Contribution from the Department of Chemistry,
Sir George Williams Campus, Concordia University, Montreal, Quebec, Canada H3G 1M8

Configurational Rearrangements in *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ Complexes. 6. Bis(chelate)bis(2,6-diisopropylphenoxy)titanium Systems (Chelate = Acetylacetonate, 8-Hydroxyquinolinate, and 8-Hydroxyquinaldinate)[1-6]

DOUGLAS G. BICKLEY and NICK SERPONE*

Received November 3, 1978

For a series of bis(chelate)bis(2,6-diisopropylphenoxy)titanium complexes [chelate = acetylacetonate (acac), 8-hydroxyquinolinate (ox), and 8-hydroxyquinaldinate (quin)] an NMR total line shape analysis of isopropyl methyl group exchange (inversion) is reported, along with data for acetylacetonate (acac) methyl group exchange for the corresponding acac complex. Activation energies (kcal/mol) and entropies (eu), in *m*-dichlorobenzene solutions, for inversion are respectively 6.3 ± 1.7 and −36.5 ± 5.7 (acac), 14.7 ± 0.8 and −9.7 ± 2.2 (quin), and 21.2 ± 1.3 and 2.2 ± 3.3 (ox). For acac methyl group exchange, the corresponding kinetic data are (in *m*-dichlorobenzene solution) 13.8 ± 0.3 and −10.6 ± 1.0. Dramatic differences between kinetic parameters suggest that the ox and quin complexes possess a different rearrangement route than that for the acac complex. On the assumption that the ox and quin complexes retain the same structure in solid and solution phases, the isopropyl methyl group exchange is identified as resulting from the process cis(phenoxy),cis(N),trans(O)-Δ(Λ) ⇄ cis(phenoxy),cis(N),trans(O)-Λ(Δ). This rearrangement stereochemistry can only be generated via a Ti–N bond-rupture mechanism occurring through a trigonal-bipyramidal axial intermediate.

Introduction

Several nuclear magnetic resonance studies of configurational rearrangements in complexes of the type *cis*-$M(AA)_2X_2$, *cis*-$M(AA)_2XY$, and *cis*-$M(AB)_2X_2$ have been reported[7] in recent years. These studies have utilized mainly 1,3-diketones as the chelating ligand and M = Si(IV),[8] Sn(IV),[9,10] Ge(IV),[8] and Ti(IV).[2,3,11-14] All these complexes undergo exchange processes which result in the NMR equivalence of the terminal groups on the chelating ligand.

Recent work has been directed toward resolving the question of whether enantiomerization of these optically active complexes occurs during the configurational rearrangements.[2-4,14-17] Diastereotopic probes (generally isopropyl groups) have been positioned on the terminal sites of the AA ligands,[4] on the 3-position of the AA diketonate ligand,[3] and on the monodentate ligand X[2,14,17] of the *cis*-$M(AA)_2X_2$ framework. Enantiomerization processes have been detected in these systems (except for the Ti(3-*i*-Pr(acac))$_2$Cl$_2$ case[3]) which, in combination with complete permutational[6] and topological and mechanistic[5] analyses, led to more detailed mechanistic understanding of the rearrangement processes.

We recently reported[2] kinetic data for acetylacetonate methyl group exchange in a series of Ti(acac)$_2$(phenoxy)$_2$ complexes. Some of these compounds contained isopropyl substituents on the phenoxy ligand, and in some cases isopropyl methyl group exchange was observed and assigned to enantiomerization of these C_2-type complexes.

Harrod and Taylor[18,19] have prepared a series of complexes of the type Ti(chelate)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ (chelate = acetylacetonate, oxinate, and quinaldinate) and observed isopropyl methyl group exchange in variable-temperature NMR experiments. Unfortunately, the kinetic data were obtained from an approximate line shape analysis[18] and were therefore subject to considerable systematic errors.[20] Crystal structure studies[21] on these complexes have shown that the complexes adopt a structure in which the phenoxy ligands are cis, as are the two nitrogen donor atoms of the oxinate and quinaldinate ligands. In addition, in the acetylacetonate and oxinate complexes, the phenoxy rings are directed away from one another, whereas in the quinaldinate they are more nearly parallel. It also appears that the bond strength of the Ti–N bond in the quinaldinate complex is weaker relative to the analogous bond in the oxinate analogue; the Ti–O(quin) bond strength is slightly larger. Even such studies,[21] however, did not afford clues as to why barriers of suggested[18] phenoxy group rotation and isopropyl group rotations are so much lower in the case of the acetylacetonate complex.

