

## Carbon-13 Nuclear Magnetic Resonance Study of Some Alkoxides of Titanium

By Clive E. Holloway, Department of Chemistry, York University, Downsview, Ontario, Canada

Variable-temperature  $^{13}\text{C}$  n.m.r. studies of niobium pentaethoxide, and titanium tetraethoxide, tetra-*n*-propoxide, tetra-*n*-butoxide, tetraisopropoxide, tetraisobutoxide, tetra-neopentyl oxide, and tetra-*t*-butoxide have been obtained. The coexistence of trimers and trimer aggregates is suggested for the straight-chain alkoxides of titanium. For the branched-chain derivatives, monomer-dimer-trimer equilibria are proposed for the isobutoxide, and monomer-dimer equilibria for the isopropoxide and neopentyl oxide. Use of previously published  $^1\text{H}$  n.m.r. data permits estimation of the enthalpy and entropy of dimerization for the isopropoxide and neopentyl oxide as *ca.*  $-14$  kcal mol $^{-1}$  and  $-50$  cal K $^{-1}$  mol $^{-1}$  respectively.

METAL alkoxides in solution tend to form oligomers which are fluxional in behaviour, and consequently n.m.r. techniques have been of use in the determination of structural and kinetic features of a number of derivatives. Not included among these, however, have been the alkoxides of Group 4, in particular those of titanium. This is puzzling since the corresponding derivatives of niobium and tantalum readily reveal the structural features<sup>1</sup> of their edge-shared octahedra. Bradley's proposed structure<sup>2</sup> for the titanium tetra-alkoxide trimers involves face-shared octahedra and might therefore be expected to be equally rigid on the n.m.r. time scale. Indeed, ligand scrambling and alcoholysis rates of known six-co-ordinate niobium, tantalum, and titanium alkoxy-pentane-2,4-dionates are all very similar.<sup>3</sup> By contrast, the alcoholysis rates of titanium tetra-alkoxides are considerably faster.<sup>4</sup>

Adoption of the open-ended trimeric unit which has been found by Russo and Nelson,<sup>5</sup> based on light-scattering data, helps to clarify the situation. In this structure [Figure 1(a)] the central six-co-ordinate titanium atom is flanked by two five-co-ordinate units. The presence of these co-ordinatively unsaturated metal atoms provides a relatively easy associative route for either internal ligand scrambling or external ligand exchange. In the ligand-scrambling process the structure proposed by Bradley as the normal ground state can now be envisaged as that of an unstable intermediate. Ligand scramblings and ligand exchange in the above six-co-ordinate systems, on the other hand, require some degree of bond breaking which is probably less energetically favourable. In any event the possibility of two different mechanisms for scrambling processes would rationalize the noticeably different rates observed for the two types of unit, co-ordinatively saturated and unsaturated.

Since more facile exchange requires lower temperatures or larger chemical shifts to effect freezing out of structural features in the n.m.r. spectrum, it seemed logical to investigate the possibilities of  $^{13}\text{C}$  n.m.r. which generally affords larger shifts than the previously employed  $^1\text{H}$  n.m.r. An additional bonus is the simplified spectra that  $^1\text{H}$ -decoupled  $^{13}\text{C}$  n.m.r. can give. The

<sup>1</sup> D. C. Bradley and C. E. Holloway, *J. Chem. Soc. (A)*, 1968, 219.

<sup>2</sup> D. C. Bradley, *Nature*, 1958, **182**, 1211.

<sup>3</sup> D. C. Bradley and C. E. Holloway, *J. Chem. Soc. (A)*, 1969, 282; A. E. Sentek, M.Sc. Dissertation, York University, Ontario, 1970.

greatest drawback lies in the unreliable nature of peak area to site population relations due both to different nuclear Overhauser enhancement (n.o.e.) factors and longitudinal relaxation times ( $T_1$ ) of carbon atoms in different sites. It was therefore decided to test these features with an alkoxide of known structure and fluxional behaviour such as niobium pentaethoxide. The alternative method of individually determining n.o.e.

