by gentle heating and stirring. The antimony(V) chloride (1.4 ml, 8.7 mmoles) was added, at which point the solution became bright yellow, and a precipitate formed. The mixture was allowed to reflux for two hours. The volume of the solution was reduced to one-third

and cooled, at which point a precipitate formed. The precipitate was filtered, dried, and then dissolved in 100 ml of methylene chloride. The volume was reduced to half and ten ml of hexane was added. The mixture was cooled overnight in the freezer. The prismatic crystals were then filtered and dried. The yield was 79.8% and the melting point was 221-223°.

Anal. Calcd. for $[Ge(C_{15}H_{11}O_2)_3][SbCl_6]$: C, 50.19; H, 3.10; Cl, 19.75. Found: C, 49.22; H, 2.97; Cl, 20.25.

10. Titanium Complexes.

The titanium analogs of the above germanium complexes were prepared in a similar manner by Luis Matienzo (24).

C. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were obtained with a Varian A-60 analytical spectrometer (60.00 MHz) fitted with a Varian variable temperature controller, Model V-6040. The chemical shifts of methanol and ethylene glycol were used to determine the low and high temperatures respectively. A calibration standard containing seven compounds was used to correct the magnetic sweep width at 250 Hz and 500 Hz. This standard was also employed for chemical shift determinations of several new compounds. In this case calibrations of magnetic sweep widths were determined for sweep widths of 500, 250, and 50 Hz.

Signal areas used in the determination of equilibrium constants were measured by planimetry. In general, eight to ten spectra were measured for each equilibrium constant to minimize the error due to minor variations in the individual spectrum. Spectra were run at various radiofrequency fields and examined to avoid errors caused by saturation effects. The optimum radiofrequency at room temperature was found to have an amplitude of 0.10 mG.

Signal areas used in the determination of the rate of isomerization of trans-$Ge(dpm)_2Cl_2$ were measured by electronic integration. In general, three spectra were measured for the concentration of trans and cis isomer at half hour intervals for four hours. To insure the establishment of equilibrium, subsequent measurements were taken at six and fifteen hours.

III. RESULTS AND DISCUSSION

A. Synthesis and Observations of Some New Germanium β-diketonates

The investigation of germanium complexes led to the preparation of four new compounds. They are: cis- and trans-$Ge(dpm)_2Cl_2$, $[Ge(dpm)_3][SbCl_6]$, and $[Ge(bzbz)_3][SbCl_6]$. Originally, the object of the preparative phase of this research was to prepare a mixed ligand complex from three different tris(β-diketonato)germanium(IV) complexes. These complexes are not formed directly from the metal halide and β-diketones. Their preparation requires the following sequence of reactions:

a. $GeCl_4 + 2Hdik \longrightarrow Ge(dik)_2Cl_2 + 2HCl(g)$.

b. $3Ge(dik)_2Cl_2 + 2SbCl_5 \longrightarrow 2[Ge(dik)_3][SbCl_6] + GeCl_4$.

As in the case of germanium, the reactions of titanium or tin tetrachloride with various β-diketones give the dichlorobis(β-diketonato)metal complexes. However, tin and titanium β-diketonates usually take less than two hours to prepare. The reaction, in the first attempt to prepare cis-$Ge(dpm)_2Cl_2$ in methylene chloride, was allowed to reflux for eight hours. No product was recovered. The cis-$Ge(dpm)_2Cl_2$ was successfully prepared in methylene chloride

when the reaction was allowed to reflux for approximately 120 hours. It was noted that the time required to prepare the dihalobis(β-diketonato)germanium(IV) complexes varied considerably as compared to their titanium and tin analogs. In Table II are tabulated reaction times and reaction solvents for several Metal(IV)$(dik)_2Cl_2$ complexes. In all cases, the preparation involved the reaction of the metal chloride with the free ligand. The yields for most reactions were from 75% to 90%.

Table II. Reaction times for several $M(dik)_2Cl_2$ complexes.

Ligand	M = Germanium Time, hrs	Solvent	M = Titanium Time, hrs	Solvent
Hacac	2	$CHCl_3$	0.33	$CHCl_3$[5]
Hetac[a]	8	$CHCl_3$[17]		
Hbzac	10	$CHCl_3$[21]	0.25	C_6H_6[6]
Hpivac[b]	110	$CHCl_3$[29]	1	$CHCl_3$[29]
Hbzbz	110	C_6H_6	0.25	C_6H_6[6]
Hdpm	119	$CHCl_3$	2	CH_3CO_2H[29]

[a] $CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$

[b] $(CH_3)_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}CH_3$

Although Table II indicates that there is some variation in the polarity of the solvents used in the reactions of a given ligand, the longer reaction times for the germanium complexes

indicate that other factors may be involved. Table II lists no tin complexes, although $Sn(acac)_2Cl_2$ (17), $Sn(bzac)_2Cl_2$ (30), and $Sn(bzbz)_2Cl_2$ (30) have been prepared in methylene chloride. The preparation of $Sn(acac)_2Cl_2$ required less than an hour, but no times were reported for $Sn(bzac)_2Cl_2$ or $Sn(bzbz)_2Cl_2$.

The ionic radii of germanium(IV), titanium(IV) and tin(IV) are 0.44 Å, 0.64 Å, and 0.74 Å respectively (31). Because germanium(IV) has the smallest radius it would be the most sensitive to steric factors. The ligands in Table II are listed in increasing order of size of the terminal R groups. The reaction times for the germanium compounds increase as the steric hindrance increases.

The reluctance of germanium(IV) chloride to form etherates has been noted by Udovenko and Fialkov (18). The explanation given was that since germanium(IV) has the smallest radius of the three tetrachlorides, it is the most screened and therefore the slowest to react. The calculated ratio of metal to chloride ionic radii are germanium, 0.24; titanium, 0.37; and tin, 0.41. Since both etherate and dihalobis formation require the formation of a metal-oxygen bond, the screening factor for germanium could also contribute to the difference in the time required for the preparation of complexes which differ only in their metal moiety.

Both the screening factor and ionic radii of germanium(IV) chloride should affect the reaction rate if the mechanism

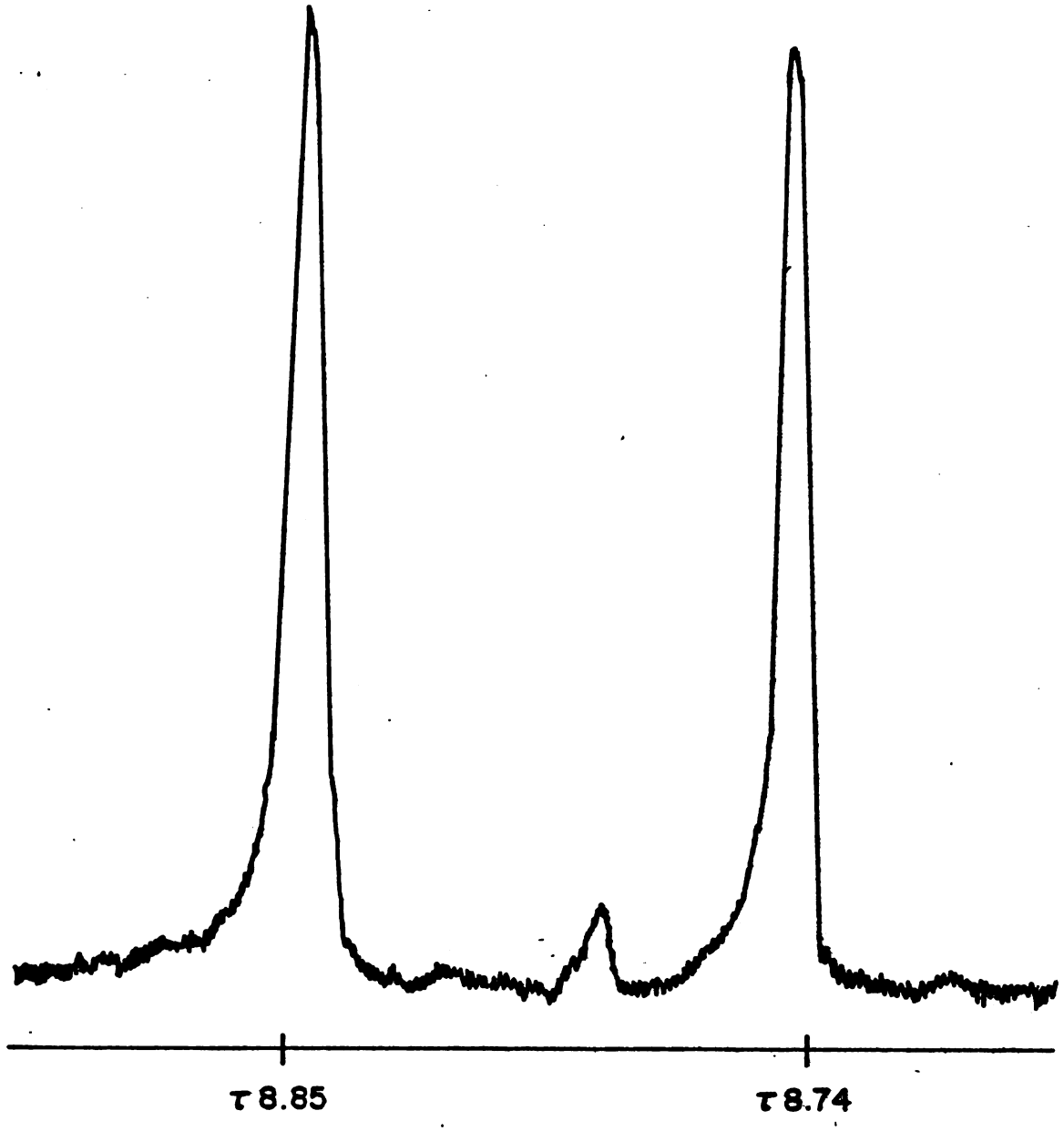
is S_{N2}. This mechanism requires nucleophilic attack and subsequent formation of a five-coordinate intermediate. The S_{N1} mechanism requires bond rupture and subsequent formation of a three coordinate intermediate. This mechanism is influenced by the bond energy of the species which must dissociate, in this instance a metal-chlorine bond. Mean thermochemical bond energies in kcal/mole for the three metal chlorides in question are: germanium, 104 (32), tin, 76 (33), and titanium, 48 (34). An increase in reaction time with increase in bond energy is observed. These arguments predict that either an S_{N1} or S_{N2} mechanism would lead to lower reaction rates for germanium.