In this work we report our studies on isopropyl methyl group exchange in the above series of complexes, as well as acac methyl group exchange in the Ti(acac)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ complex. Apparently, the only other complexes of the type Ti(chelate)$_2$X$_2$ for which kinetic data on rearrangements are available and the chelate is *not* a 1,3-diketone are the bis(methoxy) and bis(dimethylamino) complexes with chelate = dimethylmalonato and *N,N,N',N'*-tetramethylmalonamidato.[22] The Ti(chelate)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ (chelate = acac, ox, quin) series of complexes affords a study of the effect of the bidentate ligand on the rates and energetics of inversion about the Ti core.

Experimental Section

Reagents and Solvents. The following reagent grade chemicals were obtained from commercial sources and used without further purification: titanium(IV) isopropoxide (Research Organics/Inorganics), 2,4-pentanedione (acetylacetone, Fisher), 8-quinolinol (oxine, Eastman), 2-methyl-8-quinolinol (quinaldine, Aldrich), and 2,6-diisopropylphenol (Aldrich).

All organic solvents used in the preparation and purification of compounds were reagent grade and were dried by refluxing over CaH_2 chips for at least 12 h 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.[2,4] Melting points were measured in sealed capillaries (modeling clay) and are uncorrected.

Bis(2,6-diisopropylphenoxy)bis(2,4-pentanedionato)titanium(IV).[23] Recrystallizations from dichloromethane–hexane and benzene–hexane gave a red solid, mp 136–138 °C dec (lit.[19] mp 128–139 °C).

Bis(2,6-diisopropylphenoxy)bis(8-quinolinolato)titanium(IV).[23] Two recrystallizations from benzene–hexane solutions gave an orange solid, mp 270–271 °C dec (lit.[19] mp 259–260 °C).

Bis(isopropoxy)bis(2-methyl-8-quinolinolato)titanium(IV). This complex was prepared by the direct reaction of titanium(IV) isopropoxide with 2-methyl-8-quinolinol (1:2 mole ratio) in benzene, and the crude yellow product was used without further purification in subsequent syntheses.

Bis(2,6-diisopropylphenoxy)bis(2-methyl-8-quinolinolato)titanium(IV). Direct reaction of Ti(quin)$_2$(O-*i*-C$_3$H$_7$)$_2$ with 2,6-diisopropylphenol in refluxing benzene produced the desired compound. Recrystallization from benzene–hexane gave an orange solid, mp 268–270 °C dec (lit.[19] mp 258–259 °C).

Nuclear Magnetic Resonance Spectra. Since these complexes exhibit varying degrees of sensitivity toward moisture, all handling of solids and preparations of solutions were conducted entirely under anhydrous conditions in a dry nitrogen-filled glovebag. Techniques used to prepare the NMR samples, to calibrate the NMR spectrometer, to obtain the

0020-1669/79/1318-2200$01.00/0

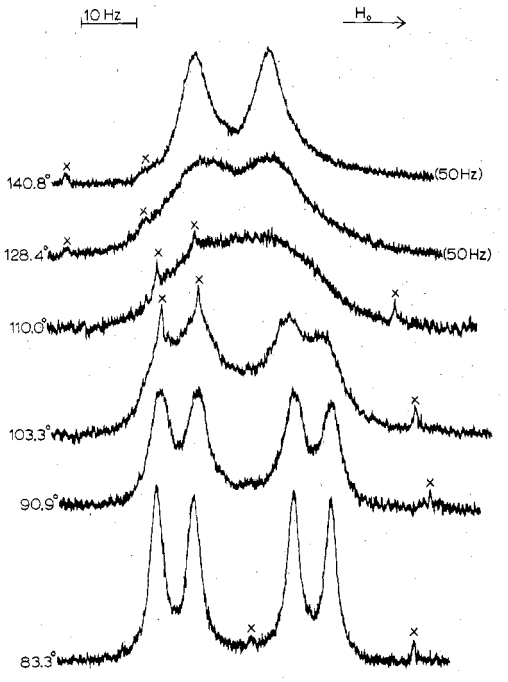


Figure 1. Temperature dependence of the isopropyl methyl resonances of the $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex in *m*-dichlorobenzene solution (0.145 M). Lines labeled × are either spinning side bands or very small amounts of thermal decomposition products. The top two spectra were taken at a 50-Hz sweep width; the remaining four were taken at a 100-Hz sweep width.