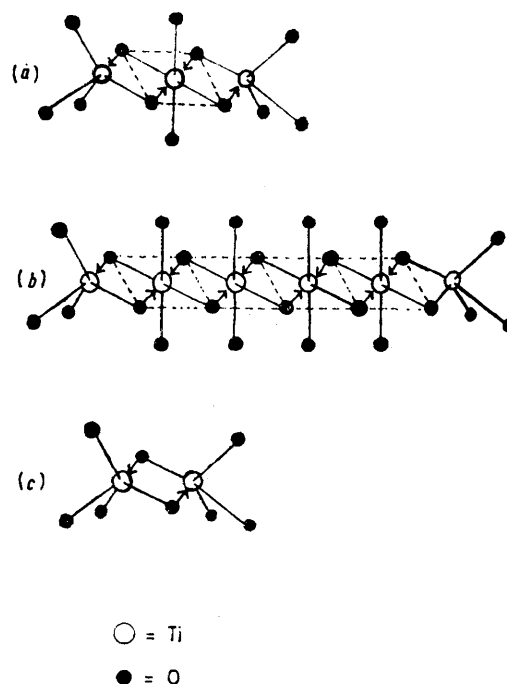


FIGURE 1 Structure of titanium(IV) alkoxide oligomers

and  $T_1$  data for each system at each temperature, although theoretically preferable, is much less feasible from a practical point of view. Some quantitative work using  $^{13}\text{C}$  n.m.r. has been accomplished<sup>6</sup> using paramagnetic reagents which shorten  $T_1$  and destroy the n.o.e. This is not possible in the present cases because the reagents are able to undergo ligand scrambling with metal alkoxides, thus altering their behaviour.

<sup>4</sup> C. E. Holloway and R. Ward, 54th Canad. Chem. Conf., Halifax, 1971, paper Inorg. IV 7.

<sup>5</sup> W. R. Russo and W. H. Nelson, *J. Amer. Chem. Soc.*, 1970, **92**, 1521.

<sup>6</sup> G. E. Hawkes, K. Herwig, and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 1017.

## EXPERIMENTAL

All the  $^{13}\text{C}$  n.m.r. spectra were obtained on a Varian CFT-20 n.m.r. unit at 20 MHz with an 8K 620L-100 computer. The variable-temperature system takes an 8-mm outside diameter sample tube which was filled to a depth of ca. 2 cm, using techniques described elsewhere,<sup>7</sup> with a ca. 0.1 mol dm<sup>-3</sup> solution of the alkoxide in  $\text{CDCl}_3$ . Temperature measurements were obtained by calibrating the V-6040 temperature controller against an alcohol thermometer inside the 8-mm sample tube containing  $\text{CDCl}_3$ , with the lock,  $^1\text{H}$  decoupler, and pulse in action to simulate actual experimental conditions.

In general, where structural features were observed, the splittings were insufficient to permit use of the electronic integrator for estimation of peak area. Measurements were therefore made manually in most cases. The accuracy is not expected to be better than  $\pm 5\%$  in either case. Peak positions are recorded as differences from the reported peak of free alcohol.<sup>8</sup> Actual shift measurements were made relative to  $\text{CDCl}_3$  and corrected to  $\text{SiMe}_4$  by choosing the appropriate reference-line parameter in the instrumental-data table. A pulse width of 5  $\mu\text{s}$  (flip angle  $32^\circ$ ) was used at a sweep width of 4 000 Hz with an acquisition time of 0.5 s. Spectra were accumulated for ca. 0.5 h, corresponding to ca. 4 000 scans.