In addition to the small ionic radius, large screening factor, and high bond energy of germanium(IV) chloride, all complexes are octahedral and the hybridization of germanium to $4sp^3d^2$ requires more energy than the hybridization of titanium to $3d^24sp^3$. Since tin has the largest ionic radius, but also requires hybridization of outer d orbitals the reaction times for tin are expected to be somewhere between those of titanium and germanium.

There are two possible isomers for the octahedral $Ge(dpm)_2Cl_2$, <u>cis</u> and <u>trans</u>. Figure 7 shows the structure of the <u>cis</u> isomer. Since this isomer has one two fold axis of rotation there are two nonequivalent sets of <u>t</u>-butyl groups which give rise to a doublet in the <u>t</u>-butyl region of the nmr spectrum as shown in Figure 8. The peak heights of the <u>cis</u> isomer doublet in Figure 8 are not exactly equal

Figure 7. cis-$Ge(dpm)_2Cl_2$.

Figure 8. t-Butyl proton resonance lines (60 MHz) of 0.4M cis-$Ge(dpm)_2Cl_2$ in methylene chloride at 44.0°.


τ 8.85
τ 8.74

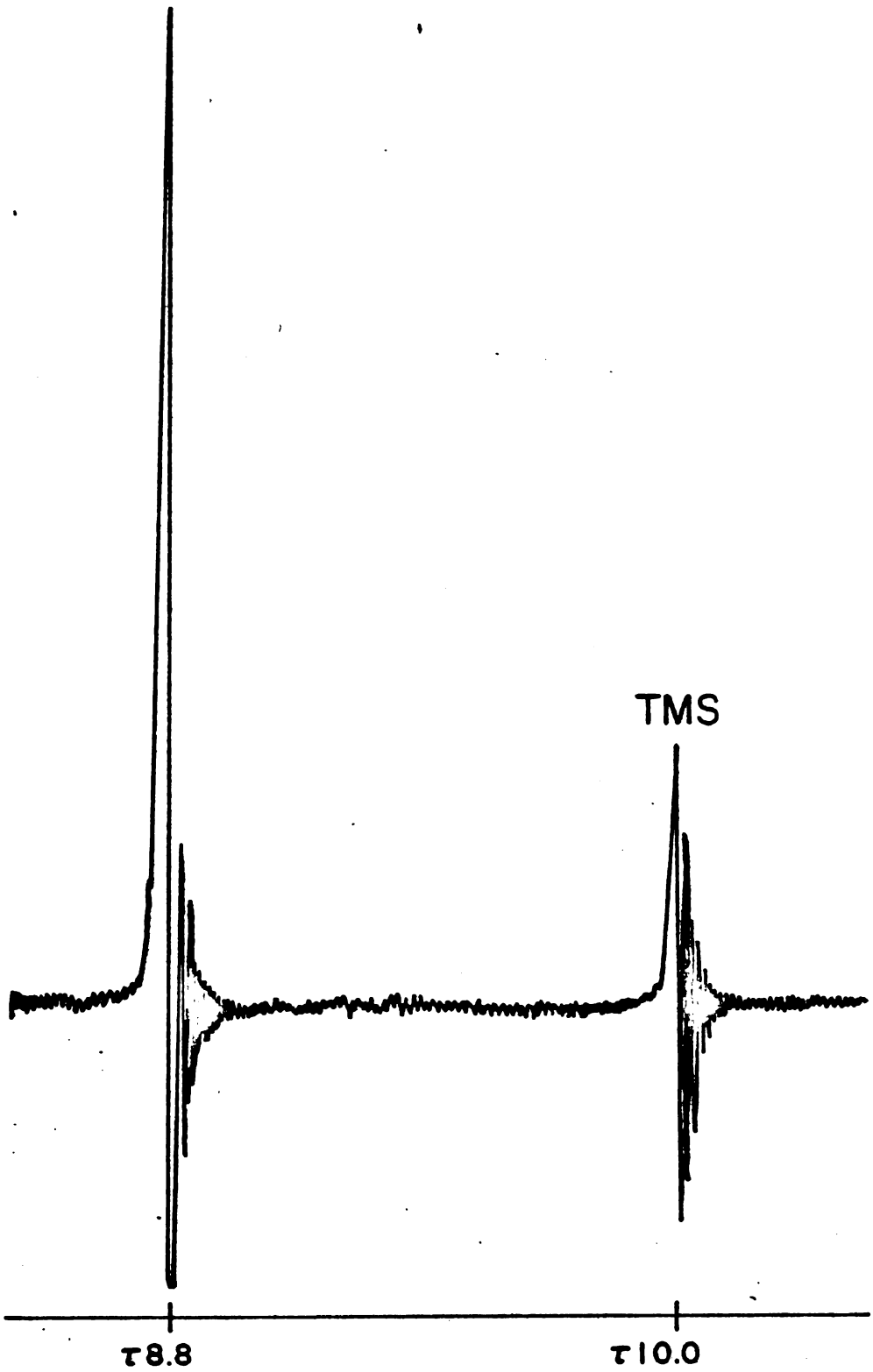
due to the presence of some of the trans isomer. The t-butyl resonance line for the trans isomer occurs at the same position as the downfield resonance line in the doublet for the cis isomer. The small peak between the two lines of the cis doublet is attributed to free ligand whose t-butyl resonance line occurs at approximately τ 8.8. This small peak at τ 8.8 appears after the solution has aged a few hours. The solvent for this spectrum was methylene chloride. Figure 9 shows the structure of the trans isomer. In this isomer all t-butyl groups are equivalent and the nmr spectrum gives rise to a singlet in the t-butyl region. Figure 10 shows the singlet of the trans isomer in relation to tetramethylsilane for a saturated solution at 44^0, taken in benzene where trans-cis isomerization is slow.

The solid germanium complexes react slowly with atmospheric moisture. A few crystals of $Ge(dpm)_2Cl_2$ were exposed to the atmosphere and after twelve hours the melting point had dropped ten degrees, although no deterioration of the crystals was detected visually. After three days, the crystals were no longer hard and the compound only partially melted leaving a white residue. After eight days the crystals had changed to a white, wet powder. This powder partially melted twenty degrees below the original melting point and left a white residue, probably germanium dioxide.

The cis-$Ge(dpm)_2Cl_2$ complex is very soluble in chlorinated hydrocarbons but only slightly soluble in hexane. If a solution of cis-$Ge(dpm)_2Cl_2$ is allowed to stand for more

Figure 9. trans-$Ge(dpm)_2Cl_2$.

Figure 10. t-Butyl proton resonance line (60 MHz) of a saturated solution of trans-$Ge(dpm)_2Cl_2$ in relation to TMS at 500 sweep width in benzene at 44.0^0.


TMS
τ8.8
τ10.0

than a few hours in a capped nmr tube, the solution develops a faint yellow color and the spectrum shows a weak peak between the two peaks of the doublet in the t-butyl region. This peak corresponds to the chemical shift of the t-butyl resonance line for the free ligand. Since freshly prepared samples of $Ge(dpm)_2Cl_2$ did not show the spurious peak, the possibility that this weak peak was due to the trans complex and not decomposition was considered. Samples were dissolved in o-dichlorobenzene and heated at 100^0, 180^0, and 210^0 for periods of fifteen minutes to twenty-four hours. The spectra showed that the area of the spurious peak remained constant within experimental error. The subsequent preparation of the trans isomer ruled out the assignment of this spurious peak as the resonance line for the trans isomer. Apparently, in o-dichlorobenzene an equilibrium is established between the complex and the dissociation products, one of which is the free ligand.

The trans isomer of $Ge(dpm)_2Cl_2$ can be prepared by either slow crystallization of the $Ge(dpm)_2Cl_2$ reaction mixture or by digestion of the cis isomer. In either method the solvent pairs methylene chloride-hexane or benzene-hexane work well. In methylene chloride the trans isomer required about fifteen minutes to isomerize which was also the required time for dissolution of the sample used, (10 mg in 0.4 ml). In benzene the isomerization was much slower and an equilibrium constant, $K_{eq} = [cis]/[trans]$, of 4.6 was found for this process. The rate of trans-cis isomerization

in benzene will be discussed in greater detail later. Steric and electronic factors predict that the trans isomer of $M(dik)_2X_2$, where X is a halogen and M is metal, is favored. Except for trans-$Ge(dpm)_2Cl_2$ reported here, no other trans isomers of the type $M(dik)_2Cl_2$ have been reported either in the solid state or in solution. X-ray studies have been done on $M(acac)_2X_2$, where M is titanium or germanium and X is fluorine, chlorine, or bromine (35). IR studies of the solids have also been done for the above compounds and also the tin analogs (36). Nmr techniques have been used to study the geometry of these complexes in solution (6,26,37,38). In all cases, the $M(dik)_2X_2$ complexes have been found to possess cis symmetry. To explain this fact two opposing arguments have been put forward. Both invoke electronic effects as the cause of the stabilization of the cis configuration. In both arguments, the cis stabilization is assumed to arise from the fact that in the cis isomer all three t_{2g} orbitals can participate in p —> d π-bonding, whereas, in the trans isomer only two of the orbitals can participate. In dispute, however, is whether the halogen or oxygen atoms are more important in p —> d π-bonding. From infrared spectral data, Nelson (39) has concluded that halogen-metal p —> d π-bonding is more important than the oxygen-metal p —> d π-bonding in $Sn(acac)_2Cl_2$ complexes. From nmr and IR data Bradley (39) concluded that electron donation of the oxygen atoms to the metal is the more important factor in $Ti(dik)_2X_2$ complexes. This latter view is also held by Fay (37).

Another unusual property of germanium complexes was also noted when an attempt was made to find the coalescence temperature of $Ge(dpm)_2Cl_2$. At room temperature this complex shows a doublet, which indicates there is slow terminal group exchange. This observation is also true for $Ge(acac)_2Cl_2$ (26) and $Sn(acac)_2Cl_2$ (40), but not $Ti(acac)_2Cl_2$ (5). The coalescence temperature for $Ti(acac)_2Cl_2$ (5) and $Sn(acac)_2Cl_2$ (40) are -50^0 and 90^0, respectively, but neither $Ge(acac)_2Cl_2$ (41) nor $Ge(dpm)_2Cl_2$ coalesce below 180^0. The spectrum of 0.67M $Ge(dpm)_2Cl_2$ in o-dichlorobenzene indicated that the complex may be close to coalescence at 180^0 since the lines of the doublet had begun to broaden and the peak separation had decreased from 7.9 Hz at room temperature to 5.6 Hz at 180^0.

The chemical shifts of some tris(β-diketonates) and cis-$Ge(dpm)_2Cl_2$ were determined and are reported in Table III. The solvent in all cases was methylene chloride and tetramethylsilane was used as the internal standard. The concentration of the germanium complexes was 0.20M and the concentration of the titanium complexes was 0.10M. The proton between the two carbonyl groups in the β-diketonate anion, $[RCOCHCOR]^-$, is referred to as the ring proton.

