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Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ Complexes. 5. The *cis*-$M(AA)_2X_2$ System – Diastereotopic Probe on the Monodentate X Ligands

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Total lineshape analyses of acetylacetonate (acac) methyl group site exchange in a number of cis-*Ti(acac)$_2$(phenoxo)$_2$ complexes, and isopropyl methyl group exchange (inversion) in the isopropyl-substituted phenoxo complexes Ti(acac)$_2$(2-^{i}PrC$_6$H$_4$O)$_2$ and Ti(acac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$ are reported. For the former exchange phenomena, activation energies (kcal/mol) and entropies of activation (eu) in CH_2Cl_2 solutions are, respectively: 8.7 ± 0.5 and −15.7 ± 2.1 (2,6-Cl$_2$C$_6$H$_3$O), 10.4 ± 0.6 and −16.8 ± 2.2 (2-ClC$_6$H$_4$O), 11.6 ± 0.6 and −13.2 ± 2.0 (2-IC$_6$H$_4$O), 11.9 ± 0.8 and −13.7 ± 2.6 (4-ClC$_6$H$_4$O), 11.9 ± 0.6 and −14.5 ± 2.2 (4-^{i}PrC$_6$H$_4$O), 12.5 ± 0.4 and −13.7 ± 1.2 (2-^{i}PrC$_6$H$_4$O), 15.6 ± 0.4 and −3.2 ± 1.4 (2-(C$_6$H$_5$)C$_6$H$_4$O), and 12.4 ± 1.7 and −15 ± 6 (2,6-^{i}Pr$_2$C$_6$H$_3$O). For inversion, the corresponding kinetic data are (CH_2Cl_2 solutions): 4.9 ± 0.2 kcal/mol and −40.7 ± 0.8 eu for Ti(acac)$_2$(2-^{i}PrC$_6$H$_4$O)$_2$, and 7.1 ± 0.7 kcal/mol and −32.6 ± 2.3 eu for Ti(acac)$_2$(2,6-^{i}Pr$_2$C$_6$H$_3$O)$_2$. Comparison of the rates for exchange of acac methyl groups indicate that electronic effects play a major role in the rearrangement processes. The probable mechanism(s) is identified as predominantly twist motions with some contribution from SP-axial and/or TBP-equatorial intermediates* [1].

Introduction

Recent work from this laboratory has addressed itself to the stereochemistry of, and configurational rearrangements in complexes of the type $M(AA)_2X_2$, $M(AA)_2XY$, and $M(AB)_2X_2$ in which the chelating ligands have generally been 1,3-diketones and M = Sn(IV) [2], Si(IV) [3] and Ge(IV) [3, 4]. In the course of these studies, complete permutational [5, 6] and topological and mechanistic[7] analyses have been carried out for these general classes of complexes. Such analyses have been applied to the complexes of the type *cis*-$M(AA)_2X_2$ in which a diastereotopic probe (the isopropyl group) was positioned either on the terminal sites of the AA bidentate ligands (*e.g.* $Me_2CHCOCHCOCHMe_2$) [8] or at the 3-position of the AA diketonate ligand [9]. An important consequence of the presence of a diastereotopic probe on a *cis*-$M(AA)_2X_2$ complex is the possibility of following the steric course of configurational rearrangements in which reversal of helicity in these C_2 optically active species may occur. Work by Finocchiaro [10] and his coworkers [11] on Sn(diketonato)$_2$Cl$_2$ complexes has also addressed itself to the question of whether or not configurational changes co-involve enantiomeric changes.

An interesting position for the diastereotopic probe in these *cis*-$M(AA)_2X_2$ complexes is on the monodentate ligand, X. The simplest possibility is the direct attachment of an isopropyl group on the metal ion; unfortunately, where M is Ti(IV), as in the present case, titanium–carbon σ bonds are notoriously unstable [12]. The isopropoxo group and other alkoxo ligands constitute a good choice and such complexes have recently been studied by Jennings and coworkers [13], and by Fay and Lindmark [14]. However, alkoxo groups afford little possibility of varying the electronic and steric factors which may affect the steric course and/or the energetics of the configurational changes. The phenoxide and substituted phenoxide groups, on the other hand, not only provide for such variations by suitable choice of substituents, but have the added advantage of leading to larger chemical shift differences for exchanging groups that might result from the magnetic anisotropy effect of the aromatic ring.

Harrod and Taylor [15, 16] have prepared and studied a number of Ti(acac)$_2$(phenoxo)$_2$ (acac = anion of 2,4=pentanedione) complexes with a variety of substituents on the phenoxo ligand. Unfortunately, the kinetic data were obtained from an approximate lineshape analysis [16] and therefore subject to considerable systematic errors [17]. Several of these complexes were shown to be stereochemically nonrigid *cis* diastereomers on the basis of

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variable temperature proton nuclear magnetic resonance (nmr), and dipole moment studies [15, 18].

In this work we report our studies on acac terminal methyl group exchange and on exchange of isopropyl methyl groups using a total lineshape analysis in a series of *cis*-$Ti(acac)_2(phenoxo)_2$ complexes with various substituents on the phenoxo ligand (phenoxo = 2,6-$Cl_2C_6H_3O$, 2-ClC_6H_4O, 2-IC_6H_4O, 4-ClC_6H_4O, 4-$^iPrC_6H_4O$, 2-$^iPrC_6H_4O$, 2-$(C_6H_5)C_6H_4O$, and 2,6-$^iPr_2C_6H_3O$). Such systems afford another possibility of establishing a relationship between AA terminal group exchange and inversion of the molecular configuration. All the complexes exhibit acac methyl group exchange and in the case of some isopropyl-substituted phenoxo complexes, isopropyl methyl group exchange is also observed. The study of the former process has been conducted in an attempt to delineate the effect of the X ligand in $M(AA)_2X_2$ on the rate of exchange of acetylacetonate methyl groups. Reference is also made to the earlier permutational [6], and topological and mechanistic [7] analyses in an effort of discriminating between the various physical rearrangement pathways [19].

Experimental

Reagents and Solvents

The following reagent grade chemicals were procured from commercial suppliers and used without further purification: titanium(IV) isopropoxide (Research Organic/Inorganic), 2,4-pentanedione (acetylacetone, Fisher), 4-isopropylphenol (Aldrich), 2-phenylphenol (Eastman), 2-isopropylphenol and 2,6-diisopropylphenol (Aldrich).

All organic solvents used in the preparation and purification of compounds, and in the preparation of nmr samples were reagent grade and were dried by refluxing over calcium hydride chips for at least 12 hr and distilled therefrom immediately prior to use.