Calculation of the monomer-dimer equilibria from previously obtained  $^1\text{H}$  n.m.r. data was carried out as follows. The shift of the monomer is designated  $a$ , and the averaged shift of the dimer is  $b$ . The quantity of monomer is  $x$  and the quantity of dimer is  $y/2$ . Thus the total concentration of alkoxide calculated as monomer is  $x + y = c$ . For a mixture of monomers and dimers, the averaged chemical shift,  $M$ , is then  $(ax + by)/c$ ; substituting for  $y = c - x$ , we obtain  $M = (ax + cb - bx)/c$  from which  $x = c(M - b)/(a - b)$ . The equilibrium constants are then calculated for the depolymerization from  $K = 2x^2/y$ .

## RESULTS AND DISCUSSION

The  $^{13}\text{C}$  n.m.r. data for the alkoxides are given in Table I. The shifts relative to the parent alcohol are considerably larger than those found for  $^1\text{H}$  n.m.r. spectra. However, by contrast, the differences between shifts for polymerized and non-polymerized derivatives are much less striking. Thus the diagnostic value of the  $^1\text{H}$  n.m.r. shifts<sup>7</sup> are not paralleled by the  $^{13}\text{C}$  shifts.

The spectra for niobium pentaethoxide were exactly in accord with the previous  $^1\text{H}$  n.m.r. spectra.<sup>1,9</sup> That is, at room temperature the alkoxy-resonances were split into terminal and bridging sites in the ratio of 4:1, with the smaller bridging peak to high field. The expected larger shifts were observed, and the largest terminal-bridging shift was obtained for the carbon atom  $\beta$  to the oxygen. Apparently the anisotropic contributions to the net chemical shift are sufficiently important to match or outweigh changes in electron density due to bridge formation. Both the  $\alpha$  proton and the  $\beta$  carbon are in similar positions with respect to the C-O bond and the lone pairs of electrons on the

\* 1 cal = 4.184 J.

<sup>7</sup> D. C. Bradley and C. E. Holloway, *J. Chem. Soc. (A)*, 1968, 1316.

oxygen, and might therefore be expected to show similar neighbour anisotropy effects.

On cooling further, the terminal alkoxy  $\beta$ -carbon resonance splits again into two resonances of equal area separated by a much larger shift of 77.5 Hz, compared to the 6 Hz observed in the  $^1\text{H}$  n.m.r. spectrum.<sup>9</sup> The respective coalescence temperatures of  $-15$  (for  $^{13}\text{C}$ ) and  $-60$   $^\circ\text{C}$  (for  $^1\text{H}$ ) reflect this change in separation. Using the simple formula  $\tau_c = (2\pi\delta\nu)^{-1}$  and the Arrhenius relation between rate and temperature, it is possible to estimate respective rates at coalescence of

TABLE I  
 $^{13}\text{C}$  N.m.r. chemical shift data (p.p.m.)

Compound	$\theta_c/^\circ\text{C}$	Chemical shift <sup>a</sup>			
		$\alpha$	$\beta$	$\gamma$	$\delta$
Nb(OEt) <sub>5</sub>	34	11.5(4), <sup>b</sup> 10.6(1)	0.9(4), -0.2(1)		
	-30	13.8, 9.9,	1.1, 0.1		
		10.8			
Ti(OEt) <sub>4</sub>	34	13.1	1.25		
	-55	13.6, 12.9	2.0, 0.5		
		12.9	0.4		-0.2
Ti(OPr) <sub>4</sub>	34	12.9	1.2		0.4
	-55	13.4, 12.8	0.5, -0.3		0.0
		12.9	0.4		-0.3
Ti(OBu) <sub>4</sub>	34	12.9	1.0		0.0
	-55	13.4, 12.8	0.5, -0.35		0.4
		12.9	0.7		-0.2
Ti(OBu <sup>t</sup> ) <sub>4</sub>	34	12.8	1.05		0.25
	-45	12.9	0.5, -0.35		0.25
Ti(OPr <sup>t</sup> ) <sub>4</sub>	34 <sup>c</sup>	12.4	1.0		
Ti(OBu <sup>t</sup> ) <sub>4</sub>	34 <sup>c</sup>	12.8	1.4		0.25
Ti(OBu <sup>t</sup> ) <sub>4</sub>	34 <sup>c</sup>	11.0	0.5		

<sup>a</sup> Downfield relative to parent alcohol (ref. 8) to nearest 0.05 p.p.m. <sup>b</sup> Relative peak areas in parentheses; for others see text. <sup>c</sup> Only minor changes in chemical shift were observed on cooling to  $-55$   $^\circ\text{C}$ .