The chemical shift of the ring proton of cis-$Ge(dpm)_2Cl_2$ is 0.1 ppm downfield from the shift for $Al(dpm)_3$ in $CDCl_3$ (14). This downfield shift for $M(dik)_2X_2$ as compared to the analogous $M(dik)_3$ complex is typical and attributed to the fact that the cis-dihalobis(β-diketonates) have a dipole, whereas, the symmetric tris(β-diketonates) do not (26).

Table III. Chemical shifts for germanium and titanium β-diketonates[a].

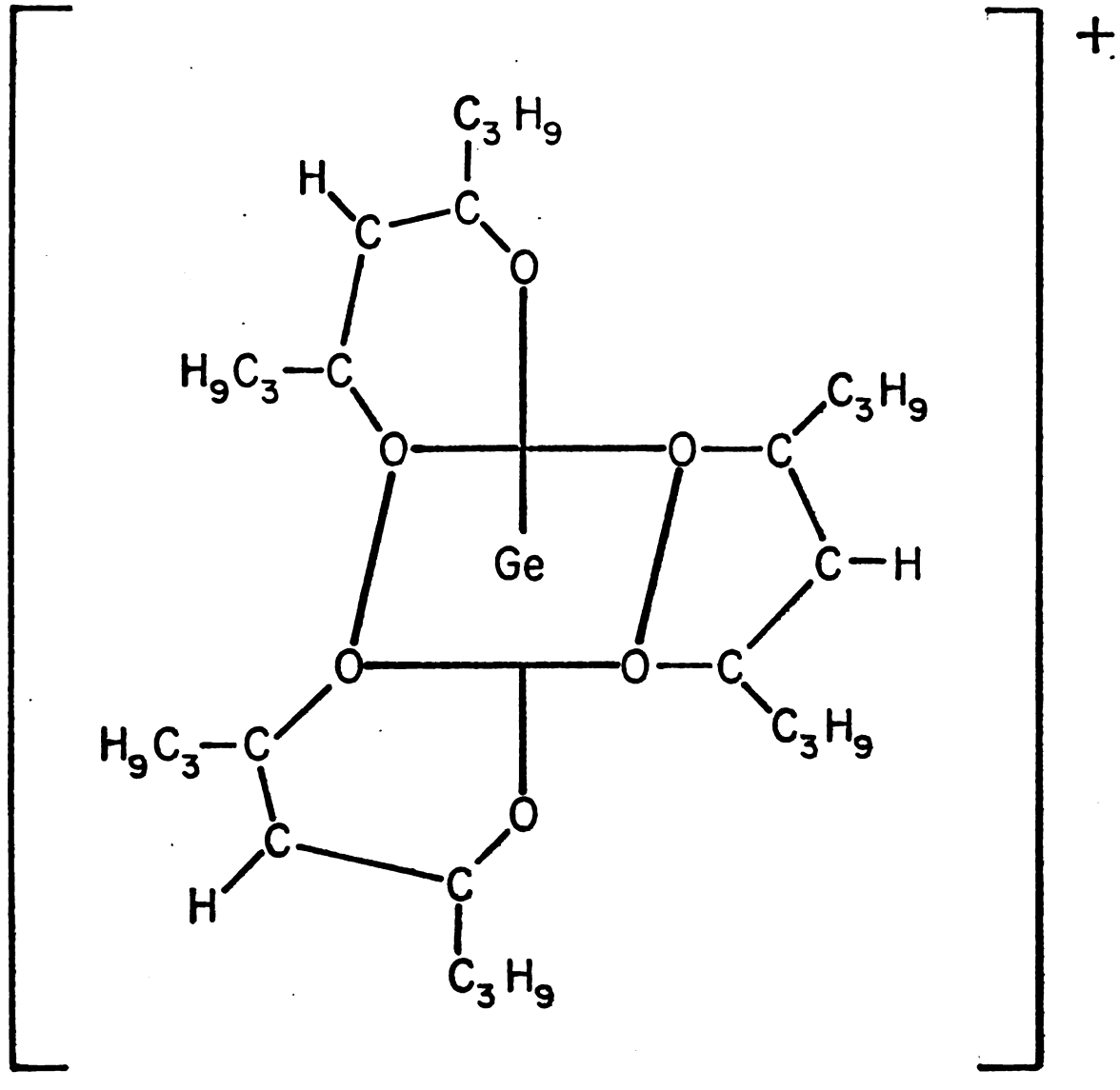
Compound	τ, -CH	τ, $-CH_3$	τ, t-C_4H_9
cis-$Ge(dpm)_2Cl_2$	4.06		8.74, 8.85
$[Ge(acac)_3][SbCl_6]$	4.03	7.76	
$[Ge(dpm)_3][SbCl_6]$	3.82		8.77
$[Ti(acac)_3][SbCl_6]$	3.80	7.75	
$[Ti(dpm)_3][SbCl_6]$	3.61		8.78

[a]See text for solvents and concentrations used.

The values for $[Ge(acac)_3][SbCl_6]$ and $[Ti(acac)_3][SbCl_6]$ in Table III, are in good agreement with the values recently reported by Fay and Serpone (28). The ring proton resonances of the cationic complexes are shifted to lower fields than their analogous neutral complexes. Fay and Serpone attribute this fact to the positive charge and not to benzenoid ring currents. The trend of this downfield shift is germanium < tin < titanium. A comparison of the values of the chemical shifts reported in Table III illustrate this trend.

The $M(dik)_2Cl_2$ compounds were used to prepare the $[M(dik)_3][SbCl_6]$ complexes. When $Ge(dpm)_2Cl_2$ was refluxed with antimony pentachloride in glacial acetic acid for two hours the analysis of the product corresponded to the expected $[Ge(dpm)_3][SbCl_6]$ complex. Since all terminal groups of this complex are in an equivalent environment, see Figure 11, a singlet is expected in the t-butyl region of the nmr

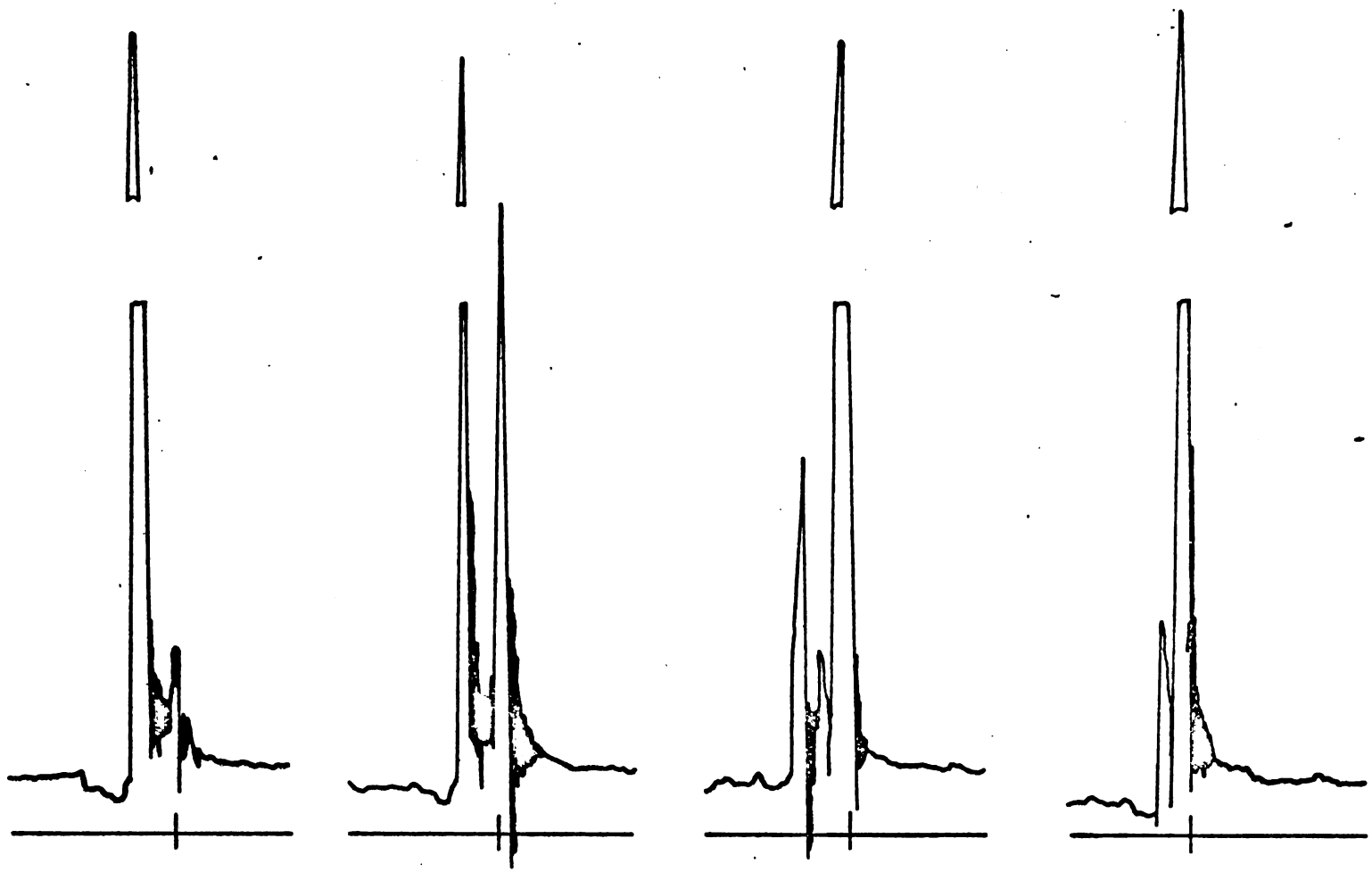
Figure 11. The cation $[Ge(dpm)_3]^+$.


C3 H9
H
C
C
O
H9C3
C
O
O
C
C3H9
Ge
C
H
O
O
C
H9C3
C3H9
C
O
H
C
C3 H9
+

spectrum. The expected singlet was observed at τ 8.7. If however, antimony pentachloride is added to $Ge(dpm)_2Cl_2$ in methylene chloride in the absence of tetramethylsilane, and allowed to age for 0.5 hour at room temperature, the crystalline product gives a set of two lines in the t-butyl region. A very weak peak is seen at τ 8.7, and corresponds to the expected resonance of $[Ge(dpm)_3][SbCl_6]$. A second, much larger peak is seen about seven cps downfield. As the solution ages the downfield peak decreases and the upfield peak for $[Ge(dpm)_3][SbCl_6]$ increases. After thirty-two hours the peak heights are inverted. This change in spectra with time is illustrated in Figure 12. The spectral observations, the analysis, and the manner of preparation indicate that the isolated compound may be a reaction intermediate in the preparation of $[M(dik)_3][M'X_n]$ from $M(dik)_2X_2$ and $M'X_m$, where n equals four to six and m equals two to five. This intermediate is postulated to be an adduct of the form $M(dik)_2X_2,M'X_m$ if the octahedral symmetry is maintained in the adduct, then for $[Ge(dpm)_2Cl_2,SbCl_5]$ the ligands must be trans since only one line is observed in the t-butyl region which is attributed to the adduct.

