Intramolecular Rearrangement in Some Bis(chelate)titanium(IV) Complexes

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Summary The rate of molecular rearrangement of bis(phenoxy)bis(chelate)titanium(IV) complexes increases with decreasing pK_a of the parent phenol and the activation entropies for the rearrangement are large and negative.

SINCE Bradley's original application of ^1H n.m.r. methods to the study of molecular rearrangement in bis(alkoxy)bis(acac)titanium(IV) complexes,[1] several similar studies have been reported.[2–4] None of these studies has thus far succeeded in establishing unequivocally which mechanism is responsible for the observed coalescence of the non-equivalent methyl proton signals of the *cis* acac ligands.

Three types of mechanism have been proposed, each involving an intermediate in which the methyl groups of the acac ligands become equivalent. (i) A torsional twist to produce a six-co-ordinate, trigonal prismatic transition state; (ii) a reversible heterolytic dissociation of the monodentate ligand to produce a five-co-ordinate, cationic intermediate, and (iii) a reversible dissociation of one end of the chelate ligand to produce either a neutral, or a cationic, five-co-ordinate intermediate.

We have applied the Bradley technique to many bis(phenoxy)bis(chelate)titanium(IV) complexes. Some of our results, together with those of other workers, are summarized in Table 1. Two features should be noted. Firstly, the large negative $\Delta S^‡$ values observed by Bradley for the alkoxy-complexes are real and are also typically observed with the phenoxy-analogues. Secondly, there is a strong correlation between the electron-withdrawing power of the monodentate ligand and the coalescence temperature for the acac methyl resonance (T_c). This correlation has some obvious anomalies, such as the relative positions of the 2-iodophenoxy- and 4-chlorophenoxy-complexes relative to the parent phenoxy-complex. In these cases the small changes in electronic effects (as reflected in the relatively minor changes in pK_a) are probably less important than steric effects, or ground-state dipole effects. In spite of these anomalies, there is a correlation over a wide range.

We believe that the anomalously large negative $\Delta S^‡$ values typical of the phenoxy- and alkoxy-complexes cannot be reconciled with a mechanism involving only torsional twisting of the co-ordination faces of a pseudo-octahedral complex. Such $\Delta S^‡$ values indicate a large difference in polarity between the ground state and the transition state, a condition that cannot result from converting a pseudo-octahedron into a pseudo-trigonal prism. On the other hand, Bradley could not detect n.m.r. line broadening with the parent alcohol as solvent for bis(alkoxy)-complexes, suggesting that intermolecular exchange of alkoxy-groups was slower than the racemization process. We have observed that powerful donor ligands, such as pyridine, have virtually no effect on the coalescence temperatures of the present bis(phenoxy)-complexes. Such observations render an ionic dissociation mechanism unlikely.

TABLE 1

Coalescence temperatures and activation parameters for bis(acac)TiX$_2$ *complexes*

Ligand (X)	E_a/kcal	$\Delta S^\ddagger$ e.u.	T_c/°C[b]	Solvent	Ref.	pK_a
MeO	10·1 ± 0·4	−19 ± 2	+13	CCl_4	1	—
Cl	11·2 ± 0·6	−10 ± 2	−25	CH_2Cl_2	2	—
PhO	10·1 ± 2·1	−20	+10	CS_2[a]	This work	9·98
p-Me·C_6H_4·O	9·9 ± 2·2	−20	+14	"	"	10·26
p-AcC_6H_4·O	—	—	+ 1	$CHCl_3$	"	8·47
p-MeO·CO·C_6H_4·O	—	—	− 5	"	"	8·05
p-ClC_6H_4·O	6·7 ± 1·6	−31	+12	"	"	9·42
p-NO_2·C_6H_4·O	6·7 ± 1·1	−29	−12	"	"	7·15
o-MeC_6H_4·O	7·6 ± 1·3	−29	+18	"	"	10·28
o-Pr^iC_6H_4·O	—	—	+35	CS_2[a]	"	—
o-IC_6H_4·O	8·1 ± 1·1	−25	+ 5	$CHCl_3$	"	8·51
o-ClC_6H_4·O	6·0 ± 1·3	−32	−12	"	"	8·48
2,6-Cl_2·C_6H_3·O	—	—	−58	"	"	7·00
2,4,6-Cl_3·C_6H_2·O	—	—	−65[c]	"	"	—
C_6F_5·O	—	—	−80[c]	"	"	—

[a] No change in T_c was observed using $CHCl_3$. [b] Temperature at which CH_3 resonances of the acac ligand coalesce. [c] Upper limits.

TABLE 2

Coalescence temperatures and activation parameters for isopropoxy and isopropyl-substituted phenoxy complexes of titanium(IV)

Chelate	Ligand	$E_a^\ddagger$/kcal	$\Delta S^\ddagger$ e.u.	T_c/°C[c]	Solvent
acac	Isopropoxy	9·2 ± 0·9	−33·0	+12	$CHCl_3$
acac	Isopropoxy	10·2 ± 1·0	−20	+17[e]	CCl_4
oxin[a]	"	9·4 ± 1·8	−37·0	+55	Dichlorobenzene
quin[b]	"	—	—	<−70	$CHCl_3$
acac	2-Isopropylphenoxy	—	—	−45	$CHCl_3$
oxin	"	—	—	<−35[d]	Pyridine
quin	"	—	—	+35	$CHCl_3$
acac	2,6-Di-isopropylphenoxy	—	—	<−70	$CHCl_3$
oxin	"	12·2 ± 0·2	−34·7	+120	Dichlorobenzene
quin	"	8·0 ± 1·1	−44·1	+75	Dichlorobenzene

[a] 8-Hydroxyquinolinate. [b] 2-Methyl-8-hydroxyquinolinate. [c] Coalescence of resonances owing to inequivalent methyl protons on isopropyl groups. [d] Insolubility of this complex precluded exact measurement of T_c. [e] Reference 1.

In our opinion, the only type of mechanism that fits the large body of data now available would be one involving a transition state, or reactive intermediate, resembling a tightly bound ion-pair. Molecular rearrangement would occur *via* migration of the anion across the surface of the cationic complex, followed by collapse of the ion-pair to a neutral six-co-ordinate species.

We have also investigated the coalescence of non-equivalent methyl group resonances in isopropoxy- and 2,6-di-isopropylphenoxy-complexes. Bradley observed that the activation parameters for coalescence of the acac methyl resonances and the isopropyl methyl resonances of bis(isopropoxy)bis(acac)titanium(IV) were identical. In the complex bis-(2,6-di-isopropylphenoxy)bis(acac)titanium(IV) the isopropyl groups are apparently unhindered and give only a single doublet down to −70 °C. However, in the oxinate and quinaldinate analogues, the isopropyl groups give rise to two separate doublets of equal intensity at room temperature and these coalesce to a single doublet at 120 and 75 °C, respectively. The activation parameters for these coalescence phenomena are strikingly similar to those observed with acac complexes, particularly with respect to the large negative $\Delta S^\ddagger$ values. Some data for these types of complex are in Table 2. The similarity of the activation parameters suggests that the coalescence of the methyl resonances in the isopropylphenoxy-complexes probably occurs as a result of a similar process to that operating in the acac complexes. The large variations in actual coalescence temperatures in Table 2 for the various types of complex reflects the gross differences in molecular properties of the complexes and cannot be assigned any special significance at present.

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