$3 \times 10^{-3}$  (at  $-15$   $^\circ\text{C}$ ) and  $4 \times 10^{-2}$  s<sup>-1</sup> (at  $-60$   $^\circ\text{C}$ ). From this an activation energy of ca. 9 kcal mol<sup>-1</sup> is obtained for the terminal-terminal exchange process.\* This is consistent with the thermodynamic data available for this and other Group 5 alkoxides.<sup>1,9</sup> Thus  $^{13}\text{C}$  n.m.r. appears to live up to expectation and to give reasonable peak intensities, indicating that factors affecting intensity, other than site populations, are not important in this case. However, it is probably still wise to compare peak intensities only of carbon atoms identically situated in the alkoxy-group, in order to eliminate the effects of differing rates of molecular motion on  $T_1$  which can occur along a carbon chain effectively anchored at one end.

By contrast, the low-temperature n.m.r. spectra of the titanium derivatives were less straightforward. For the unbranched-chain derivatives, where molecular-weight studies have indicated trimers in each case,<sup>7,10</sup> three types of behaviour were observed. Among the

<sup>8</sup> J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. Reich, *J. Amer. Chem. Soc.*, 1970, **92**, 1338.

<sup>9</sup> C. E. Holloway, *J. Co-ordination Chem.*, 1971, **1**, 253.

<sup>10</sup> D. C. Bradley and C. E. Holloway, *Inorg. Chem.*, 1964, **3**, 1163.

branched-chain derivatives, three showed no variable-temperature changes and one gave splitting similar to that of a trimer. If certain established trends in the general behaviour of alkoxides are taken into account, these spectra can be interpreted on the basis of varying degrees of oligomer formation.

First it is necessary to accept that the *n*-alkoxides, except for the isobutoxide, are at least trimeric under the conditions studied and that the most likely structure is that of the open-ended trimer [Figure 1(a)] as postulated by Russo and Nelson.<sup>5</sup> This structure, with its bridging-terminal ratio of 1:2, appears to be the simplest explanation for the low-temperature <sup>13</sup>C n.m.r. spectrum of titanium tetra-*n*-butoxide (Figure 2). Thus at *ca.* -55 °C the high-field bridging peak and the low-field terminal peak, in a *ca.* 1:2 ratio, coalesced. The rate of ligand scrambling in the Group 5 alkoxides<sup>9</sup> has been shown to depend on the size of the alkoxy-group, and using the same trends one would expect that the *n*-propoxide and ethoxide derivatives of titanium would coalesce at slightly lower temperatures than the

trimer is capable of further aggregation to give open-ended hexamer and higher units [Figure 1(b)]. The degree to which this would happen would be governed by the known relative abilities of the alkoxy-groups to form bridges.<sup>9,13</sup> This would be in the order ethoxide > *n*-propoxide > *n*-butoxide for the three systems of interest. The ethoxide then represents the case where at the coalescence temperature of the hexamer aggregate very little of the trimer remains. The *n*-propoxide represents a situation where at the coalescence temperature of the hexamer appreciable amounts of trimer remain thus giving three peaks, the outer two being due to the hexamer and the inner one to the trimer. The *n*-butoxide represents the other extreme where little or no hexamer is formed. It is interesting to note, however, that on prolonged soaking at low temperature the spectrum of the *n*-butoxide changes to become more comparable to that of the ethoxide, suggesting that the approach to a hexamer-trimer equilibrium is slow in this case. In the absence of molecular-weight data at these temperatures, the above interpretation must