The reaction of dihalobis(β-diketonato)metal complexes with Lewis acids, in particular, ferric chloride, cupric chloride, auric chloride, and antimony pentachloride, to give the tris(β-diketonates) is well known. However, no work appears to have been done on the mechanism involved. During the preparation of $[Ge(dpm)_3][SbCl_6]$, it was observed

Figure 12. The change in the t-butyl proton resonance spectra (60 MHz) with time for 0.20M [$Ge(dpm)_2Cl_2$,$SbCl_5$] in methylene chloride at 33.0°.


τ8.7
t=.25hrs
τ8.7
t=2 hrs
τ8.7
t=3hrs
τ8.7
t=32 hrs

that the solvent plays an important role in this reaction. In glacial acetic acid $[Ge(dpm)_3][SbCl_6]$ precipitates immediately on addition of antimony(V) chloride to $Ge(dpm)_2Cl_2$. In methylene chloride the reaction is slow enough to detect a mixed compound, probably $[Ge(dpm)_2Cl_2,SbCl_5]$, prior to formation of $[Ge(dpm)_3][SbCl_6]$.

Considerable effort and time was invested in an attempt to make $Ge(hfac)_2Cl_2$ (cf. experimental section). Neither the method of preparation used for the other bis-(β-diketonates), nor the addition of germanium tetrachloride to hexafluoroacetylacetone in the absence of solvent gave a discernible reaction. The addition of sodium hexafluoroacetylacetoneate to germanium tetrachloride did give a reaction but no product was recovered. Since these complexes were to be used in the investigation of mixed ligand complexes, the preparation of the hexafluoro analog was especially desirable. The reason for this is that the mixed ligand complexes are appreciably favored at the expense of the parent complexes when one complex contains very electronegative terminal groups and the other does not.

B. Isomerization of trans-$Ge(dpm)_2Cl_2$

The t-butyl resonance line for trans-$Ge(dpm)_2Cl_2$ is located at the same position as the downfield peak of the doublet which corresponds to the cis isomer. When the trans isomer was dissolved in methylene chloride, it required less than fifteen minutes for the compound to isomerize. At this

point the spectrum was characteristic of an equilibrium mixture of the isomers. This is also about the length of time it took to dissolve the sample, (10 mg in 0.4 ml).

In benzene the isomerization is much slower. Since trans-$Ge(dpm)_2Cl_2$ is only slightly soluble in benzene, a saturated solution was prepared and decanted after an hour. The change in concentration with time was followed by measuring the change in peak areas. Usually three measurements were taken at each time and the concentration of the cis and trans isomers were determined by electronic integration. Data was collected at half hour intervals for four hours and subsequent measurements were taken at six and fifteen hours to assure the establishment of equilibrium. The reaction was followed at 43.8^0. If the isomerization is a simple first order reaction as written in reaction "c",

c. trans ——> cis

then a plot of the log (f_{trans}) versus time, where f_{trans} is the fraction of trans isomer, should give a straight line. This plot is Figure 13 and shows that an equilibrium was established after approximately 260 minutes. Table IV lists the data used to calculate the rate of isomerization. Table V lists the data used to calculate the equilibrium constant, $K_{eq} = [f_{cis}]/[f_{trans}]$. The equilibrium constant was found to be 4.64 ± .31 calculated at the 95% confidence level. A better fit of the data is obtained if it is assumed that the reaction is reversible and first order as described in reaction "d".

Figure 13. Plot of log [$f_{\underline{trans}}$] *vs* time for the isomerization of *trans*-$Ge(dpm)_2Cl_2$ in benzene at 43.8°.

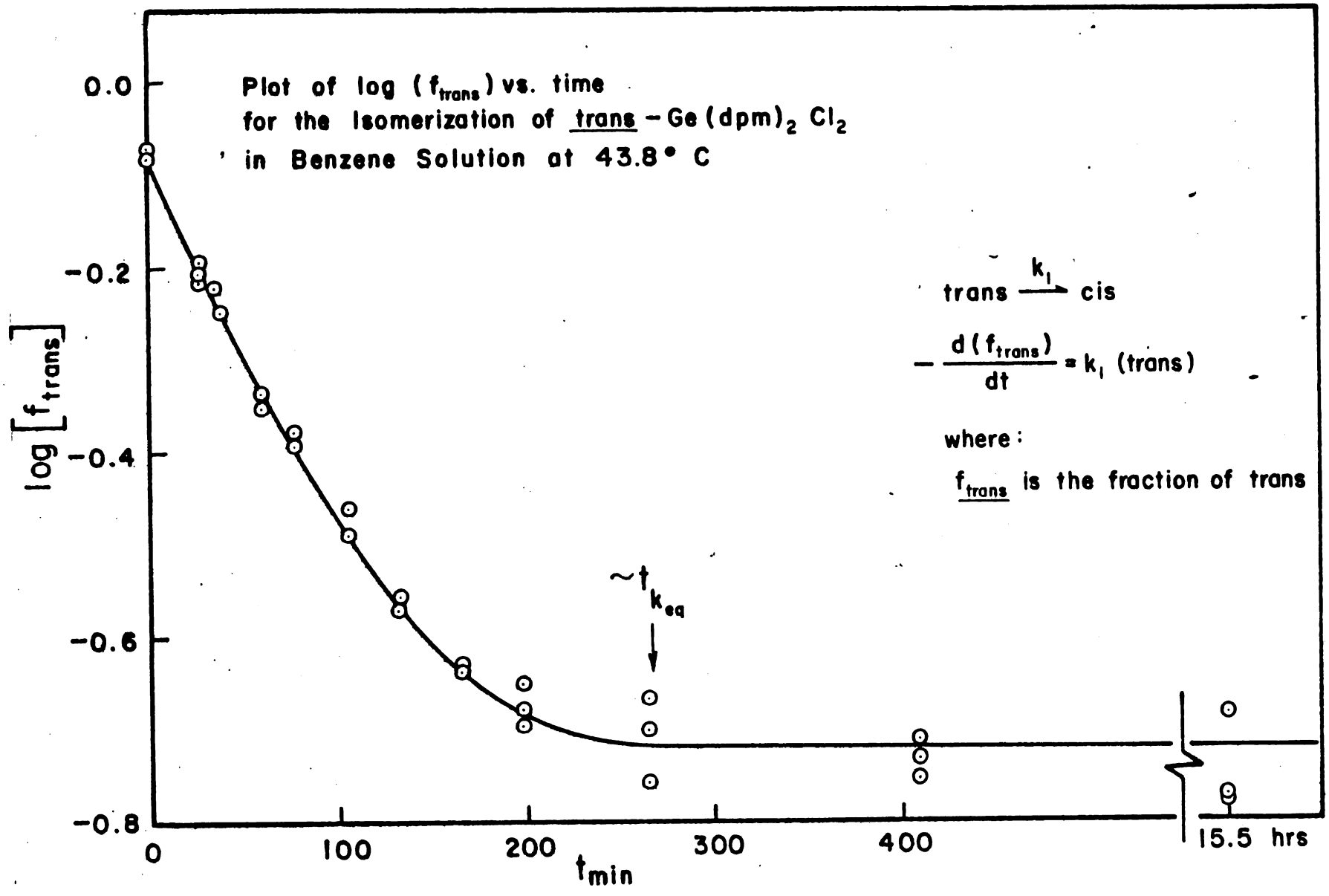

Plot of log (f_{trans}) vs. time
for the Isomerization of trans - Ge(dpm)$_2$ Cl$_2$
in Benzene Solution at 43.8° C
trans $\xrightarrow{k_1}$ cis
$-\frac{d(f_{trans})}{dt} = k_1$ (trans)
where:
f_{trans} is the fraction of trans
$\sim t_{k_{eq}}$
log [f_{trans}]
0.0
-0.2
-0.4
-0.6
-0.8
0
100
200
300
400
t_{min}
15.5 hrs

Table IV. Kinetic data for isomerization of trans-$Ge(dpm)_2Cl_2$ in benzene at 43.8°.

Time min	f_{trans}	f_{cis}	log (f_{trans})	log[f_{trans}-(1-f_{trans})/K_{eq}]
0	0.826	0.174	-0.08328	-0.1033
0	0.857	0.143	-0.07308	-0.08291
27	0.591	0.419	-0.1903	-0.3004
	0.620	0.380	-0.2076	-0.2691
	0.610	0.390	-0.2145	-0.2791
33	0.596	0.404	-0.2246	-0.2925
	0.592	0.408	-0.2274	-0.2975
37	0.598	0.402	-0.2519	-0.2998
	0.596	0.404	-0.2246	-0.2925
60	0.443	0.557	-0.3536	-0.4908
	0.461	0.539	-0.3364	-0.4622
77	0.404	0.596	-0.3940	-0.5607
	0.417	0.583	-0.3796	-0.5361
105	0.322	0.678	-0.4917	-0.7545
	0.316	0.654	-0.4604	-0.6883
	0.323	0.677	-0.4914	-0.7520
133	0.269	0.731	-0.5711	-0.9547
	0.277	0.723	-0.5576	-0.9172
	0.277	0.723	-0.5571	-0.9172
165	0.229	0.771	-0.6395	-1.201
	0.232	0.768	-0.6340	-1.179
	0.229	0.771	-0.6395	-1.201
197	0.200	0.800	-0.6988	-1.656
	0.222	0.778	-0.6527	-1.268
	0.209	0.791	-0.6793	-1.420

Table V. Equilibrium constant data for
trans-$Ge(dpm)_2Cl_2$ $\overset{K_{eq}}{\rightleftharpoons}$ cis-$Ge(dpm)_2Cl_2$.

Time min	f_{trans}	f_{cis}	K_{eq}
265	0.165	0.835	5.07
	0.214	0.786	3.67[a]
	0.172	0.828	4.81
411	0.178	0.822	4.62
	0.192	0.808	4.21
	0.183	0.817	4.47
15.5 hrs	0.167	0.833	4.99
	0.206	0.793	3.85[a]
	0.189	0.811	4.29
		Average:	4.64 ± .31[b]

[a]Dropped for 95% confidence level calculation.