General Techniques and Syntheses

The general techniques in preparing the complexes under a dry nitrogen atmosphere have been described earlier [8]. Melting points were measured in capillaries, sealed with modeling clay, and are uncorrected. All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, USA.

Bis(isopropoxo)bis(2,4-pentanedionato)titanium-(IV)

This complex was prepared by direct reaction of titanium(IV) isopropoxide with 2,4-pentanedione (1:2 mol ratio) in benzene, and was used without further purification in the syntheses of the phenoxo complexes.

Bis(2-chlorophenoxo)bis(2,4-pentanedionato)titanium(IV) [20]

Recrystallization from a dichloromethane-hexane solution gave a yellow solid; mp 166–168 °C (dec).

Anal Calcd for $TiC_{22}H_{22}O_6Cl_2$: C, 52.72; H, 4.42. Found: C, 52.39; H, 4.40.

Bis(2-iodophenoxo)bis(2,4-pentanedionato)titanium(IV) [20]

Recrystallization from dichloromethane–hexane produced a yellow-orange solid; mp 141–143 °C (dec). Lit. [18] mp 145–146 °C.

Anal Calcd for $TiC_{22}H_{22}O_6I_2$: C, 38.63; H, 3.24. Found: C, 38.47; H, 3.16.

Bis(2,6-dichlorophenoxo)bis(2,4-pentanedionato)-titanium(IV) [20]

Recrystallization from dichloromethane–hexane gave a yellow-orange solid; mp 112–114 °C (dec).

Anal Calcd for $TiC_{22}H_{20}O_6Cl_4$: C, 46.35; H, 3.54. Found: C, 46.23; H, 3.73.

Bis(4-chlorophenoxo)bis(2,4-pentanedionato)titanium(IV) [20]

Recrystallization from dichloromethane–hexane yielded a yellow solid; mp 114–116 °C (dec). Lit. [18] mp 124–125 °C.

Anal Calcd for $TiC_{22}H_{22}O_6Cl_2$: C, 52.72; H, 4.42. Found: C, 52.64; H, 4.42.

Bis(2,6-diisopropylphenoxo)bis(2,4-pentanedionato)titanium(IV) [20]

Recrystallizations from dichloromethane–hexane and benzene-hexane gave a red solid; mp 136–138 °C (dec). Lit. [18] mp 139–140 °C. The purity of this complex was further verified by infrared and proton nmr spectroscopy.

Bis(2-isopropylphenoxo)bis(2,4-pentanedionato)-titanium(IV)

A solution of 6.30 g (46.3 mmol) of 2-isopropylphenol in 50 ml of benzene was added to a solution of 8.05 g (22.1 mmol) of $Ti(acac)_2(^iC_3H_7O)_2$ in 10 ml benzene. The resulting red solution was stirred at room temperature for 4 hr; removal of solvent under reduced pressure gave a viscous red liquid. This liquid was dissolved in *ca.* 50 ml of hexane and upon concentrating and cooling the solution, a red-orange solid formed which was collected, washed with hexane, and dried *in vacuo*. Recrystallization from dichloromethane–hexane solution gave an orange solid; mp 102–103 °C (dec). Lit. [18] mp 106–107 °C.

Anal Calcd for $TiC_{28}H_{36}O_6$: C, 65.11; H, 7.03. Found: C 65.11; H, 7.07.

Bis(4-isopropylphenoxo)bis(2,4-pentanedionato)titanium(IV)

This compound was prepared in 48% yield by reacting 4.30 g (31.6 mmol) of 4-isopropylphenol with 5.53 g (15.2 mmol) of $Ti(acac)_2(^iC_3H_7O)_2$ in 50 ml of benzene using the same procedure as the 2-isopropylphenoxo complex. Recrystallization from benzene–hexane produced an orange solid; mp 147–149 °C (dec).

Anal Calcd for $TiC_{28}H_{36}O_6$: C, 65.11; H, 7.03; Ti, 9.27. Found: C, 64.91; H, 7.04; Ti, 9.05.

Bis(2-phenylphenoxo)bis(2,4-pentanedionato)titanium(IV)

This product was prepared in 67% yield by a method analogous to the one above. Recrystallization from dichloromethane–hexane gave an orange powder; mp 123–125 °C (dec).

Anal Calcd for $TiC_{34}H_{32}O_6$: C, 69.87; H, 5.52. Found: C, 69.97; H, 5.60.

Nuclear Magnetic Resonance Spectra

Because of the possible hydrolytic instability of the complexes investigated, all handling of solids and preparations of solutions were carried out entirely under anhydrous conditions in a dry nitrogen-filled glove bag. Techniques to prepare the nmr samples, to calibrate the nmr spectrometer, to obtain the nmr spectra, and to determine the sample temperature in the variable temperature nmr experiments are the same as those described earlier [8].

Method of Calculation

The rate of exchange of chemically equivalent nuclei between two nonequivalent, uncoupled sites A and B can be calculated by determining τ_A (or τ_B), the mean lifetime of a nucleus on site A (or B). The nmr experiment provides access to the quantity τ_A (or τ_B). For such a simple system, the Gutowski–Holm [21] (GH) lineshape function expresses transverse magnetization as a function of frequency and of the three parameters: (1) the chemical shift or frequency separation between the two absorption maxima in the absence of exchange, $\delta\nu = \nu_A - \nu_B$ (in Hz); (2) T_{2A} and T_{2B}, the transverse relaxation time for nuclei in site A and site B, respectively, in the absence of exchange; and (3) the first order rate constant, $k = \frac{1}{2}\tau$, where $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$. In using the GH equation it is assumed that the fractional population of sites A and B are equal, $P_A = P_B = 0.5$; also, $T_{2A} = T_{2B}$. In addition, the dependence of both $\delta\nu$ and T_{2A} (and T_{2B}) on temperature must be known in the slow exchange region [22].

For the complexes investigated in this work, T_2 values are temperature dependent as evidenced by viscosity broadening in the region of slow exchange Also, the chemical shift separation between the sites A and B in the absence of exchange is temperature dependent. T_2 values for the acetylacetonate methyl groups were obtained from the linewidths of the related *cis*-$Zr(acac)_2Cl_2$; this complex is not affected by exchange broadening because at all accessible temperatures the rate of exchange is fast on the nmr time scale [23]. The temperature dependence of the linewidth at one-half maximum amplitude ($= 1/\pi T_2$) of the acetylacetonate methyl resonance of *cis*-$Zr(acac)_2Cl_2$ in CH_2Cl_2 solution has been reported by Fay and Lowry [24]. Their data were taken to estimate the appropriate T_2 value to be used for lineshape calculations *at each temperature* for the complexes studied in CH_2Cl_2 solution. Failure to correct for the temperature dependence of T_2 in the lineshape calculations may result in curvature of the Arrhenius plots of log k *vs.* 1/T in the slow exchange region, with a consequent increase in the "random" errors in E_a and $\Delta S^{\neq}$ obtained by linear least-squares analysis [25].