TABLE 2  
Monomer-dimer equilibrium calculations

Compound	$\theta_c$ °C	Concentration mol dm <sup>-3</sup>	Average $K_{diss}$ mol dm <sup>-3</sup>	Arrhenius data
Ti(OPr <sup>i</sup> ) <sub>4</sub>	0	0.41—2.43	0.52 ± 0.14 *	$\Delta H = 14.9$ kcal mol <sup>-1</sup> $\Delta S = 53.5$ cal K <sup>-1</sup> mol <sup>-1</sup> Correlation coefficient = 0.9983
	-10		0.21 ± 0.13	
	-20		0.053 ± 0.04	
	-30		0.019 ± 0.002	
Ti(OCH <sub>2</sub> CMe <sub>3</sub> ) <sub>4</sub>	-4	0.05—0.38	0.58 ± 0.25	$\Delta H = 14.2$ kcal mol <sup>-1</sup> $\Delta S = 51.8$ cal K <sup>-1</sup> mol <sup>-1</sup> Correlation coefficient = 0.9988
	-12		0.22 ± 0.09	
	-23		0.072 ± 0.034	
	-30		0.032 ± 0.005	
Ti(OBu <sup>t</sup> ) <sub>4</sub>	120	0.15—0.51	0.93 ± 0.08	$\Delta H = 12.5$ kcal mol <sup>-1</sup> $\Delta S = 32.0$ cal K <sup>-1</sup> mol <sup>-1</sup> Correlation coefficient = 0.9880
	100		0.42 ± 0.21	
	79		0.23 ± 0.39	
	60		0.064 ± 0.064	
	50		0.026 ± 0.013	

\* Standard deviation.

*n*-butoxide. This is not the case since both begin to reveal structural features at -45 °C. Furthermore, the peak ratios in these two derivatives are indicative of the presence of different species than found for the *n*-butoxide. A similar effect has been observed previously in the <sup>1</sup>H n.m.r. spectrum of the ethoxide,<sup>11</sup> where new peaks appeared on cooling below -20 °C and were tentatively assigned to the tetrameric structure known to exist in the solid state.<sup>12</sup> In such a structure two different types of bridge are present and the overall bridging to terminal ratio is 5:3, which does not fit the observed <sup>13</sup>C n.m.r. spectrum (Figure 2). If it is assumed that a face-shared species represents the activated state in the observed ligand scrambling, it is most unlikely that the low-temperature species would be the totally six-co-ordinate structure originally proposed by Bradley, even though the observed peak ratios in the <sup>13</sup>C n.m.r. spectrum of the ethoxide are temptingly close to the 1:1 expected for such a molecule. Instead it seems more logical to recognize that the open-ended

remain open to speculation; however, the observed peak ratio in the ethoxide case (and outer peak ratio in the *n*-propoxide case) is 6:5 which is close to the expected 7:5 ratio of the hexamer [Figure 1(b)].

The question of why the hexamer units would be more resistant to ligand exchange than the trimer can be clarified by considering how bridging-terminal exchange would be transmitted through two or more edge-shared octahedra. As in the Group 5 cases, some degree of bridge dissociation must be involved thus making the exchange in the hexamer more akin to that of the niobium or tantalum penta-alkoxide dimers as discussed in the introduction.

The isobutoxide has been shown by molecular-weight studies<sup>7</sup> to be less than trimeric but more than dimeric at 5 °C. The <sup>13</sup>C n.m.r. spectrum (Figure 2) shows structural features at *ca.* -30 °C which resolve into a triplet, the inner component of which decreases with decreasing temperature. The outer components of the

<sup>12</sup> J. A. Ibers, *Nature*, 1963, **197**, 686.

<sup>11</sup> D. C. Bradley and C. E. Holloway, *Proc. Paint. Res. Inst.*, 1965, **37**, 487.