NMR spectra, and to determine the sample temperature in the variable-temperature NMR experiments are identical with those described earlier.[4]

Treatment of Data. The data were treated by a total line shape calculation based on the Gutowsky–Holm (GH) line shape equation[24] which, for an uncoupled, equally populated ($P_A = P_B = 0.5$), two-site exchange process, expresses transverse magnetization as a function of the frequency and of the three parameters: (1) $\delta\nu_{ae}$, the chemical shift separation in the absence of exchange; (2) $T_{2A} = T_{2B}$, the transverse relaxation time for nuclei in site A and B, respectively, in the absence of exchange; (3) the first-order rate constant for exchange $k = 1/2\tau$, where $\tau = \tau_A\tau_B/(\tau_A + \tau_B)$, and $\tau_{A(B)}$ is the lifetime of a nucleus on site A (or B).

The temperature dependence of T_2 values for the series of complexes was assayed by using the line width, $W_{1/2}$, of the quinaldinate methyl resonance of the $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex in the slow-exchange to fast-exchange region. From 54 to 158 °C, the average $W_{1/2}$ is 1.03 ± 0.05 Hz. A constant T_2 was assumed for this series of complexes in *m*-dichlorobenzene.

The appropriate value of $\delta\nu_{ae}$ to be used in the calculations was determined from the measurements of $\delta\nu_{ae}$ at a series of temperatures in the slow-exchange region. From the plot of $\delta\nu_{ae}$ vs. temperature, the straight-line portion in the slow-exchange region was extrapolated[25] into the intermediate- and fast-exchange regions. Values of $\delta\nu_{ae}$ were then read directly from such a plot.

Values of the mean residence times were obtained by numerically comparing the experimental spectra with theoretical spectra computer-calculated by using the GH total line shape function at intervals of 0.005 Hz for an appropriate range of ca. 240 values of τ. In the case of the ox and quin complexes, spectra were calculated at intervals of 0.01 Hz because of the large chemical shift differences involved. Input parameters to the computer program consisted of a value for $\pi\delta\nu_{ae}$, T_{2A}, and T_{2B}, and P_A and P_B, at each temperature. In general, the following characteristic line shape parameters were used to numerically compare the theoretical and experimental NMR spectra: line widths at one-quarter ($W_{1/4}$), one-half ($W_{1/2}$), and three-quarters ($W_{3/4}$) maximum amplitude; below coalescence, $\delta\nu_e$, the experimental frequency separation during exchange, and R, the ratio of the maximum amplitude to the central minimum, were also used. The τ values giving the best agreement between theoretical and experimental spectra for each line shape parameter were averaged, with each line shape parameter being given equal weight.

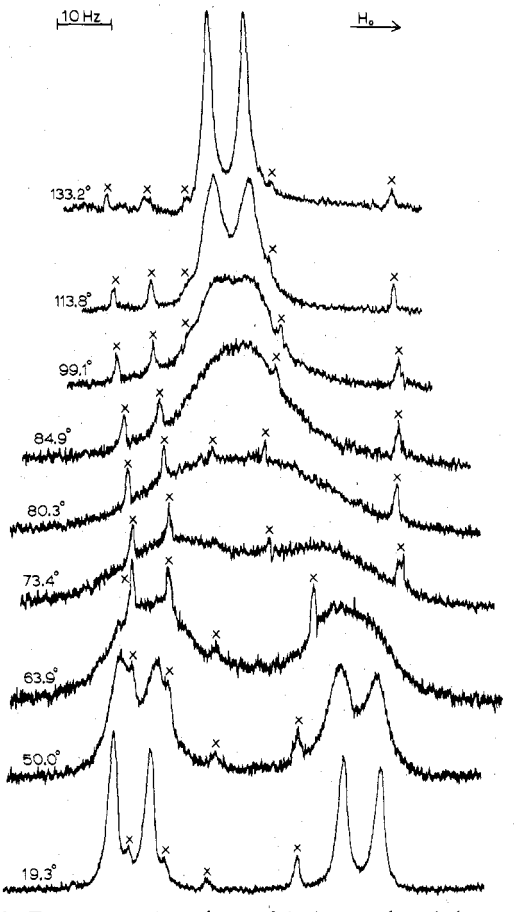


Figure 2. Temperature dependence of the isopropyl methyl resonances of the $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex in *m*-dichlorobenzene solution (0.111 M). Spinning side bands and/or small amounts of thermal decomposition products are labeled ×.

For isopropyl methyl group exchange in $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ the low-field doublet of the isopropyl quartet was analyzed, though either doublet may be used to extract kinetic data. For the oxinate and quinaldinate analogues, the low-field components of the two doublets were used. Below coalescence, only $\delta\nu_e$ was used in all cases to obtain τ values.

For acac methyl group exchange in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex, all line shape parameters were used in evaluating τ values.

The resulting mean lifetimes for isopropyl methyl group exchange in $Ti(chelate)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ (chelate = acac, ox, quin) complexes and for acac methyl group exchange in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex are presented in Table I.