The appropriate value of $\delta\nu$ to be used in the calculations was determined from the measurements of $\delta\nu$ at a series of temperatures in the slow exchange region. From the plot of $\delta\nu$ *vs.* temperature, the straight line portion in the slow exchange region was extrapolated [3, 26] into the intermediate and fast exchange regions. Values of $\delta\nu$ appropriate to the particular temperature were then read directly from such a plot.

Where the dependence of $\delta\nu$ on temperature was known, values of the mean residence times were obtained by comparing the experimental spectra with theoretical spectra computer-calculated using the GH total lineshape function at intervals of 0.005 Hz for an appropriate range of *ca.* 240 values of τ. Input parameters to the computer program consisted of values of $\pi\delta\nu$, T_{2A} and T_{2B}, and P_A and P_B at each temperature. Generally, the following characteristic line-shape parameters were used to numerically compare theoretical and experimental spectra: linewidths at one-quarter ($W_{1/4}$), one-half ($W_{1/2}$), and three-quarters ($W_{3/4}$) maximum amplitude, and, below coalescence, $\delta\nu_e$, the experimental frequency separation during exchange between the two absorptions, and R, the ratio of the maximum amplitude to the central minimum. The τ values giving the best agreement between theoretical and experimental spectra for each lineshape parameter were averaged with each lineshape parameter being given equal weight. The τ values for acetylacetonate methyl group exchange studied in this work are summarized in Table I.

A similar total lineshape analysis was carried out for the isopropyl methyl group exchange in dichloromethane solution of the complexes $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$. The analysis was performed on the more intense lowfield doublet of the isopropyl quartet; either doublet may be used to extract kinetic data (see *e.g.* Figure 1). The appropriate τ values are collected in Table II.

TABLE I. Mean Residence Times for Acetylacetonate Methyl Group Exchange in $Ti(acac)_2(phenoxo)_2$ Complexes.

2-ClC_6H_4O[a]		2-IC_6H_4O[a]		4-ClC_6H_4O[b]	
Temp.,[c] °C	$\tau \times 10^2$, sec	Temp.,[c] °C	$\tau \times 10^2$, sec	Temp.,[c] °C	$\tau \times 10^2$, sec
−15.5	9.4	−13.4	13	−9.1	17
−11.0	7.0	−9.1	8.2	−2.7	13
−7.6	4.9	−2.7	5.5	0.2	9.0
−3.2	3.6	0.2	4.4	4.6	7.3
0.8	2.9	4.6	3.5	7.5	5.6
3.5	2.4	7.5	2.7	11.1	4.3
7.3	1.8	11.1	2.2	12.0	3.0
11.4	1.3	12.0	1.9	15.2	3.0
16.9	1.1	16.1	1.4	16.1	2.8
26.8	0.50	19.1	1.0	16.8	2.5
		25.2	0.75	18.9	2.0
		30.0	0.48	19.1	2.1
		34.8	0.35	20.8	2.0
		38.1	0.36	25.2	1.6
				30.0	0.90
				34.8	0.72
				38.1	0.73
2-$^i PrC_6H_4O$[b]		4-$^i PrC_6H_4O$[b]		2-$(C_6H_5)C_6H_4O$[b]	
Temp.,[c] °C	$\tau \times 10^2$, sec	Temp.,[c] °C	$\tau \times 10^2$, sec	Temp.,[c] °C	$\tau \times 10^2$, sec
14.6	8.8	6.4	8.9	20.5	6.3
15.5	8.3	8.5	7.5	22.9	5.0
17.9	7.5	12.3	5.9	24.3	4.3
20.3	6.3	14.1	5.1	27.3	3.3
22.1	5.4	17.5	4.3	29.4	2.8
25.0	4.2	20.2	3.7	30.2	2.5
25.1	4.4	20.9	3.1	32.6	2.2
28.6	3.5	23.8	2.9	36.2	1.6
30.2	2.9	25.2	2.4	37.4	1.4
32.2	2.6	26.8	2.2	41.5	1.0
33.6	2.4	27.9	2.1		
36.1	2.1	30.0	1.7		
40.0	1.5	32.0	1.3		
43.6	1.3	37.2	1.1		
47.0	1.0	39.7	0.91		
2,6-$^i PrC_6H_3O$[b]					
Temp.,[c] °C	$\tau \times 10^2$, sec				
13.8	13				
16.1	11				
22.7	7.6				
25.2	7.5				
28.6	4.5				
29.5	4.2				
33.3	3.7				
35.2	3.0				
37.9	2.9				
40.6	1.9				

[a] 0.250*M* in dichloromethane. [b] 0.300*M* in dichloromethane. [c] Calculated from the Van Geet equation for methanol and/or ethyleneglycol (see text).

For the $Ti(acac)_2(2,6\text{-}Cl_2C_6H_3O)_2$ complex, the slow exchange region could not be attained; this necessitated the use of a computer-fitting of digitized spectra, as described earlier [27]. The *cis*-$Zr(acac)_2$-

TABLE II. Mean Residence Times for Isopropyl Methyl Group Exchange in $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$.

$2\text{-}^iPrC_6H_4O$[a]		$2,6\text{-}^iPr_2C_6H_3O$[a]	
Temp.,[b] °C	$\tau \times 10^2$, sec	Temp.,[b] °C	$\tau \times 10^2$, sec
−8.4	25	3.0	15
−1.0	20	7.7	12
1.7	18	13.8	9.3
3.8	18	16.1	8.6
4.9	17	22.4	7.5
7.3	15	22.7	6.8
8.2	14	25.2	6.5
12.1	13	28.6	5.2
12.6	13	29.5	4.6
14.6	13	33.3	4.6
15.5	11	35.2	3.7
17.9	11	40.6	3.3
19.9	10		
20.3	10		
22.9	9.4		
24.8	9.1		
25.0	9.2		

[a]0.300*M* in dichloromethane. [b]Calculated from the Van Geet equation for methanol and/or ethylene glycol (see text).