[b]95% confidence level.

d. trans $\overset{k_1}{\underset{k_2}{\rightleftharpoons}}$ cis

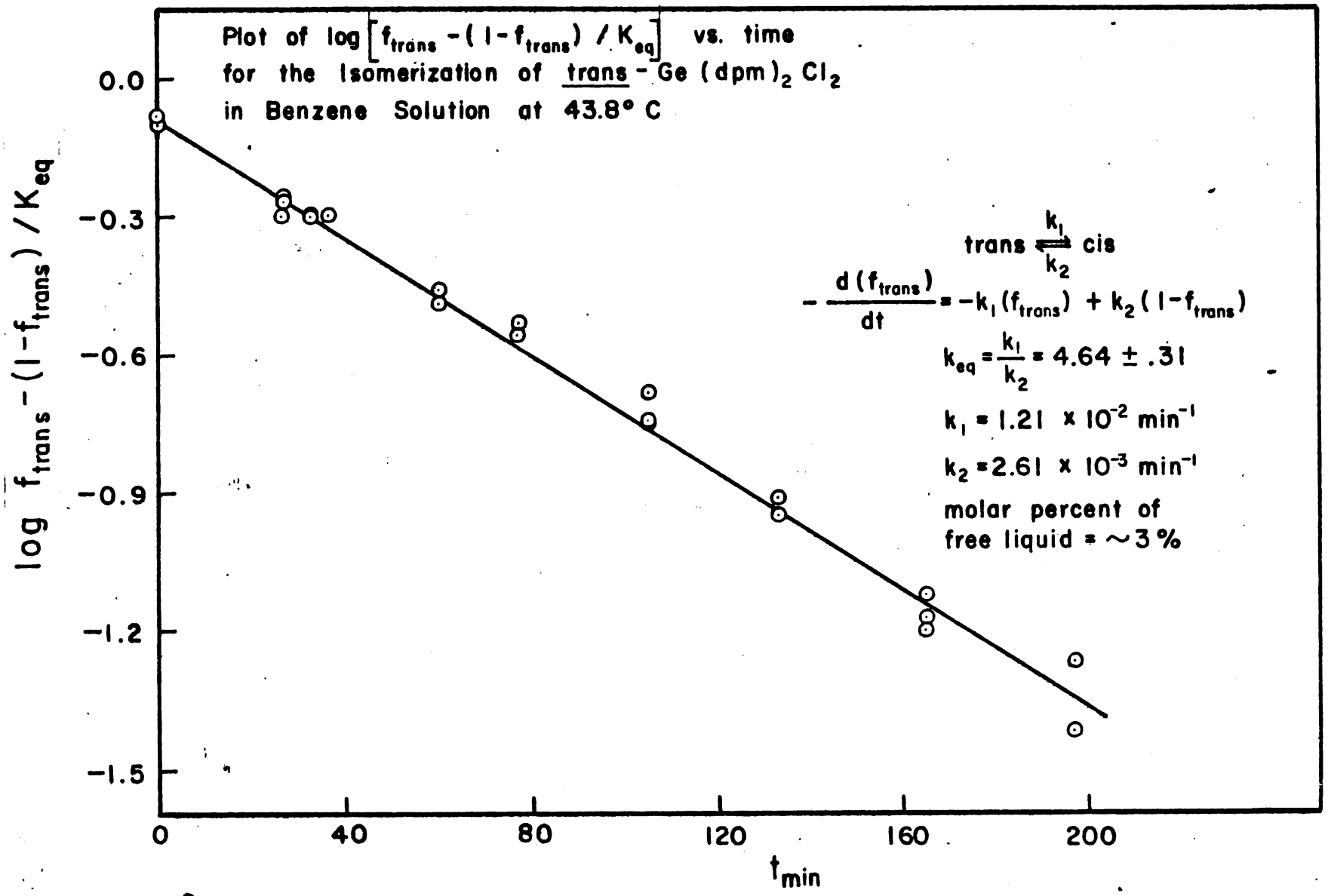
The integrated rate equation for this reaction is:

$$\log [f_{trans} - (1-f_{trans})/K_{eq}] = -k_1(1 + 1/K_{eq})t,$$

where $K_{eq} = k_1/k_2$.

k_1 calculated from the slope was 1.21×10^{-2} min^{-1}. From k_1 and K_{eq}, k_2 was calculated to be 2.61×10^{-3} min^{-1}. Although the plot in Figure 14 implies that there is good correlation between the rate equation for reaction "d" and the data, the spectra showed that a small amount of free ligand (about 3 % of the total concentration) had formed as the solution aged. It was not determined if the

Figure 14. Plot of log [$f_{\underline{trans}} - (1 - f_{\underline{trans}})/K_{eq}$] *vs* time for the isomerization of *trans*-$Ge(dpm)_2Cl_2$ in benzene at 43.8°.


Plot of log [f_trans - (1 - f_trans) / K_eq] vs. time
for the Isomerization of trans - Ge (dpm)2 Cl2
in Benzene Solution at 43.8° C
log f_trans - (1-f_trans) / K_eq
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
0
40
80
120
160
200
t min
trans ⇌ cis (k1, k2)
-d(f_trans)/dt = -k1 (f_trans) + k2 (1-f_trans)
k_eq = k1/k2 = 4.64 ± .31
k1 = 1.21 x 10^-2 min^-1
k2 = 2.61 x 10^-3 min^-1
molar percent of
free liquid = ~3 %

free ligand resulted from isomerization or from hydrolysis and the formation of the free ligand was not taken into account when the rate equation was derived. In any case, the calculated rates are intended to be only a first approximation.

There are no examples of $M(dik)_2X_2$ isomerization to use as a comparison. Fay (3) has studied the cis-trans isomerization of cis-tris(1,1,1-trifluoro-2,4-pentanedionato)-cobalt(III), $Co(tfac)_3$. Fay found that the rate equation based on reaction "d" fit the data. The equilibrium constant was 0.25, k_1 equaled 9.8×10^{-3} min^{-1}, and k_2 equaled 4.2×10^{-4} min^{-1} for the isomerization of cis-$Co(tfac)_3$ at 66^0 in methylene chloride. In both cases, the isomerization follows a reversible, first order rate law.

Since, the isomerization of trans-$Ge(dpm)_2Cl_2$ is reversible and first order, three mechanisms are possible, (1) bond rupture of the ligand; (2) dissociation of chlorine; and (3) dissociation of ligand. Also the observations indicate that the rate of isomerization is influenced by the solvent. However, the data do not permit the evaluation of the three possible mechanisms.

C. Exchange Reactions

The relative inertness of germanium tris(β-diketonate) complexes was illustrated when the compounds were mixed so that exchange might occur. These reactions, for neutral β-diketonates, are numerous and have been studied

extensively. The exchanges proceed smoothly and quickly to form a large variety of mixed ligand complexes. That the germanium systems examined did not undergo any perceptible ligand exchange reactions was, therefore, somewhat unusual. The systems studied were $[Ge(acac)_3]^+$ - $[Ge(dpm)_3]^+$ and $[Ge(acac)_3]^+$ - $[Ge(bzbz)_3]^+$.

The expected spectra for the exchange reaction between $[Ge(acac)_3]^+$ and $[Ge(dpm)_3]^+$ may have a total of eight lines in the t-butyl and methyl regions of the nmr spectrum. They are: two singlets which correspond to the parent complexes; a doublet in the t-butyl region and a singlet in the methyl region which correspond to the mixed ligand complex $[Ge(acac)(dpm)_2]^+$ (the t-butyl groups exist in two non-equivalent environments); and a doublet in the methyl region and a singlet in the t-butyl region which correspond to the mixed ligand complex $[Ge(acac)_2(dpm)]^+$ (the methyl groups exist in two non-equivalent environments). An equimolar solution of $[Ge(acac)_3]^+$ and $[Ge(dpm)_3]^+$ in methylene chloride was allowed to age for ten hours at room temperature. The sample was periodically checked *via* nmr but after ten hours the spectra indicated that no exchange had occurred. Only the two original singlets which corresponded to the parent compounds were present and unchanged.

The system $[Ge(acac)_3]^+$ - $[Ge(bzbz)_3]^+$ was investigated next. In this case, the electronegativity of the two ligands was much larger and, therefore, the possibility of exchange was enhanced. The spectrum may have a maximum of

four lines in the methyl region; two singlets which correspond to $[Ge(acac)_3]^+$ and $[Ge(acac)(bzbz)_2]^+$, and one doublet which corresponds to $[Ge(acac)_2(bzbz)]^+$. An equimolar mixture of $[Ge(acac)_3]^+$ and $[Ge(bzbz)_3]^+$ in methylene chloride, was sealed in a heavy walled tube and heated for eight hours at 210^0. Since $[Ge(bzbz)_3]^+$ is only partially soluble, the supernatant was decanted into a nmr tube in a nitrogen atmosphere. The spectra gave one line in the methyl region which corresponded to $[Ge(acac)_3]^+$. The presence of $[Ge(bzbz)_3]^+$ was indicated by a complicated peak in the phenyl region.