Results

Figures 1 and 2 illustrate the temperature dependence of the isopropyl methyl resonances of the $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ and $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes, respectively, in *m*-dichlorobenzene solutions. Both complexes display two isopropyl methyl doublets at ambient temperature; as the temperature is increased the two doublets begin to coalesce, and eventually a single isopropyl methyl doublet is observed. With the ox and quin complexes, the large chemical shift differences between the two isopropyl methyl doublets (ca. 20–40 Hz) necessitate the crossing and merging of the low- and high-field components of the two doublets into a broad featureless resonance before resharpening to form a single, time-averaged doublet. Only temperatures above and below this coalescence region could be used to extract mean lifetimes for isopropyl methyl group exchange.

The temperature dependence of the acetylacetonate and isopropyl methyl group resonances of the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex (Figure 3) is very similar to that ex-

Table I. Mean Residence Times for Isopropyl Methyl Group Exchange in Ti(chelate)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ Complexes and for Acetylacetonate Methyl Group Exchange in the Ti(acac)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ Complex

Isopropyl Methyl Group Exchange

acac[a]		ox[b]		quin[c]	
temp,[d] °C	$10^2\tau$, s	temp,[d] °C	$10^3\tau$, s	temp,[d] °C	$10^3\tau$, s
16.7	17	94.9	39	54.5	41
19.7	13	99.9	26	63.9	13
25.5	12	103.3	20	66.0	12
28.0	10	105.9	19	68.7	11
31.6	9.3	108.2	18	73.4	7.4
37.0	8.1	134.3	2.7	80.3	5.7
		140.8	1.6	113.8	0.92
		154.4	0.68	117.5	0.73
				121.8	0.57
				125.8	0.42
				133.2	0.25

Acetylacetonate Methyl Group Exchange

temp,[d] °C	$10^2\tau$, s	temp,[d] °C	$10^2\tau$, s	temp,[d] °C	$10^2\tau$, s
22.0	10	35.6	3.8	48.1	1.6
25.5	8.5	37.0	3.4	51.5	1.2
28.0	6.9	40.4	2.6	54.4	1.1
31.6	5.0	40.8	2.5	62.5	0.64
33.3	4.6	44.5	1.9		

[a] 0.250 M in *m*-dichlorobenzene. [b] 0.145 M in *m*-dichlorobenzene. [c] 0.111 M in *m*-dichlorobenzene. [d] Calculated from the Van Geet equation for methanol and/or ethylene glycol.

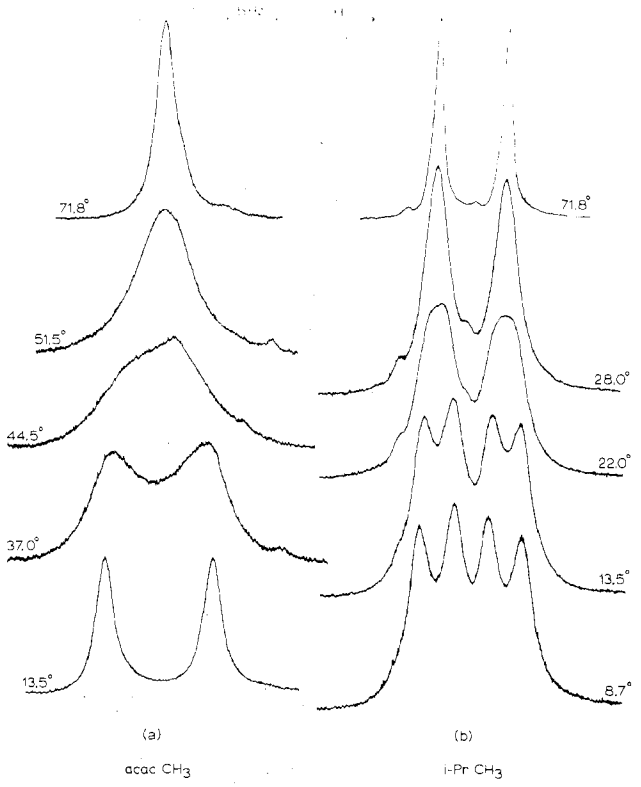


Figure 3. Temperature dependence of the (a) acetylacetonate and (b) isopropyl methyl resonances of the Ti(acac)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ complex in *m*-dichlorobenzene solution (0.250 M).

hibited by dichloromethane solutions of Ti(acac)$_2$(2-*i*-PrC$_6$H$_4$O)$_2$; namely, the NMR spectra consist of a single acetylacetonate methyl group resonance and a single isopropyl methyl doublet at room temperature. When the sample is cooled, the acac methyl resonance broadens and splits into two equally intense signals; the isopropyl resonance also broadens, and eventually two doublets are observed at low temperatures. A slightly different temperature range and peak separation are observed in *m*-dichlorobenzene solution.