<sup>13</sup> C. G. Barraclough, R. L. Martin, and G. Winter, *J. Chem. Soc.*, 1964, 758.

triplet are similar in relative intensities to the corresponding peaks of the *n*-butoxide, and can be assigned to a trimer species of the same structure. In the Group 5 series, the isobutoxide dimers undergo coalescence at *ca.* 30 °C above the temperature for the *n*-alkoxide dimers, presumably due to the increased bulk

some polymerization at low temperature from  $^1\text{H}$  chemical-shift studies.<sup>7</sup> The extent of this aggregation could not be determined at that time. However, the  $^{13}\text{C}$  n.m.r. spectrum showed no significant changes with temperature in either case. From the above discussion, the bulkier isopropoxide and neopentyl oxide groups

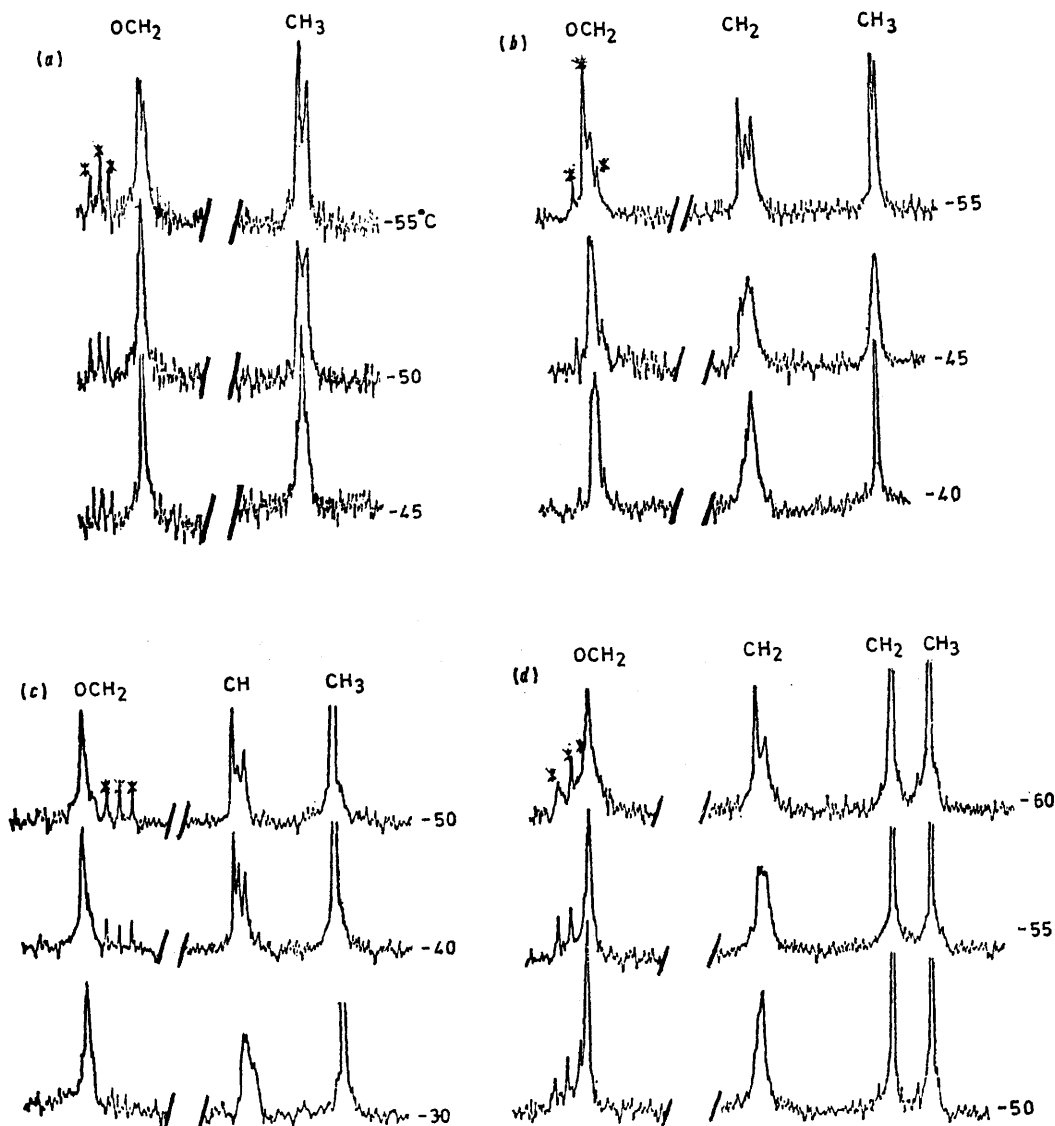


FIGURE 2 Variable-temperature  $^{13}\text{C}$  n.m.r. spectra of titanium(IV) alkoxides. (Peaks marked \* are due to  $\text{CDCl}_3$ )

of the ligand.<sup>9</sup> Thus a similar increase in coalescence temperature between the *n*-butoxide and isobutoxide in the present case is not unexpected. The inner peak of the triplet can be assigned to an averaged or accidentally degenerate monomer-dimer resonance. Previous  $^1\text{H}$  n.m.r. studies<sup>7</sup> have also indicated a change in degree of polymerization with temperature.

The tertiary butoxide shows no changes in either the  $^1\text{H}$  or  $^{13}\text{C}$  n.m.r. spectra and can be safely considered to represent a non-polymerizing system. The isopropoxide and neopentyl oxide have both been shown to undergo

should be undergoing much slower exchange; thus if trimer units were present they would be resolved out at temperatures higher than observed for the isobutoxide. The absence of such features strongly suggests that no significant amounts of trimer are present, limiting the degree of aggregation to the dimer. The previously obtained  $^1\text{H}$  shifts were therefore subjected to a monomer-dimer equilibrium analysis to test this idea. The results are summarized in Table 2 together with estimates of the enthalpy of depolymerization obtained from plots of  $\ln K_{\text{diss}}$  against  $T^{-1}$ . The