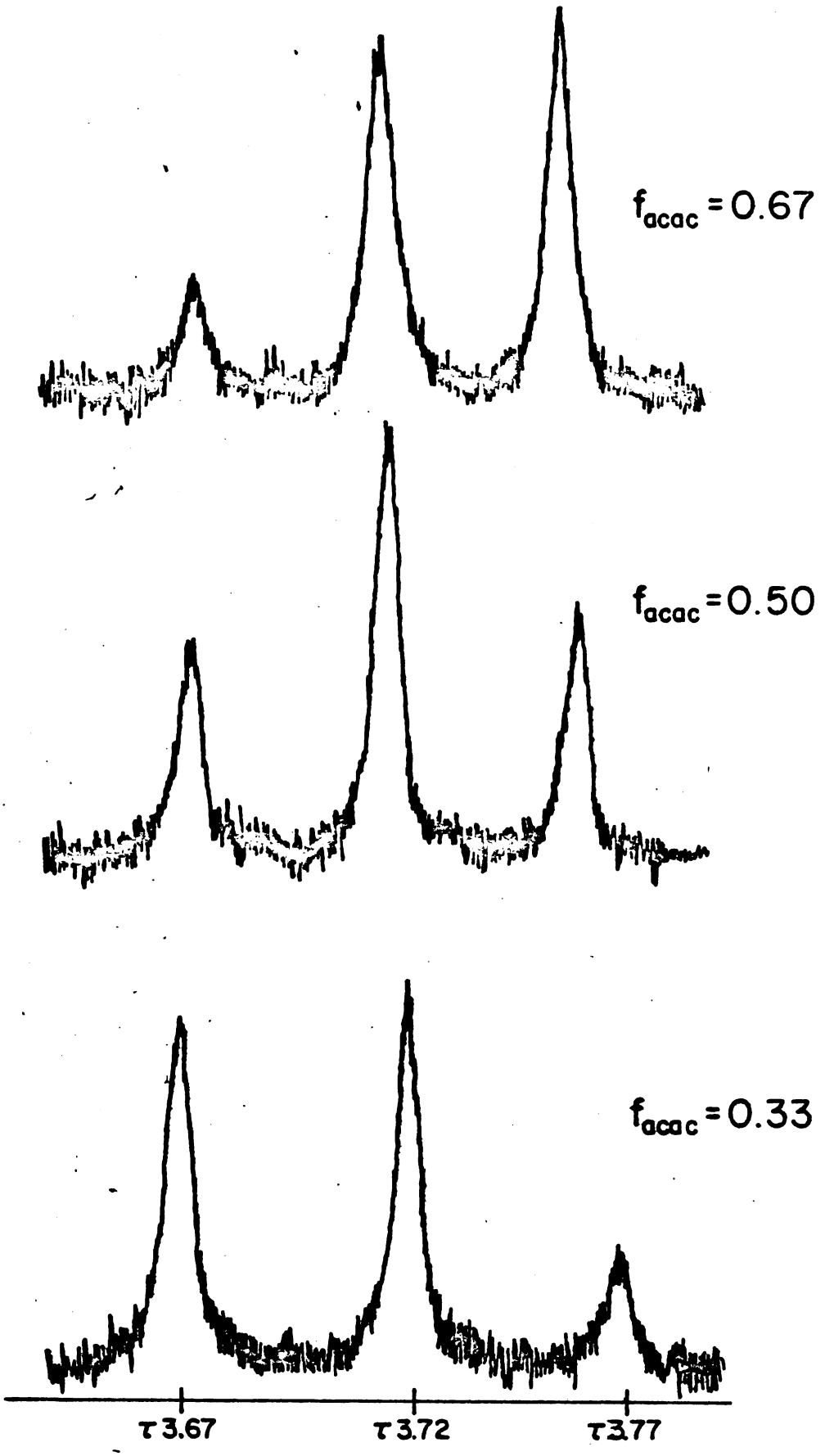
Since the cationic germanium systems did not undergo exchange reactions a comparable set of cationic titanium complexes were investigated, they are: $[Ti(acac)_3][SbCl_6]$, $[Ti(dpm)_3][SbCl_6]$, and $[Ti(bzbz)_3][SbCl_6]$. These complexes were studied in pairs and all three sets, $[Ti(acac)_3]^+$ - $[Ti(dpm)_3]^+$, $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$, and $[Ti(dpm)_3]^+$ - $[Ti(bzbz)_3]^+$ were found to readily undergo exchange reactions. An examination of the relative intensities of the nmr lines as a function of time showed that in all cases equilibrium was established in less than five minutes after dissolution of the complexes. The total molarity of titanium was varied from 0.1M to 0.6M and the equilibrium was observed in a variety of solvent; methylene chloride, benzene, chlorobenzene, and o-dichlorobenzene. For each system there are four possible species in solution, the two parent complexes, and two mixed ligand complexes, $[Ti(dik)_2(dik')]^+$

and $[Ti(dik)(dik')_2]^+$. The resonance lines of the complexes in both the ring proton and terminal group region were assigned by examination of the changes in relative signal intensities as a function of ligand composition. Examples of spectra in the ring proton region of an equilibrium mixture are shown in Figure 15. The system illustrated is $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$ in methylene chloride and at equilibrium. The term f_{acac} is defined as the fraction of total ligand present as acetylacetonate. The resonance lines at τ3.67, τ3.72, and τ3.77 are assigned to the acetylacetonate ring protons of $[Ti(acac)(bzbz)_2]^+$, $[Ti(acac)_2(bzbz)]^+$, and $[Ti(acac)_3]^+$, respectively.

The chemical shifts for both the parent and mixed complexes were determined in methylene chloride with tetramethylsilane as an internal standard and $f_{acac} = 0.50$. They are reported in the appropriate sections. Resonance lines for the ligand dibenzoylmethanate in either the parent complex or in the mixed ligand complexes were not examined. Both the terminal phenyl groups and the ring protons are much farther downfield than the resonances attributed to the other ligands.

Some difficulty was encountered in the resolution of lines in the t-butyl and methyl regions and the corresponding ring proton regions. This led to the spectral examination of these three systems in methylene chloride and chlorobenzene at 100 MHz. The spectra were run by Dr. J. Heeschen of the Chemical Physics Lab, Dow Chemical Company, Midland.

Figure 15. Changes in relative signal intensities as a function of ligand composition for the acetylacetonate ring proton spectra (60 MHz) of 0.30M $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$ at equilibrium in methylene chloride at 33.0^0.

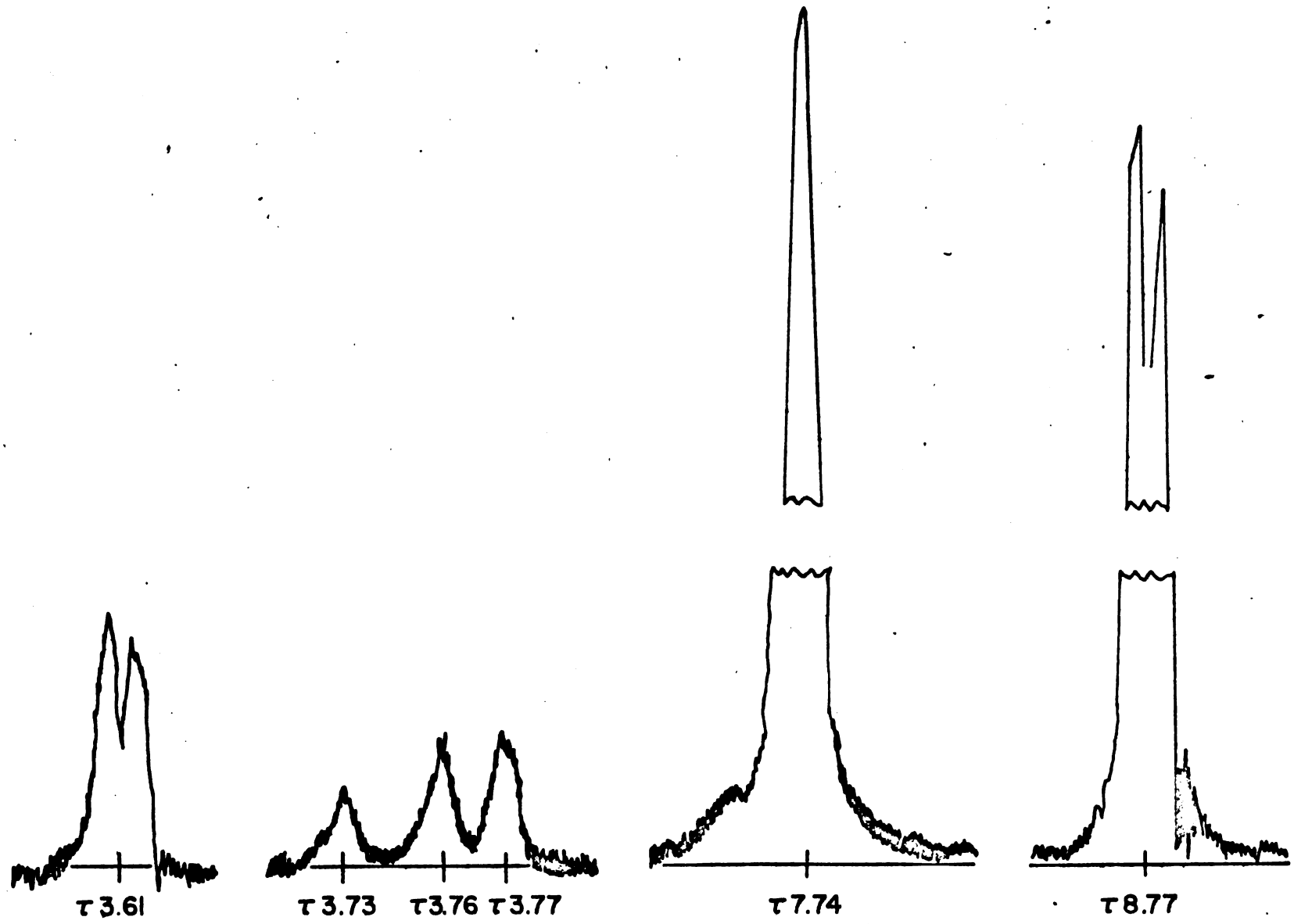

$f_{acac} = 0.67$
$f_{acac} = 0.50$
$f_{acac} = 0.33$
τ3.67
τ3.72
τ3.77

A variety of solvents were used in an attempt to resolve the expected peaks of the spectrum. The increase in resolution with solvent was in the order: benzene < chlorobenzene < o-dichlorobenzene < methylene chloride.

The first system studied was $[Ti(acac)_3]^+ - [Ti(dpm)_3]^+$. A set of eight lines analogous to those described earlier for $[Ge(acac)_3]^+ - [Ge(dpm)_3]^+$ are possible in the methyl and t-butyl regions. In the downfield region τ3.0-4.0, two sets of three peaks should be present, with each set a representation of the ring protons which correspond to the mono, bis, and tris complexes of a given ligand.

This system was studied in benzene, chlorobenzene, o-dichlorobenzene, and methylene chloride. The total titanium concentration was varied from 0.1M to 0.4M. In benzene both ring proton regions and the methyl region showed a broad singlet with a shoulder. The t-butyl region showed only a broad singlet. In chlorobenzene and o-dichlorobenzene the ring proton regions were obscured by the solvent or solvent impurities, and the methyl and t-butyl regions showed broad peaks similar to those found when benzene was used as a solvent. A sample dissolved in chlorobenzene was examined in the t-butyl and methyl regions at 100 MHz, but neither peak was further resolved. Figure 16 illustrates the results of the spectrum obtained in methylene chloride at 0.30M titanium and $f_{acac} = 0.67$ at 60 MHz. The dipivalolmethanate ring region was partially resolved and gave two greatly overlapped peaks. The half width of the

Figure 16. Proton resonance line spectrum (60 MHz) of an equilibrium mixture of 0.30M $[Ti(acac)_3]^+$ - $[Ti(dpm)_3]^+$, f_{acac} = 0.67 in methylene chloride at 33.0°.