Table II. Concentration Dependence of Mean Residence Times for Isopropyl Methyl Group Exchange in Ti(chelate)$_2$(2,6-(*i*-Pr)$_2$-C$_6$H$_3$O)$_2$ (chelate = acac, ox, and quin) Complexes and Acetylacetonate Methyl Group Exchange in the Ti(acac)$_2$-(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ Complex, in *m*-Dichlorobenzene Solution

complex	temp,[a] °C	concn, M	τ, s
Isopropyl Methyl Group Exchange			
Ti(acac)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$	13.5	0.250	0.267
		0.150	0.281
	25.5	0.250	0.120
		0.150	0.117
	37.0	0.250	0.085
		0.150	0.078
Ti(ox)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$	99.9	0.145	2.6×10^{-2}
		0.101	2.6×10^{-2}
	134.4	0.145	2.7×10^{-3}
		0.101	2.9×10^{-3}
Ti(quin)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$	66.0	0.111	1.2×10^{-2}
		0.070	1.2×10^{-2}
	121.8	0.111	5.7×10^{-4}
		0.070	5.1×10^{-4}
Acetylacetonate Methyl Group Exchange			
Ti(acac)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$	37.0	0.250	0.034
		0.150	0.034
	44.5	0.250	0.019
		0.150	0.020
	48.1	0.250	0.016
		0.150	0.017

[a] Calculated from the Van Geet equation for methanol and/or ethylene glycol.

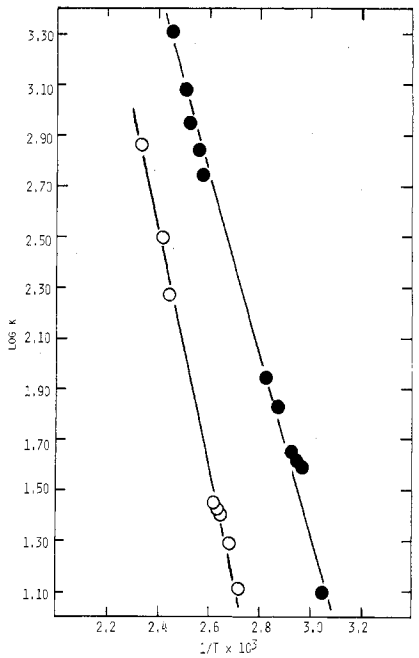


Figure 4. Arrhenius least-squares plots for isopropyl methyl group exchange in the Ti(ox)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ (○) and Ti(quin)$_2$-(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ (●) complexes in *m*-dichlorobenzene solution.

The concentration dependence of the mean residence times for isopropyl methyl group exchange in Ti(chelate)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ (chelate = acac, ox, quin) complexes and acac methyl group exchange in the Ti(acac)$_2$(2,6-(*i*-Pr)$_2$C$_6$H$_3$O)$_2$ complex is summarized in Table II. These data demonstrate that the rate of exchange is independent of concentration, and exchange is a first-order process.

Table III. Kinetic Data for Isopropyl Methyl Group Exchange in $Ti(chelate)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ (chelate = acac, ox, and quin) Complexes and Acetylacetonate Methyl Group Exchange in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ Complex

chelate	k_{298}, s^{-1}	$\Delta H^{\ddagger}_{298}$, kcal/mol	$\Delta S^{\ddagger}_{298}$, eu	$\Delta G^{\ddagger}_{298}$, kcal/mol	E_a, kcal/mol	log A
			Isopropyl Methyl Group Exchange			
acac[a,b]	4.2	5.7 ± 1.7[c]	−36.5 ± 5.7	16.60 ± 0.04	6.3 ± 1.7	5.3 ± 1.2
acac[d]	8.3	6.3 ± 0.7	−32.6 ± 2.3	16.19 ± 0.03	7.1 ± 0.7	6.10 ± 0.50
quin[a,e]	2.0	14.1 ± 0.8	−9.7 ± 2.2	17.1 ± 0.3	14.7 ± 0.8	11.10 ± 0.49
ox[a,f]	0.013	20.7 ± 1.3	2.2 ± 3.3	20.0 ± 0.3	21.2 ± 1.3	13.69 ± 0.72
			Acetylacetonate Methyl Group Exchange			
acac[a,b]	5.9	13.2 ± 0.3	−10.6 ± 1.0	16.39 ± 0.02	13.8 ± 0.3	10.91 ± 0.22
acac[d]	8.1	11.8 ± 1.7	−15 ± 6	16.21 ± 0.05	12.4 ± 1.7	10.0 ± 1.2

[a] In *m*-dichlorobenzene. [b] 0.250 M. [c] All errors are random errors estimated at the 95% confidence level. [d] 0.300 M in dichloromethane; from ref 2. [e] 0.111 M. [f] 0.145 M.