Cl_2 complex was employed as the source of linewidths for the program input, and these were held constant at each temperature. Below coalescence, the only fixed parameter employed was the linewidth; the program was allowed to search for the best combination of τ_A, τ_B, and $\delta\nu$ which produced the closest fit to the observed spectrum. For temperatures above coalescence, problems were encountered in obtaining reasonable computer-fittings when $\delta\nu$ was allowed to vary. To overcome this problem, the values of $\delta\nu$ obtained below coalescence were extrapolated into the intermediate exchange region. Values for $\delta\nu$ from this extrapolation were used as input data for temperatures above coalescence and remained fixed. The resulting mean lifetimes obtained through this procedure are listed in Table III.

Results

Figures 1 and 2 illustrate the temperature dependence of the acetylacetonate and isopropyl methyl resonances of the $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(4\text{-}^iPrC_6H_4O)_2$ complexes, respectively, in dichloromethane solutions. A single acetylacetonate methyl resonance is observed at ambient temperature; on cooling the signal broadens and splits into two resonances of equal intensity, indicative of a *cis* structure in solution [2–4, 8, 9, 13, 14]. Such behaviour is typical of all the $Ti(acac)_2(phenoxo)_2$ complexes studied; only the coalescence temperatures differ. For the $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ complex, the isopropyl methyl resonance appears as a single doublet at room temperature. On cooling, this doublet broadens and eventually two doublets are observed below ~8 °C. Similar behaviour occurs for the isopropyl methyl resonances of the $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complex. However, as Figure 2(b) reveals, the isopropyl methyl resonances of the $Ti(acac)_2(4\text{-}^iPrC_6H_4O)_2$ complex fail to split into two doublets at low temperatures. The $W_{1/2}$ values for the isopropyl methyl doublet change only from 1.09, 1.07 Hz at 39.7 °C to 1.80, 1.90 Hz at −46.3 °C. This reflects line broadening due to viscosity and solvation changes at low temperature.

The concentration dependence of the mean residence times for acetylacetonate methyl group exchange in the $Ti(acac)_2(phenoxo)_2$ complexes and for isopropyl methyl group exchange in the complexes $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ is summarized in Tables IV and V, respectively. These data demonstrate that the rate

TABLE III. Temperature Dependence of Mean Residence Times for Exchange of Acetylacetonate Methyl Groups in $Ti(acac)_2(2,6\text{-}Cl_2C_6H_3O)_2$ from Computer-Fitted Spectra.[a,b]

Temp.,[c] °C	τ_A, sec	τ_B, sec	2τ, sec	k (= $1/2\tau$), sec^{-1}	$\delta\nu_o$, Hz
−63.7	0.20	0.19	0.20	5.0	10.30
−61.1	0.16	0.15	0.16	6.3	10.39
−57.1	0.11	0.11	0.11	9.0	10.28
−51.5	0.059	0.058	0.058	17.2	10.73
−47.9	0.044	0.045	0.044	22.7	10.69
−42.6	0.026	0.030	0.028	35.7	10.23
−38.4	0.018	0.028	0.022	45.5	10.06[d]
−35.6	0.013	0.018	0.015	66.7	10.04[d]
−29.5	0.0099	0.013	0.011	90.9	9.98[d]

[a]0.250 *M* in dichloromethane. [b]The τ_A, τ_B, and $\delta\nu_o$ parameters were allowed to vary in the computer-fitting procedure unless noted otherwise. [c]Calculated from the Van Geet equation for methanol (see text). [d]Fixed parameter.

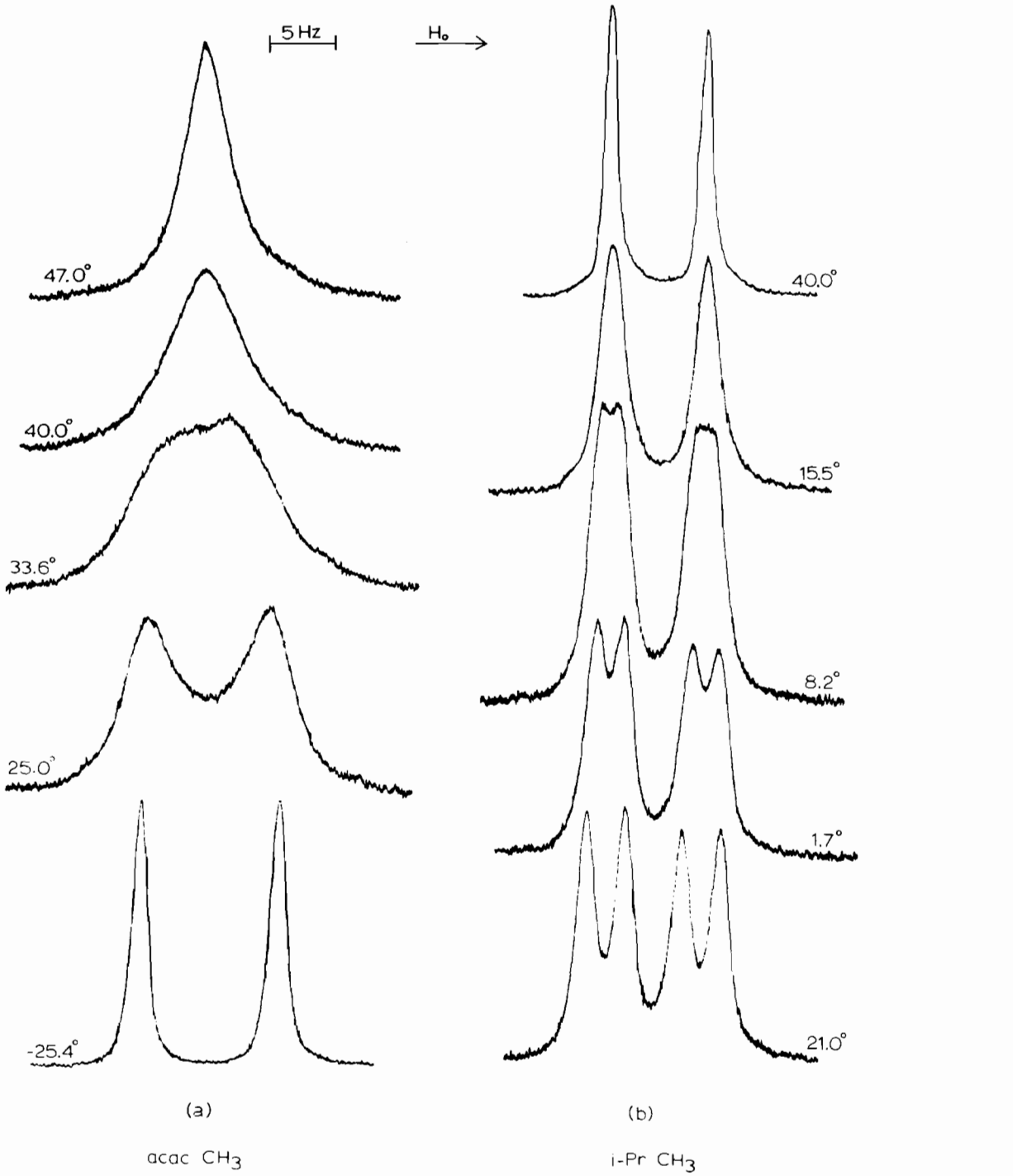

Figure 1. Temperature dependence of the (a) acetylacetonate and (b) isopropyl methyl resonances in the proton nmr spectrum of the $Ti(acac)_2(2\text{-}^{i}PrC_6H_4O)_2$ complex in dichloromethane solution, 0.300 *M*.

of exchange is independent of concentration and that exchange is a first-order process.