τ 3.61
τ 3.73
τ 3.76
τ 3.77
τ 7.74
τ 8.77

overlapped peaks is 0.8 cps. The two overlapped peaks are separated by 0.3 cps and the chemical shifts in τ values for both is τ3.61, in cps the chemical shifts are 383.4 and 383.1. The acetylacetonate ring proton region gave a set of three peaks, the two upfield peaks are slightly overlapped. The peak assignment and corresponding chemical shifts are: $[Ti(acac)(dpm)_2]^+$, τ3.73; $[Ti(acac)_2(dpm)]^+$, τ3.76; $[Ti(acac)_3]^+$, τ3.77. The methyl region gave a broad singlet with a chemical shift of τ7.74 and a half width of 0.77 cps. The t-butyl region gave what appeared to be two peaks with a great deal of overlap. They are separated by only 0.3 cps and the half width is 0.69 cps. The chemical shifts for both peaks is τ8.77, in cps the values are 73.7 and 73.4. The 100 MHz spectrum did not show a change in the t-butyl region but the methyl peak was resolved into two greatly overlapped peaks, Figure 17.

In both the t-butyl and methyl regions, one of the two peaks which overlap should be a doublet which corresponds to the respective bis ligand complex. Other titanium complexes are known to undergo rapid terminal group exchange at room temperature and give singlets instead of the predicted doublets. Therefore, spectra of these systems were run at low temperature to see if any of the peaks could be resolved into doublets. Methylene chloride solutions which were 0.30M in titanium and had a ligand composition of f_{acac} = 0.33 or 0.67 were examined at -62.8°. The results are: t-butyl region, one broad line with a half width of 2.0 cps;

Figure 17. Proton resonance lines (100 MHz) for an equilibrium mixture of 0.30M $[Ti(acac)_3]^+$ - $[Ti(dpm)_3]^+$, f_{acac} = 0.50 in methylene chloride at room temperature.

methyl region, one broad line with a slight shoulder and a half width of 2.0 cps; in both ring proton regions, broader peaks.

Although the $[Ti(acac)_3]^+$ - $[Ti(dpm)_3]^+$ system did undergo ligand exchange, the system was found to be unsuitable for quantitative work. The requirement that a set of peaks in at least one of the regions be complete, well defined, and separable was not met. Apparently, the chemical shifts in all regions for the system are so similar that the individual peaks are not separable.

The system $[Ti(dpm)_3]^+$ - $[Ti(bzbz)_3]^+$, theoretically, should give rise to four lines in the t-butyl region; two singlets which correspond to $[Ti(dpm)_3]^+$ and $[Ti(dpm)(bzbz)_2]^+$, and a doublet which corresponds to $[Ti(dpm)_2(bzbz)]^+$. There should also be a set of three singlets in the dipivaloylmethanate ring proton region which correspond to the mono, bis, and tris dipivaloylmethanate complexes. The system was insoluble in benzene but fairly soluble in methylene chloride. The spectrum with methylene chloride as the solvent, f_{dpm} = 0.50, and a titanium concentration of 0.30M, gave the following results. The ring proton region gave a set of three lines with a small amount of overlap at the base line. The chemical shifts for the ring protons are: $[Ti(dpm)(bzbz)_2]^+$, τ3.55, $[Ti(dpm)_2(bzbz)]^+$, τ3.57, and $[Ti(dpm)_3]^+$, τ3.59. The t-butyl region gave two greatly overlapped peaks separated by 0.6 cps with chemical shifts of τ8.75 and τ8.76. The half width was 0.50 cps. The spectrum of an equilibrium

mixture of 0.30M $[Ti(dpm)_3]^+$ - $[Ti(bzbz)_3]^+$ in both the t-butyl and dipivaloylmethanate ring proton regions is illustrated in Figure 18. The spectrum was also examined at 100 MHz. Although the ring proton region was completely resolved, the t-butyl region was unchanged. As in the case of the $[Ti(acac)_3]^+$ - $[Ti(dpm)_3]^+$ system, although ligand exchange did take place, the resulting spectra were not well enough resolved to permit quantitative study of the system.

The system $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$ theoretically should give rise to four lines in the methyl region; two singlets which correspond to $[Ti(acac)_3]^+$ and $[Ti(acac)(bzbz)_2]^+$, and a doublet which corresponds to $[Ti(acac)_2(bzbz)]^+$. There should also be a set of three singlets in the acetylacetonate ring proton region which correspond to the mono, bis and tris acetylacetonate complexes. The system was insoluble in benzene and only sparingly soluble in chlorobenzene and o-dichlorobenzene. The chemical shifts were done in methylene chloride with a total titanium concentration of 0.40M and $f_{acac} = 0.50$. Figure 19 illustrates the spectrum obtained under these conditions. In the acetylacetonate ring proton region three well defined peaks were present: $[Ti(acac)(bzbz)_2]^+$, τ3.67; $[Ti(acac)_2(bzbz)]^+$, τ3.72; and $[Ti(acac)_3]^+$, τ3.77. The methyl region gave three peaks which overlapped near the base line. The chemical shift assignments are: $[Ti(acac)(bzbz)_2]^+$, τ7.66; $[Ti(acac)_2(bzbz)]^+$, τ7.70; and $[Ti(acac)_3]^+$, τ7.73.

Figure 18. Ring proton and t-butyl nmr lines (60 MHz) of an equilibrium mixture of 0.30M $[Ti(dpm)_3]^+$ - $[Ti(bzbz)_3]^+$, f_{dpm} = 0.50, in methylene chloride at 33.0°.

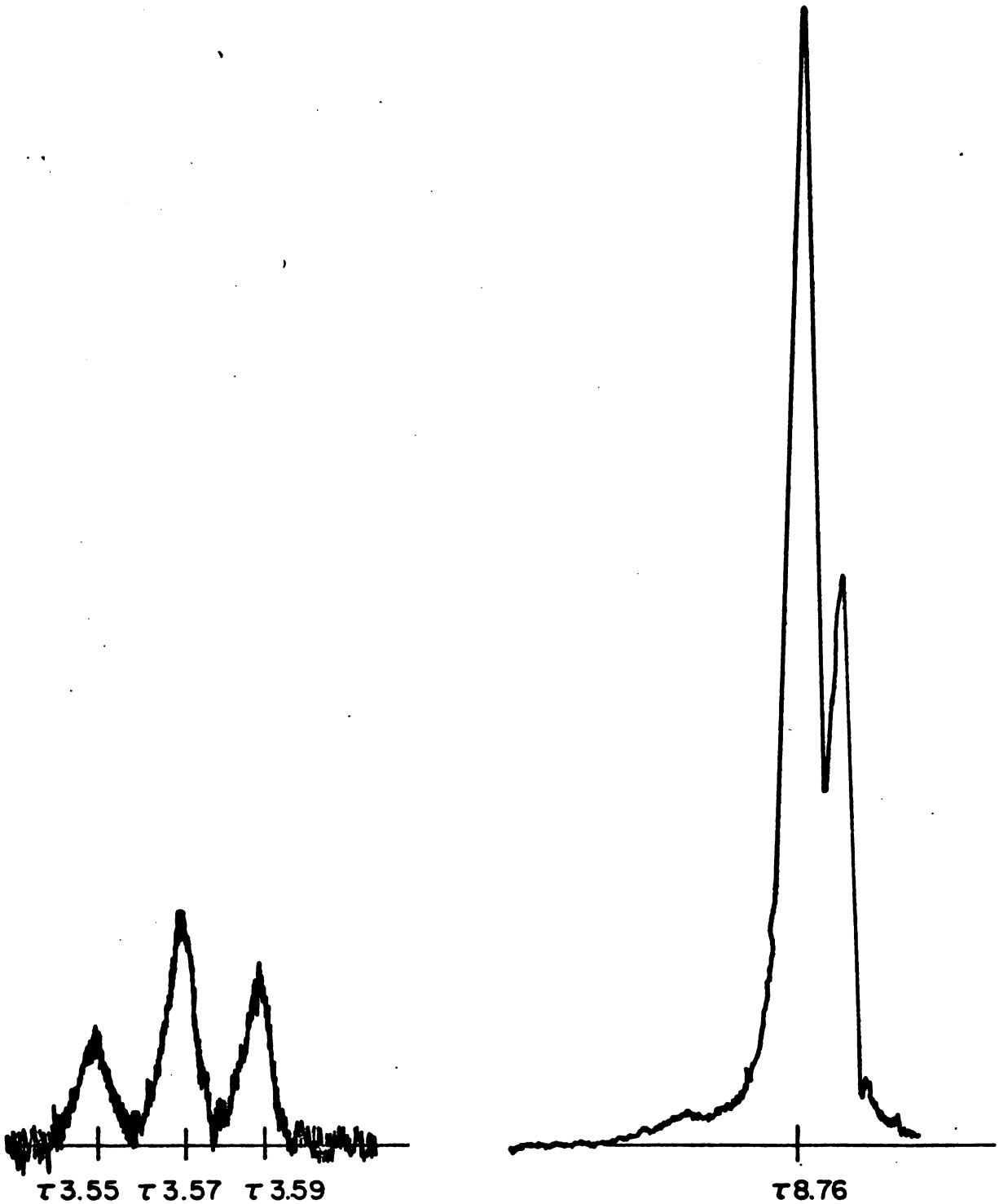
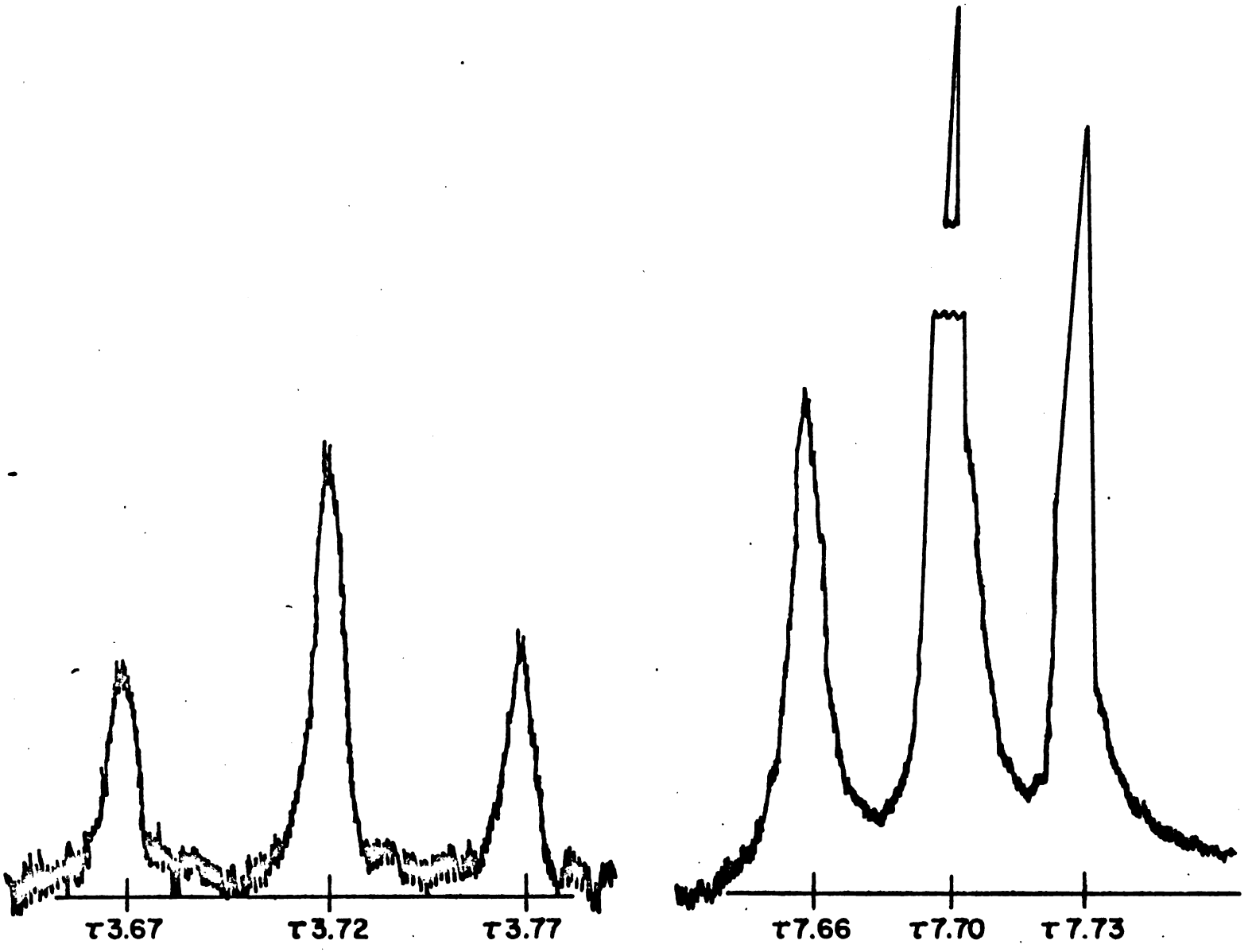