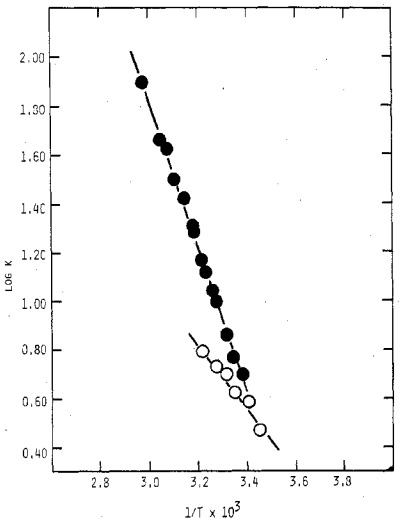


Figure 5. Arrhenius least-squares plots for acetylacetonate methyl groups (●) and isopropyl methyl group (○) exchange in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex in *m*-dichlorobenzene solution.

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-squares straight-line plots of log k vs. $1/T$ (see Figures 4 and 5), where k $(=1/2\tau)$ is the first-order rate constant for exchange. Activation entropies, $\Delta S^{\ddagger}$, were obtained from the expression $\Delta S^{\ddagger} = R[\ln A - \ln RT/Nh] - R$.[10]

Arrhenius and Eyring activation parameters for exchange of isopropyl methyl groups in the $Ti(chelate)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes and for acac methyl groups in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex are listed in Table III. 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.[9]

Discussion

The kinetic data of Table III indicate that the rate of isopropyl methyl group exchange in $Ti(chelate)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes decreases in the order chelate = acac > quin > ox. Differences in the activation parameters between the acac and the ox and quin complexes suggest that a different physical process may be responsible for the rearrangement in the ox and quin complexes (but see below).

Comparison of the kinetic data for isopropyl methyl and acac methyl group exchange in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex in dichloromethane and *m*-dichlorobenzene reveals no startling differences, though rearrangement appears to be slower in the aromatic solvent.

The $Ti(chelate)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ investigated here have been structurally characterized in the solid state.[21] All members of this series adopt a distorted octahedral geometry with cis phenoxy ligands. The ox and quin groups coordinate with nitrogen atoms cis and oxygen atoms trans, the stereochemistry being denoted as cis(phenoxy),cis(N),trans(O). The cis(N),trans(O) arrangement of oxinate donor atoms appears to be the favored configuration for octahedral complexes containing two oxinate ligands as this arrangement has been found in $(CH_3)_2Sn(ox)_2$,[26] $Ti(ox)_2Cl_2$,[27] $Ti(ox)_2Cl(\eta^5\text{-}C_5H_5)$,[28] $Mo(ox)_2(O)_2$,[29] and $V(ox)_2(O)(O\text{-}i\text{-}C_3H_7)$.[30]

For complexes of the type $M(ox)_2X_2$ and $M(quin)_2X_2$, three diastereomers are possible, assuming the X groups maintain their cis relationship. These isomers differ in the relative orientation of the chelate donor atoms around the octahedral core and may be designated as cis(X),cis(N),cis(O), cis(X),trans(N),cis(O), and cis(X),cis(N),trans(O). Only the cis(X),cis(N),trans(O) arrangement is observed[21] for $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ and $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$. While the oxinate complex provides no convenient means of establishing the configuration of the chelate donor atoms in solution with using the NMR technique, the quinaldinate methyl groups in the $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex may afford such information. A *m*-dichlorobenzene solution of the quin complex displays a single quinaldinate methyl group resonance. After a solution was heated at ca. 140 °C for several hours and cooled to room temperature, no changes in the quin and isopropyl methyl group NMR regions were observed. Also, the line width of the quinaldinate methyl group resonance is constant (1.03 ± 0.05 Hz) from 54 to 158 °C. It appears therefore that, in solution, the $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ and $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes retain their solid-state geometries of a single diastereomer possessing the cis(phenoxy),cis(N),trans(O) configuration.

Previous studies[2] have discussed possible causes for the observed nonequivalence of isopropyl methyl groups in $Ti(chelate)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes. The most plausible source is that the dissymmetry centered on the titanium renders the isopropyl methyl groups diastereotopic. Exchange of isopropyl methyl groups then results from inversion of the molecular configuration about the titanium core.