The Arrhenius activation energy, E_a, and frequency factor, A, were obtained in the usual manner from the slope and intercept, respectively, of the least-square straight line plots of log k *vs.* 1/T (see Figures 3 and 4 for typical plots), where k ($= \frac{1}{2}\tau$) is the first-order rate constant for exchange. Activation entropies, $\Delta S^{\neq}$, were obtained from the expression $\Delta S^{\neq} = R[\ln A - \ln RT/Nh] - R$ [2].

Arrhenius and Eyring activation parameters for exchange of acetylacetonate methyl groups in the

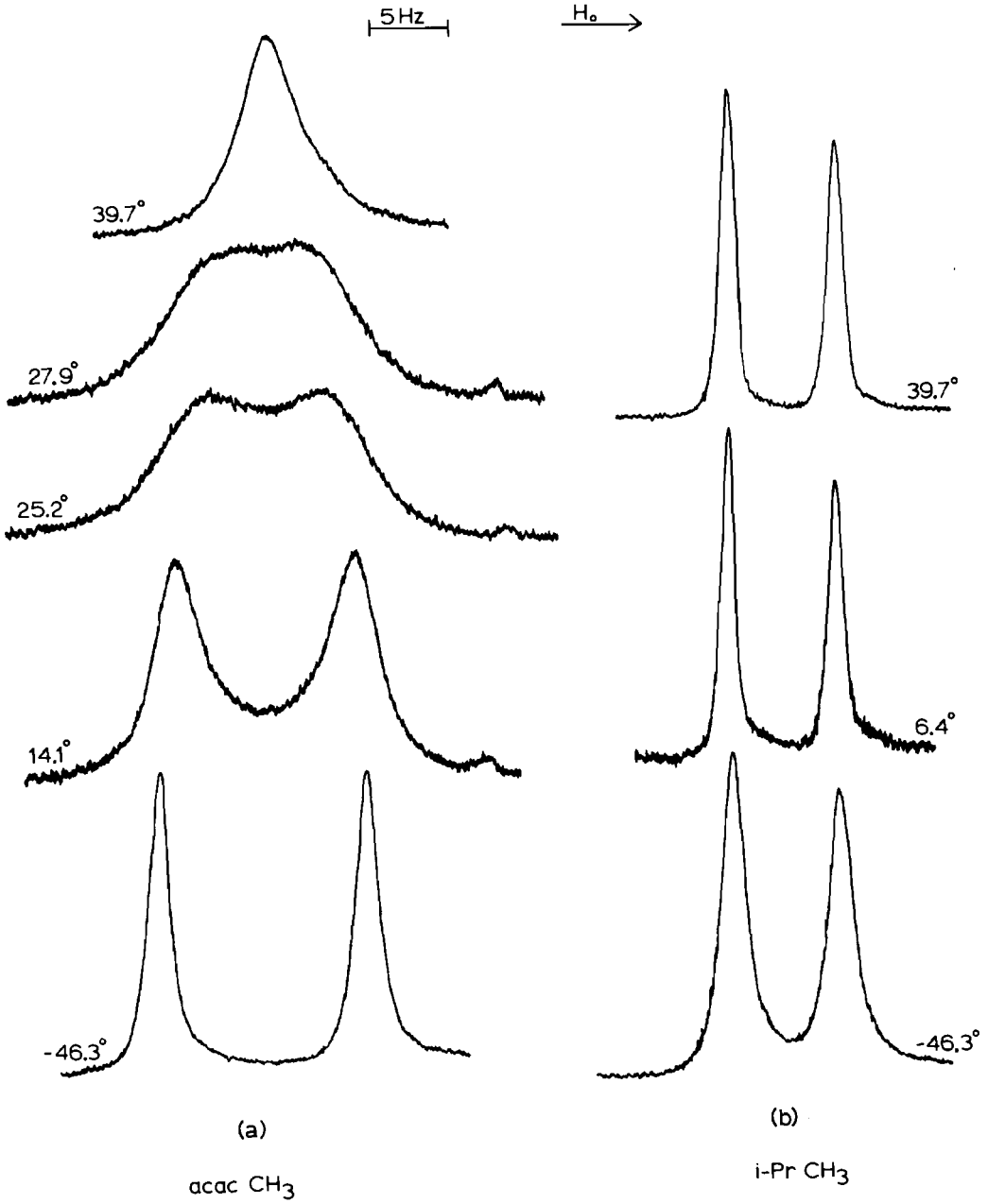

Figure 2. Temperature dependence of the (a) acetylacetonate and (b) isopropyl methyl resonances in the proton nmr spectrum of the $Ti(acac)_2(4\text{-}^{i}PrC_6H_4O)_2$ complex in dichloromethane solution, 0.300 *M*.

$Ti(acac)_2(phenoxo)_2$ complexes are collected in Table VI. The corresponding parameters for isopropyl methyl group exchange in the complexes $Ti(acac)_2(2\text{-}^{i}PrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^{i}Pr_2C_6H_3O)_2$ are listed in Table VII. The error limits attached to these activation parameters reflect only the random scatter of the data points, estimated at the 95% confidence level, and do not contain any possible contribution from systematic errors [2, 25].

Table VI also demonstrates that substantial systematic errors are introduced in kinetic parameters when the Varian methanol "thermometer" [28] is used to measure the sample temperatures. For the $Ti(acac)_2(2\text{-}ClC_6H_4O)_2$ complex, activation parameters were calculated utilizing temperatures calculated from Van Geet's equation [29] for methanol and the Varian methanol calibration curve. Use of the latter results in decreased values for $\Delta H^{\neq}$,

TABLE IV. Concentration Dependence of Mean Residence Times for Acetylacetonate Methyl Group Exchange in $Ti(acac)_2(phenoxo)_2$ Complexes[a] at Selected Temperatures.