τ 3.55
τ 3.57
τ 3.59
τ 8.76

Figure 19. Ring proton and methyl proton nmr lines (60 MHz) for an equilibrium mixture of 0.40M $[Ti(acac)_3]^+ - [Ti(bzbz)_3]^+$, $f_{acac} = 0.50$, in methylene chloride at 33.0°


τ3.67
τ3.72
τ3.77
τ7.66
τ7.70
τ7.73

The "bis" line, methyl resonance line for $[Ti(acac)_2(bzbz)]^+$, should be a doublet. The sample was run at 100 MHz but there was no indication of a doublet for the "bis" line. The system was then studied at low temperature to see if the doublet could be resolved. Low temperature spectra were examined for samples with the following listed parameters, total concentration of titanium, acetylacetonate concentration, and the lowest temperature achieved. They are: 0.60M Ti(IV), $f_{acac} = 0.33$, $T = -65.5^0$; 0.40M Ti(IV), $f_{acac} = 0.50$, $T = -86.9^0$; 0.30M Ti(IV), $f_{acac} = 0.67$, $T = -89.0^0$. All spectra gave the same results. Although there was a marked broadening of the peaks, the doublet which corresponds to $[Ti(acac)_2(bzbz)]^+$ was not observed. This may be due to the chemical shifts of the two lines in the doublet. That is, the line separation may be very small, and not to the fact that at -89.0^0 the terminal groups are still exchanging.

Although this system was not suitable for kinetic studies by nmr line broadening techniques, the sepctrum of the ring proton region was such that quantitative thermodynamic data could be obtained and this was done.

D. Equilibrium Studies of $[Ti(acac)_3]^+ - [Ti(bzbz)_3]^+$ Mixture

The equilibrium constants were determined for the system $[Ti(acac)_3]^+ - (Ti(bzbz)_3]^+$ in methylene chloride. The equilibria are described by two independent equilibrium

constants, K_1 and K_2, which were determined experimentally and are defined by the following reactions:

(1) $[Ti(bzbz)_3]^+ + [Ti(acac)_2(bzbz)]^+ \overset{K_1}{\rightleftharpoons} 2[Ti(acac)(bzbz)_2]^+$

(2) $[Ti(acac)_3]^+ + [Ti(acac)(bzbz)_2]^+ \overset{K_2}{\rightleftharpoons} 2[Ti(acac)_2(bzbz)]^+$.

For the discussion of the equilibrium in terms of the formation of one mole of the mixed ligand complexes from the parent complexes the equilibrium constants, K_{f1} and K_{f2}, are used and defined by the following reactions:

(3) $2/3[Ti(bzbz)_3]^+ + 1/3[Ti(acac)_3]^+ \overset{K_{f1}}{\rightleftharpoons} [Ti(acac)(bzbz)_2]^+$

(4) $1/3[Ti(bzbz)_3]^+ + 2/3[Ti(acac)_3]^+ \overset{K_{f2}}{\rightleftharpoons} [Ti(acac)_2(bzbz)]^+$.

K_{f1} and K_{f2} may be calculated from K_1 and K_2 from the relationships; $K_{f1} = K_1^{2/3}K_2^{1/3}$ and $K_{f2} = K_1^{1/3}K_2^{2/3}$.

For the statistical distribution of ligands the dependence of the equilibrium molar fraction of each compound, $f_{Ti(acac)_n(bzbz)_{3-n}}$, is given by:

$$f_{Ti(acac)_n(bzbz)_{3-n}} = f_{acac}^{n} f_{bzbz}^{3-n} \frac{3!}{n!(3-n)!},$$

where $n = 0, 1, 2,$ or 3; and f_{acac} and f_{bzbz} are the molar fractions of total ligand present as acetylacetonate and dibenzoylmethanate, respectively. The statistical value for both K_1 and K_2 is 3.00. The statistical value for K_{f1} and K_{f2} is also 3.00.

The concentration of the complexes which were used in the calculations of the equilibrium constants were determined

by integration of their acetylacetonate ring proton lines. The integration was done by planimetry. The concentration of $[Ti(bzbz)_3]^+$ was obtained by difference.

The equilibrium constants, K_1 and K_2 were studied as a function of total solute molarity and ligand composition at 33.3°. The results are tabulated in Tables VI and VII.

Table VI. Dependence of the equilibrium constant for the system $[Ti(acac)_3]^+ - [Ti(bzbz)_3]^+$ on total solute molarity.[a]

Total Molarity	Average Values[b]	
	K_1	K_2
0.137	2.92 ± .26[c]	3.11 ± .13
0.215	2.69 ± .24	2.86 ± .18
0.304	2.65 ± .12	2.81 ± .10
0.429	2.97 ± .22	2.80 ± .08
0.601	3.03 ± .18	2.84 ± .13

[a] In methylene chloride; temperature is 33.3°, $f_{acac} = 0.50$.

[b] Average of at least five spectral measurements.

[c] All errors estimated at the 95% confidence level.

The equilibrium constants are independent of both total solute molarity and ligand composition within experimental error. This implies that the solutions are either close to ideality or that the activity coefficient quotient is constant over the concentration ranges investigated. Tables VI and VII also show that all equilibrium constants are close to the statistical value of 3.00.

Table VII. Dependence of equilibrium constants on ligand composition for the $[Ti(acac)_3]^+$ -$[Ti(bzbz)_3]^+$ system.[a]

	Average Values[b]	
f_{acac}	K_1	K_2
0.339	2.89 ± .14[c]	
0.507	2.65 ± .12	2.81 ± .10
0.665		3.12 ± .20

[a]In methylene chloride; temperature = 33.3°; total solute molarity = 0.301.

[b]Average of at least eight spectral measurements.

[c]All errors estimated at 95% confidence level.

The temperature dependence of K_1 and K_2 was studied so that the enthalpy and entropy of the exchange reactions might be determined. The temperature range was -12.0° to 52.0°, f_{acac} = 0.33 and 0.67 for K_1 and K_2 respectively. Table VIII shows the temperature dependence of K_1 and K_2. Enthalpy and entropy changes for reactions 1 and 2 were determined from the slope and intercept of log K versus 1/T plots. The data were treated by least squares analysis, 29 points were used for K_1 and 31 points were used for K_2.

The thermodynamic data, along with the extrapolated values of K_1 and K_2 at 25° are given in Table IX. Also included in Table IX are the enthalpies, entropies, and equilibrium constants for formation of the mixed ligand complexes from the parent complexes, as defined by reactions 3 and 4. These values were calculated from the experimentally

Table VIII. Temperature dependence of equilibrium constants for the $[Ti(acac)_3]^+$ - $[Ti(bzbz)_3]^+$ system.[a]

Temperature °C	Average Values[b] K_1[c]	K_2[d]
-12.0	3.14 ± .13[e]	2.92 ± .14
9.3	2.94 ± .16	3.08 ± .12
33.3	2.92 ± .14	3.12 ± .20
52.0	2.98 ± .19	2.91 ± .14

[a] In methylene chloride.

[b] Average of at least eight spectral measurements.

[c] f_{acac} = 0.34; total solute molarity = 0.30.

[d] f_{acac} = 0.66; total solute molarity = 0.30.

[e] All errors estimated at the 95% confidence level.

Table IX. Thermodynamic data for formation of mixed ligand complexes in methylene chloride at 25°.

	Equilibrium Constant	ΔH kcal/mole	ΔS eu
K_1	3.0 ± .10	-0.16 ± .16[a]	1.63 ± .52
K_2	2.97 ± .10	0.02 ± .19	2.24 ± .33
K_{f1}	2.99 ± .10	-0.10 ± .17	1.83 ± .46
K_{f2}	2.98 ± .10	-0.04 ± .19	2.04 ± .39
stat. value	3.00	0.0	2.18

[a] All errors estimated at the 95% confidence level.

observed parameters for reactions 1 and 2 with the use of the relationships: $K_{f1} = K_1^{2/3}K_2^{1/3}$ and $K_{f2} = K_1^{1/3}K_2^{2/3}$. The results tabulated in Table IX indicate that the ligand exchange process for this system occurs in a statistical manner. That is, the cationic mixed ligand complexes are formed to the extent predicted by the statistical scrambling of ligands without regard for the chemical properties of the system. These results are consistent with those found for the ligand exchange of neutral species where both of the β-diketonates are non-fluorinated.

IV. BIBLIOGRAPHY

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