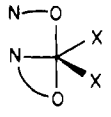
Exchange of isopropyl methyl groups in the $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ and $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes may be identified as resulting from inversion of the single diastereomer shown in reaction 1. This selectivity in the steric

$$\text{cis(phenoxy),cis(N),trans(O)-}\Delta(\Lambda) \rightleftarrows \text{cis(phenoxy),cis(N),trans(O)-}\Lambda(\Delta) \quad (1)$$

course of the rearrangement may allow definite mechanistic conclusions to be reached.

A twist mechanism about any of the four octahedral face axes cannot accommodate[31] the requirements of the rearrangement demanded by reaction 1. Similarly, a bond-rupture mechanism via a square-pyramidal axial intermediate, which

forms and decays to products through a primary process, does not generate the rearrangement required by reaction 1.[33] Rearrangements occurring via square-pyramidal intermediates which are formed and decay to products through secondary processes are considered unlikely owing to the extensive ligand motion involved. The stereochemical changes implied in reaction 1 can be generated by a bond-rupture mechanism occurring through a single trigonal-bipyramidal axial intermediate, labeled **7** in Table III of ref 5 and Figure 38a of ref 7; this intermediate is illustrated:



7

The sole intermediate capable of explaining reaction 1 for the $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ and $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complexes arises from rupture of the Ti–N bond in the equatorial plane, trans to the phenoxy groups. From the structure determinations of these two complexes it was inferred that the Ti–N bond is weaker in the quinaldinate complex relative to the oxinate.[21] If rupture of the Ti–N bond were rate determining in the rearrangement process, the quin complex should be more labile than the ox complex. The data in Table III demonstrate that the lability of the quinaldinate complex is ~2 orders of magnitude larger than that of the corresponding oxinate analogue. Further, the enthalpy of activation for enantiomerization of the quin complex is ~7 kcal/mol lower than for the oxinate, not inconsistent with the weaker nature of the Ti–N bond in the former complex.

The apparent Ti–N bond rupture mechanism for the quin and ox complexes is not surprising as this bond is expected to be the weakest of the core metal–ligand bonds from the relative electronegativities of nitrogen and oxygen. The thermochemical data for Ti–N and Ti–O bonds reveal the expected trend.[34]

Previous work on the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex suggested[2] that a twist mechanism might be predominant in the rearrangement processes; however, some contribution from SP axial and/or TBP equatorial intermediates was not precluded by the data. The significance of the ratio of the rates of acac methyl group exchange (exch) to isopropyl methyl group exchange (inv), k_{exch}/k_{inv}, has been discussed earlier.[2] For instance, twists about a single octahedral C_3 axis[7] predict $k_{exch}/k_{inv} = 1.0$ or 0.5 depending about which C_3 axis the twist motion takes place; in the case of rearrangements occurring through TBP axial and TBP equatorial intermediates, the ratio is ≤ 0.5 and ∞, respectively, since the latter intermediates never lead to inversion.[7] On the basis of such ratios, Fay and Lindmark[14] have ruled out certain intramolecular processes as sole rearrangement pathways. The observed ratio (1.4 in *m*-dichlorobenzene and 0.98 in dichloromethane) implies that in the aromatic solvent acac methyl groups are exchanged more rapidly than inversion occurs, a result which no single physical process can accommodate.[35]

If a bond-rupture mechanism is operative in the oxinate and quinaldinate complexes, the large differences in the activation parameters of Table III between the ox and quin complexes on the one hand, and the acetylactonate analogue on the other, may be suggestive of the operation of a non-bond-rupture mechanism in the rearrangement process of the latter complex (but see also ref 35) inasmuch as the Ti–O bonds are stronger than Ti–N bonds (see above). However, if every event involving acac terminal methyl group exchange is accompanied by inversion of the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ configuration, it is difficult to reconcile the differences in the activation enthalpies (ca. 6–7 kcal/mol) for the two processes (see Table III) in this complex in terms of twist motions alone. We interpret such differences as suggesting that in addition to non-bond-rupture twist motions in the rearrangement process, contributions from TBP equatorial intermediates may also be implicated inasmuch as these lead to exchange but not inversion.

Acknowledgment. Support of this work by the National Research Council of Canada is gratefully appreciated. We thank Drs. Harrod and Taylor for providing us with some of the complexes and Ms. Clements for assistance.

Registry No. $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$, 38781-11-2; $Ti(ox)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$, 38781-12-3; $Ti(quin)_2(O\text{-}i\text{-}C_3H_7)_2$, 33888-32-3; $Ti(quin)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$, 38781-13-4.