Phenoxo Ligand	Temp., °C	Concentration, *M*	τ, sec
$2,6\text{-}Cl_2C_6H_3O$	−53.3	0.250	0.036[b]
		0.150	0.041
	−43.6	0.250	0.016[b]
		0.150	0.014
$2\text{-}ClC_6H_4O$	−0.8	0.250	0.032[b]
		0.150	0.035
	5.5	0.250	0.020[b]
		0.150	0.021
$2\text{-}IC_6H_4O$	8.0	0.300	0.024[b]
		0.150	0.025
	16.7	0.300	0.013[b]
		0.150	0.014
$4\text{-}ClC_6H_4O$	11.4	0.300	0.033[b]
		0.150	0.034
	22.2	0.300	0.015[b]
		0.150	0.016
$4\text{-}^iPrC_6H_4O$	6.4	0.300	0.089
		0.150	0.109
	8.5	0.300	0.075
		0.150	0.083
	20.2	0.300	0.037
		0.150	0.038
	23.8	0.300	0.029
		0.150	0.028
	32.0	0.300	0.013
		0.150	0.014
$2\text{-}^iPrC_6H_4O$	28.6	0.300	0.035
		0.150	0.033
	36.1	0.300	0.021
		0.150	0.019
$2,6\text{-}^iPr_2C_6H_3O$	28.7	0.300	0.048[a]
		0.150	0.043
	40.0	0.300	0.023[a]
		0.150	0.021
$2\text{-}(C_6H_5)C_6H_4O$	20.5	0.300	0.063
		0.150	0.067
	24.3	0.300	0.043
		0.150	0.043
	30.2	0.300	0.025
		0.150	0.025
	36.2	0.300	0.016
		0.150	0.016

[a]In dichloromethane. [b]Calculated from the activation parameters of Table VI at the indicated temperatures.

E_a, and log A, while $\Delta S^{\neq}$ becomes more negative; these differences are outside the error limits estimated at the 95% confidence level. While other activation parameters change, the $\Delta G^{\neq}$ values are constant using these two temperature scales. This suggests that $\Delta G^{\neq}$ is insensitive to systematic errors, inasmuch as the error in $\Delta H^{\neq}$ is offset by the error in $\Delta S^{\neq}$.

Discussion

Acetylacetonate Methyl Group Exchange

Comparison of the kinetic data for exchange of acetylacetonate methyl groups in $Ti(acac)_2X_2$ (X = halide or pseudo-halide) (Table III of ref. 9) and $Ti(acac)_2(phenoxo)_2$ complexes (Table VI) reveals that, excluding the $Ti(acac)_2(2,6\text{-}Cl_2C_6H_3O)_2$ com-

TABLE V. Concentration Dependence of Mean Residence Times for Isopropyl Methyl Group Exchange in $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ Complexes in Dichloromethane Solution.

Complex	Temp., °C	Concentration, *M*	τ, sec
$Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$	3.8	0.300	0.175
		0.150	0.179
	12.6	0.300	0.133
		0.150	0.128
$Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$	15.5	0.300	0.089[a]
		0.150	0.093
	23.4	0.300	0.064[a]
		0.150	0.064

[a]Calculated from the activation parameters of Table VII at the indicated temperatures.

TABLE VI. Kinetic Data[a] for Acetylacetonate Methyl Group Exchange in $Ti(acac)_2(phenoxo)_2$ Complexes in Dichloromethane.

Phenoxo Ligand	k_{298} (sec^{-1})	$\Delta H^{\neq}_{298}$ (kcal/mol)	$\Delta S^{\neq}_{298}$ (eu)	$\Delta G^{\neq}_{298}$ (kcal/mol)	E_a (kcal/mol)	log A
$2,6\text{-}Cl_2C_6H_3O$[b]	2.6×10^3	8.1 ± 0.5[d]	−15.7 ± 2.1	12.80 ± 0.05	8.7 ± 0.5	9.79 ± 0.45
$2\text{-}ClC_6H_4O$[b]	84	9.8 ± 0.6	−16.8 ± 2.2	14.82 ± 0.06	10.4 ± 0.6	9.56 ± 0.49
	86[e]	8.9 ± 0.6	−19.7 ± 2.0	14.80 ± 0.06	9.5 ± 0.6	8.93 ± 0.45
$2\text{-}IC_6H_4O$[c]	67	11.0 ± 0.6	−13.2 ± 2.0	14.96 ± 0.04	11.6 ± 0.6	10.33 ± 0.43
$4\text{-}ClC_6H_4O$[c]	34	11.2 ± 0.8	−13.7 ± 2.6	15.36 ± 0.04	11.9 ± 0.8	10.24 ± 0.58
$4\text{-}^iPrC_6H_4O$[c]	21	11.3 ± 0.6	−14.5 ± 2.2	15.66 ± 0.02	11.9 ± 0.6	10.05 ± 0.64
$2\text{-}^iPrC_6H_4O$[c]	12	11.9 ± 0.4	−13.7 ± 1.2	16.43 ± 0.01	12.5 ± 0.4	10.24 ± 0.26
$2\text{-}(C_6H_5)C_6H_4O$[c]	12	15.0 ± 0.4	−3.2 ± 1.4	15.97 ± 0.01	15.6 ± 0.4	12.53 ± 0.31
$2,6\text{-}^iPr_2C_6H_3O$[c]	8.1	11.8 ± 1.7	−15 ± 6	16.21 ± 0.05	12.4 ± 1.7	10.0 ± 1.2

[a]Data obained using Van Geet temperatures unless otherwise noted (see text). [b]0.250 *M*. [c]0.300 *M*. [d]All errors are random errors estimated at the 95% confidence level. [e]Data calculated using Varian temperatures (see text).

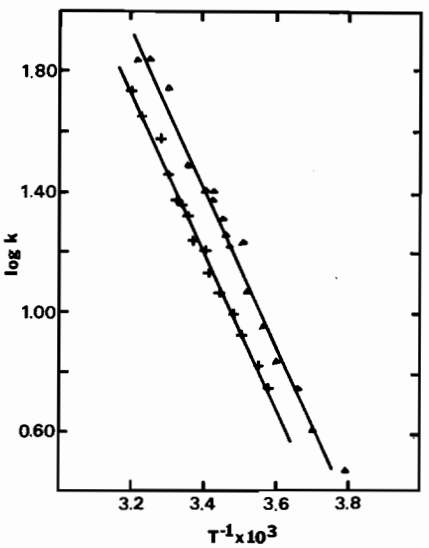

Figure 3. Arrhenius least-squares plots for acetylacetonate methyl group exchange in the $Ti(acac)_2(4\text{-}ClC_6H_4O)_2$ (+) and $Ti(acac)_2(4\text{-}^iPrC_6H_4O)_2$ (△) complexes in dichloromethane solution.