entropies of depolymerization can also be obtained from the plots, and at 51—54 cal K<sup>-1</sup> mol<sup>-1</sup> are similar to the 40—50 cal K<sup>-1</sup> mol<sup>-1</sup> found in the niobium and tantalum isopropoxide cases. The enthalpy values of 14—15 kcal mol<sup>-1</sup> are *ca.* 25% lower than the Group 5 isopropoxide systems,<sup>1</sup> indicating that the Group 4 systems involve weaker bridges, presumably due at least in part to the smaller net positive charge on the central metal atom.

The monomer-dimer equilibrium would not be expected to be appropriate for the isobutoxide system. However, the <sup>1</sup>H n.m.r. data for this derivative can be treated in the same manner to give a linear relation between ln*K* and *T*<sup>-1</sup>. In this case the correlation is poorer and the deviation in the equilibrium constants is larger; furthermore, the enthalpy obtained is less than that in the other two cases, which is not consistent with the known higher degree of polymerization. The fact that any sort of correlation was observed in this case is probably due to the variation of the <sup>1</sup>H n.m.r. shift with structure. The open-ended trimer and the five-coordinate dimer apparently have very similar averaged chemical shifts since both the n-alkoxides and branched-chain alkoxides tend to have the same low-temperature

shift differences [ $\delta(\text{alkoxide}) - \delta(\text{alcohol})$ ]. Thus the major shift changes in the isobutoxide system would occur only while appreciable amounts of monomer are present and consequently the monomer-dimer equilibrium is still an important contribution to the overall equilibrium.

To summarize, the <sup>13</sup>C n.m.r. results for titanium tetra-alkoxides are consistent with the idea of smaller oligomeric units with increasing steric hindrance of the alkoxy-group. The existence of hexamer units has been postulated to account for the fact that the coalescence temperatures do not follow a simple trend as in the Group 5 alkoxides or Group 4 bis(pentane-2,4-dionates), and for the observation of differing peak ratios from one derivative to another. The limitation of the more highly branched derivatives to dimerization has been suggested to explain the absence of low-temperature splitting in the n.m.r. spectra of these species, and is supported by the reasonable parameters obtained from the <sup>1</sup>H n.m.r. data.

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