References and Notes

(1) Taken from the M.Sc. Thesis of D. G. Bickley, Concordia University, Montreal, Canada, June 1975.
(2) Part 5: N. Serpone and D. G. Bickley, *Inorg. Chim. Acta*, **32**, 217 (1979).
(3) Part 4: D. G. Bickley and N. Serpone, *Inorg. Chim. Acta*, **25**, L139 (1977).
(4) Part 3: D. G. Bickley and N. Serpone, *Inorg. Chim. Acta*, **28**, 169 (1978).
(5) Part 2: D. G. Bickley and N. Serpone, *Inorg. Chem.*, **15**, 2577 (1976).
(6) Part 1: D. G. Bickley and N. Serpone, *Inorg. Chem.*, **15**, 948 (1976).
(7) N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).
(8) N. Serpone and K. A. Hersh, *J. Organomet. Chem.*, **84**, 177 (1975).
(9) R. W. Jones, Jr., and R. C. Fay, *Inorg. Chem.*, **12**, 2599 (1973).
(10) N. Serpone and K. A. Hersh, *Inorg. Chem.*, **13**, 2901 (1974).
(11) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **6**, 1512 (1967).
(12) A. F. Lindmark and R. C. Fay, *Inorg. Chem.*, **14**, 282 (1975).
(13) D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).
(14) R. C. Fay and A. F. Lindmark, *J. Am. Chem. Soc.*, **97**, 5928 (1975).
(15) P. Finocchiaro, *J. Am. Chem. Soc.*, **97**, 4443 (1975).
(16) P. Finocchiaro, V. Librando, O. Maravigna, and A. Recca, *J. Organomet. Chem.*, **125**, 185 (1977).
(17) N. Baggett, D. S. Poolton, and W. B. Jennings, *J. Chem. Soc., Chem. Commun.*, 239 (1975).
(18) J. F. Harrod and K. Taylor, *Chem. Commun.*, 696 (1971).
(19) J. F. Harrod and K. Taylor, *Inorg. Chem.*, **14**, 1541 (1975).
(20) N. Serpone and D. G. Bickley, *Can. J. Spectrosc.*, **19**, 40 (1974).
(21) P. H. Bird, A. R. Fraser, and C. F. Lau, *Inorg. Chem.*, **12**, 1322 (1973).
(22) H. Weingarten, M. G. Miles, and N. K. Edelmann, *Inorg. Chem.*, **7**, 879 (1968).
(23) We thank Drs. J. F. Harrod and K. Taylor for generous gifts of some of the compounds investigated here.
(24) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).
(25) T. J. Pinnavaia, J. M. Sebeson, II, and D. A. Case, *Inorg. Chem.*, **8**, 644 (1969).
(26) E. O. Schlemper, *Inorg. Chem.*, **6**, 2012 (1967).
(27) B. F. Studd and A. G. Swallow, *J. Chem. Soc. A*, 1961 (1968).
(28) J. D. Matthews, N. Singer, and A. G. Swallow, *J. Chem. Soc., A*, 2545 (1970).
(29) L. O. Atovmyan and Yu. A. Sokolova, *Chem. Commun.*, 649 (1969).
(30) W. R. Scheidt, *Inorg, Chem.*, **12**, 1758 (1973).
(31) Cf. Table II of ref 5 and the topological structure[32] in Figure 40a of ref 7.
(32) Topological correlation diagrams illustrating the consequences of the various mechanisms on the $M(AB)_2X_2$ system are the same as those of the $M(BB')_2(AA)$ system illustrated in Figures 38–40 in ref 7 but with slight modifications. In the former system, there is an additional prefix c to indicate the relative orientation of the two X groups. Also, the intermediates involving M–A bond rupture in $M(BB')_2(AA)$ are not permitted in $M(AB)_2X_2$.
(33) See for example Table IV of ref 5 and Figure 39a of ref 7.
(34) "Handbook of Chemistry and Physics", 57th ed., Chemical Rubber Co., Ceveland, OH, 1976–1977. Ti–N and Ti–O bond strengths are 111 and 161.7 ± 4.5 kcal/mol, respectively.
(35) Systematic errors arising from the line shape analysis used, which neglects overlap due to spin coupling in the $Ti(acac)_2(2,6\text{-}(i\text{-}Pr)_2C_6H_3O)_2$ complex, could explain the variance in the ratios for the two different solvents employed. If such errors were large for the data of isopropyl methyl group exchange in this complex, they could also lead to anomalous $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values (see Table III). Under these conditions, the conclusions reached regarding the operation of two different rearrangement mechanisms in the complexes reported here may be considered tenuous. However, we hasten to point out that when the rearrangements in the acac complex are taken in the context of other analogous substituted phenoxy complexes (see ref 2), the operation of a twist mechanism for the acac complex and a bond-rupture path for the oxinate and quinaldinate complexes appears reasonable.