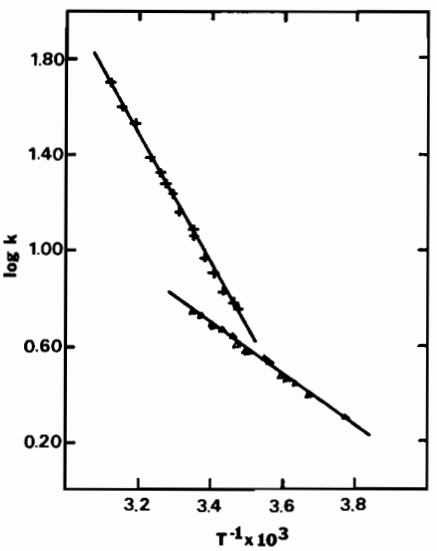

Figure 4. Arrhenius least-squares plots for acetylacetonate methyl group (+) and isopropyl methyl group exchange (△) in the $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ complex in dichloromethane solution.

TABLE VII. Kinetic Data for Isopropyl Methyl Group Exchange in Bis(acetylacetonato)titanium(IV) Complexes Containing Isopropyl-substituted Phenoxo Ligands.

Complex	k_{298} (sec^{-1})	$\Delta H^{\neq}_{298}$ (kcal/mol)	$\Delta S^{\neq}_{298}$ (eu)	$\Delta G^{\neq}_{298}$ (kcal/mol)	E_a (kcal/mol)	log A
$Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$[a]	5.5	4.3 ± 0.2[b]	−40.7 ± 0.8	16.43 ± 0.01	4.9 ± 0.2	4.32 ± 0.19
$Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$[a]	8.3	6.3 ± 0.7	−32.6 ± 2.3	16.19 ± 0.03	7.1 ± 0.7	6.10 ± 0.50

[a]0.300 *M* in dichloromethane. [b]All errors are random errors estimated at the 95% confidence level.

plex, the phenoxo complexes are considerably less labile than their halide counterparts. In general, the k_{298} values are reduced by a factor of 10^1–10^2 on progressing from halo to phenoxo complexes. This may be a result of electronic and/or steric effects. In this regard, the halo-substituted phenoxo species are slightly more labile than the alkyl- or aryl substituted analogues, with the 2,6-dichloro complex displaying a rate of exchange ~10^2–10^3× larger than that of the other complexes of Table VI. That the steric effects play only a minor role in the rate of the rearrangement process is seen by comparing the rate for the 2-chloro complex (84 sec^{-1}) with that for the 2-iodo analogue (67 sec^{-1}), and the 2-isopropyl complex (12 sec^{-1}) with the rate for the 2-phenyl substituted species (12 sec^{-1}). In contrast, comparison of the rate of exchange for the 2,6-dichloro species (2.6×10^3 sec^{-1}) with that for the 2,6-diisopropyl complex (8.1 sec^{-1}), and the 2-chloro complex (84 sec^{-1}) with the 2-isopropyl species (12 sec^{-1}) definitely indicates that electronic effects, arising from the particular substituents, play a major role in the rearrangement phenomena. It is noteworthy that the rate of acetylacetonate methyl site exchange in some $Ti(acac)_2(alkoxo)_2$ complexes decreases as the bulk of the alkoxo group increases in the order $(CH_3)_2CHCH_2O$ (19.6 sec^{-1}) > $(CH_3)_2$-CHO (8.9 sec^{-1}) > $C_6H_5(CH_3)_2CO$ (0.73 sec^{-1}) [14].

Further, within the phenoxo series of complexes there appears to be some degree of relationship between the Lewis basicity of the phenoxide anion and the rate of rearrangement of its complex. The phenol $2,6\text{-}Cl_2C_6H_3OH$ is the more acidic phenol that we have employed (least basic phenoxide) with a pK_a of 7.00 [30]; interestingly, the $Ti(acac)_2(2,6\text{-}Cl_2C_6H_3O)_2$ complex is the most labile of the phenoxo complexes studied. Alkyl-substituted phenols generally possess pK_a values in the 10–11 range [30] and their phenoxide anions are more basic than halo-substituted analogues. In bonding to the titanium centre, the more basic phenoxide anions are expected to possess the stronger Ti–O(phenoxide) bonds and thus should lead to a relative weakening of the *trans* Ti–O(acac) bonds. If a bond rupture mechanism were solely operative, the rearrangement rate would be expected to increase as the basicity of the phenoxide anion increases (pK_a of the parent phenol increases). With the limited available data this trend is not observed, which tends to argue against a bond rupture mechanism as the sole reaction pathway.

It must be pointed, however, that the use of pK_a values for aqueous solutions may not be valid in non-aqueous solvents. For example, 2-6-butylphenol is less acidic than phenol in aqueous solution but is more acidic than phenol in the gas phase [31]. The solvent medium seems to attenuate substituent effects in determining the acidities of phenols [31].

Isopropyl Methyl Group Exchange

Before discussing the kinetic data for isopropyl methyl group exchange in $Ti(acac)_2$(isopropyl-substituted phenoxo)$_2$ complexes, it is instructive to consider the origin of the observed nonequivalence of isopropyl methyl groups and of the exchange process. Two possible sources need be considered: (i) the dissymetry centred on the titanium renders the isopropyl methyl groups diastereotopic and exchange results from inversion of the molecular configuration, and (ii) hindered rotation about the Ti–O–C (phenoxide) moiety results in nonequivalent isopropyl methyl groups and rapid rotation at higher temperatures leads to exchange of the nonequivalent groups.

In the $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complex, there are a total of four different isopropyl groups in the event of no exchange processes of any kind. Sources (i) and (ii) would interconvert different pairs of isopropyl methyl groups and would result in a single doublet if both sources were implicated, or two doublets if only one source is involved. Thus, the observed behaviour [32] of two doublets coalescing into one is consistent with either source (i) or (ii). However, source (ii) cannot cause isopropyl methyl group exchange in the $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ complex and, therefore, only source (i) remains a viable explanation for the behaviour of this complex (Figure 1). Comparison of the kinetic data for isopropyl methyl group exchange in the $Ti(acac)_2$-$(2,6\text{-}^iPr_2C_6H_3O)_2$ and $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ complexes (Table VII) suggests that the same process is operative in both complexes. Thus the exchange process involving isopropyl methyl groups is iden-

tified as resulting from inversion of the molecular configuration.

Further support for this conclusion is afforded by the $Ti(acac)_2(^iC_3H_7O)_2$ complex. A single isopropyl methyl doublet is observed at room temperature; on cooling, this doublet broadens and splits into two doublets [16, 33]. Earlier workers [15, 33] attributed the two isopropyl methyl doublets to restricted rotation. However, a hindered rotation process (source (ii)) is not possible for $Ti(acac)_2(^iC_3H_7O)_2$ inasmuch as the isopropyl methyl groups remain diastereotopic in any rotational configuration and in the event of rapid rotation. Jennings and coworkers [13] also have pointed out that the geminal methyl groups in this isopropoxide complex are diastereotopic for symmetry reasons even when rotation is free. An analogous behaviour is expected for the $Ti(acac)_2(4\text{-}^iPrC_6H_4O)_2$ complex, but apparently, as Figure 2 reveals, the isopropyl methyl groups are not anisochronous. This may result from the greater distance of the diastereotopic probe from the centre of dissymmetry and/or from the isopropyl group being outside the region of magnetic anisotropy, generated by the aromatic ring, leads to unresolved chemical shift differences between the diastereotopic isopropyl methyl groups.

Mechanism(s) of the Configurational Rearrangements

Table VII summarizes the kinetic data for exchange of isopropyl methyl groups in complexes containing isopropyl-substituted phenoxo ligands. Some information on the rearrangement mechanism(s) may be deduced by comparing k_{298} and $\Delta G^{\neq}$ values for acetylacetonate and isopropyl methyl group exchange for complexes in which both processes occur simultaneously (*cf.* Table VI and VII). The relative rates for isopropyl (k_{inv}) and acetylacetonate (k_{exch}) methyl group exchange will depend on the mechanism [19, 34]; the free energies of activation are expected to be similar (*cf.* Table I of ref. 14). The $\Delta G^{\neq}$ values (Table VI and VII) for both exchange processes are identical for the $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ and $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complexes. This would suggest that a common physical pathway is responsible for exchange of acac and isopropyl methyl groups. Surprisingly the enthalpies of activation for inversion (Table VII) are 5–8 kcal/mol smaller than for acac methyl group exchange; the corresponding entropies of activation are 18–27 eu more negative.

An indication of the identity of the mechanism(s) is also afforded by the ratio of rates of acetylacetonate methyl group exchange to isopropyl methyl group exchange, k_{exch}/k_{inv} [14, 19, 34]. This ratio is 1.0, 1.4, and 2.2 for $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ in dichloromethane, $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ in m-dichlorobenzene [32], and $Ti(acac)_2(2^iPrC_6H_4O)_2$ in dichloromethane, respectively. For the analogous alkoxo complexes the ratio falls in the range 0.5 to 1.0 [13, 14] depending on the steric bulk of the alkoxide ligand [14].

The changes in signal multiplicities for isopropyl-substituted phenoxo complexes of the type *cis*-$M(AA)_2X_2$ (*cf.* Table IV of ref. 6) are consistent with either averaging set A_6 or A_5. A_6 predicts a k_{exch}/k_{inv} ratio of unity; A_5 predicts a ratio of 0.5.

The observed ratio of unity for the $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complex in dichloromethane solution allows the averaging set for this complex to be identified as A_6 (however, see also ref. 14). In the nomenclature of Figure 2 of ref. 6 this limits the rearrangement reactions to

$$cis\text{-}\Lambda_{23} \rightleftharpoons cis\text{-}\Delta_{14}$$

$$cis\text{-}\Lambda_{24} \rightleftharpoons cis\text{-}\Delta_{13}$$

and no others. No bond rupture mechanism *via* TBP (trigonal-bipyramidal) intermediates (axial and equatorial) provides a path for this rearrangement (*cf.* Figures 1–3 of ref 7). Also, no TBP intermediate undergoing pseudorotation processes generates these reactions [19]. These reactions may easily be accommodated by a twist mechanism and by a bond rupture mechanism *via* SP-axial intermediates [7]. No definitive choice between these alternatives can be made; however, the $\Delta S^{\neq}$ values for exchange are quite negative (–33 and –15 eu for isopropyl and acac methyl group exchange, respectively), and negative entropies of activation have long been argued as supporting a twist mechanism [19, 34]. However, in the light of more recent results, use of $\Delta S^{\neq}$ values as reliable indicators of mechanism may be tenuous [5].

The increase in the k_{exch}/k_{inv} ratio for the $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ complex on progressing from dichloromethane to *m*-dichlorobenzene solutions is enigmatic. As this change in ratio appears to be outside of experimental error (estimated at 10%), the most simple rationalization is that more than one physical process may be implicated. This ratio implies that acac methyl groups are exchanged more rapidly than inversion occurs, a result which no single physical process accommodates. In addition to the twist motions suggested for this complex in dichloromethane, another process which exchanges acac methyl groups but does not result in inversion must also be operative. Only TBP-equatorial and SP-axial intermediates could possibly accomodate such a process (*cf.* Figures 1–3 of ref. 7).

In a recent analogous study on inversion and diketonate R-group exchange in dialkoxobis(β-diketonato)titanium(IV) complexes, Fay and Lindmark [14] have noted that certain intramolecular pathways could be ruled out as the sole rearrangement pathway on the basis of the observed values of

k_{exch}/k_{inv}. For example, rearrangement through TBP-axial and TBP-equatorial five-coordinate intermediates with a monodentate diketonate ligand requires k_{exch}/k_{inv} to be ≤ 0.5 and ∞, respectively, while twists about a single octahedral C_3 axis [19] predict $k_{exch}/k_{inv} = 1.0$ or 0.5, depending on the C_3 axis about which the twist takes place. It was concluded that the observed variation in k_{exch}/k_{inv} (from 0.5 to 1.0) [13, 14] requires a mixture of two or more mechanisms with the relative contribution of each depending on the steric bulk of the alkoxide group. In view of this, our assignment of the rearrangements in the $Ti(acac)_2(2,6\text{-}^iPr_2C_6H_3O)_2$ to the A_6 averaging set must be regarded as equivocal; the A_5 set is by no means excluded by our data.

The $Ti(acac)_2(2\text{-}^iPrC_6H_4O)_2$ complex possesses a larger, more puzzling value of 2.2 for k_{exch}/k_{inv}. As no single physical pathway can generate such a large ratio, a mixture of rearrangement mechanisms is indicated. Participation of TBP-equatorial and SP-axial intermediates, in addition to twists, is also implied, since some component of the mixture of physical mechanisms must result in exchange without inversion.

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