

(π -Cyclopentadienyl)(π -tetraphenylcyclobutadiene)cobalt (XII). A. As described above the cobalt complex XII was made from tetraphenylcyclobutadiene-cobalt dicarbonyl bromide (XI)⁷ and either cyclopentadienyliron dicarbonyl dimer (II) or the bromide (III). Since XIII is readily soluble in benzene, it was isolated from the reaction mixture by crystallization of the residue, after the solvent had been removed, from benzene–ligroin. The yields are given in Table II.

B. A suspension of 0.20 g. (0.33 mmole) of (π -cyclopentadienyl)(π -tetraphenylcyclobutadiene)palladium bromide (VII, M = Pd) in 30 ml. of benzene was refluxed for 5 min. under nitrogen. To this was added 2.0 ml. (0.86 mmole) of a solution of dicobalt octacarbonyl in toluene (Alfa Inorganics) and the refluxing continued for 1 hr. After 15 min. of heating, metal began to be deposited and the solution turned black.

The solution was then filtered and the filtrate evaporated to dryness. The residue was dissolved in 1 ml. of benzene and chromatographed on alumina. A yellow band was eluted with 50% benzene–petroleum ether which gave 15 mg. (10%) of a yellow-brown crystalline solid. This was purified by vacuum sublimation to give pure (π -cyclopentadienyl)(π -tetraphenylcyclobutadiene)cobalt, m.p. 250–253°, m.m.p., with an authentic sample, 252–254°. The infrared spectra were identical.

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Exchange of Parts between Molecules at Equilibrium. VI. Scrambling on Titanium of the Alkoxy, Dimethylamino, and Halogen Substituents

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Scrambling of substituents on titanium was studied for the systems (1) (RO)₄Ti vs. [(CH₃)₂N]₄Ti, (2) (RO)₄Ti vs. (R'O)₄Ti, (3) (RO)₄Ti vs. TiX₄ where X stands for bromine or chlorine, and (4) [(CH₃)₂N]₄Ti vs. TiCl₄. Large enthalpies attributable to association effects were measured for an exchange corresponding to a system 1 above with R = C₂H₅ and a system 2 exchange with R = C₂H₅ and R' = (CH₃)₂CH. Even larger enthalpies were found for the reactions in systems 3 and 4, as expected for big deviations from random scrambling. An attempt is made to assess the contributions of association and non-association effects to the enthalpy of exchange reactions in system 3. The observed rapid rates of exchange are discussed, as are the structures of the various associated species noted in this study.

Previous publications from this laboratory dealing with scrambling reactions have primarily been concerned with exchange of substituents on main-group central atoms^{1,2} of groups IV, V, and VI in the periodic

(1) E. Schwarzmann and J. R. Van Wazer, *J. Am. Chem. Soc.*, **81**, 6366 (1959); E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *ibid.*, **81**, 6363 (1959); K. Moedritzer, G. M. Burch, J. R. Van Wazer, and H. K. Hofmeister, *Inorg. Chem.*, **2**, 1152 (1963); K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 139, 268 (1964); J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964).

(2) L. C. D. Groenweghe, J. H. Payne, and J. R. Van Wazer, *ibid.*, **82**, 5305 (1960); E. Schwarzmann and J. R. Van Wazer, *ibid.*, **82**, 6009 (1960); L. Maier and J. R. Van Wazer, *ibid.*, **84**, 3054 (1962); K. Moedritzer and J. R. Van Wazer, *ibid.*, **86**, 802 (1964); J. R. Van Wazer, K. Moedritzer, and D. W. Matula, *ibid.*, **86**, 807 (1964); M. D. Rausch, J. R. Van Wazer, and K. Moedritzer, *ibid.*, **86**, 814 (1964); D. Grant and J. R. Van Wazer, *ibid.*, **86**, 3012 (1964).

table. Unlike these central atoms, much of the chemistry of which is characterized by the fact that the low-energy orbitals are filled with spin-paired electrons, many of the transition elements as well as those³ of groups II and III have readily available orbitals which can accept a pair of electrons from another atom and thereby increase the coordination number of the central atom. This paper is one of several devoted to the study of scrambling reactions which are complicated by intermolecular association due to such increase in coordination number of the central atom.

Recent reviews⁴ of the chemistry of titanium show that, although scrambling of substituents on titanium is generally recognized, this phenomenon has received little study, and its significance to titanium chemistry is not well understood. Since the nuclear magnetic resonance (n.m.r.) data obtained in this investigation are pertinent to elucidation of the structure of associated molecules, this popular area for research and speculation in titanium chemistry is also treated herein.

Experiments and Data

Reagents and Equilibration. The ethyl titanate was purchased from Eastman Kodak, the isopropyl titanate from K and K Laboratories (Jamaica 33, N. Y.).

(3) H. K. Hofmeister and J. R. Van Wazer, *J. Inorg. Nucl. Chem.*, in press; M. D. Rausch and J. R. Van Wazer, *Inorg. Chem.*, **3**, 761 (1964).

(4) J. H. Haslam, *Advances in Chemistry Series*, No. 23, 1959, p. 272; I. Shiihara, W. T. Schwartz, and H. W. Post, *Chem. Rev.*, **61**, 1 (1961).

Table I. N.m.r. Results on the Various Systems TiA_4 vs. TiZ_4 at 25°

Substituent		Concn., ^a g.-atoms of Ti/l.	N.m.r. spectra	
A	Z		RO region	(CH ₃) ₂ N region
CH ₃ O	(CH ₃) ₂ N	0.5, 2	The pure (CH ₃ O) ₄ Ti showed four peaks of relative area 3:2:2:1 at -3.90, -3.77, -3.72, and -3.44 p.p.m., respectively, and this pattern persisted upon addition of the [(CH ₃) ₂ N] ₄ Ti. Another peak corresponded to all of the mixed species. This rather sharp singlet (width at half-height ≈ 4-6 c.p.s.) shifted from -3.65 p.p.m. for a CH ₃ O/Ti mole ratio = 3 to -3.08 p.p.m. for CH ₃ O/Ti = 1	Single peak for [(CH ₃) ₂ N] ₄ Ti, pure or in mixtures, at -2.49 p.p.m. Another rather sharp singlet (width ≈ 1.4 c.p.s.) for the mixed species shifting from -2.76 p.p.m. for CH ₃ O/Ti = 3 to -2.67 p.p.m. for CH ₃ O/Ti = 1. Saddle observed between end-member and mixed-species resonances
C ₂ H ₅ O	(CH ₃) ₂ N	2	Sharp triplet-quadruplet pattern, as expected for the methyl and methylene groups of C ₂ H ₅ O, corresponding to all of the ethoxyl-containing molecules. The methyl triplet shifts (width ≈ 1.3 c.p.s.) from -0.76 to -0.55 p.p.m. and the methylene quadruplet (width ≈ 1.7 c.p.s.) from -3.96 to -3.48 p.p.m. as the C ₂ H ₅ O/Ti mole ratio is decreased from 4 to 1	(CH ₃) ₂ N resonances between those of the C ₂ H ₅ O group. The compound [(CH ₃) ₂ N] ₄ Ti, either pure or in mixtures, gives a single peak at -2.51 p.p.m.. Mixed species give a single peak (width ≈ 1.4 c.p.s.) ranging from -2.76 to -2.60 p.p.m. as C ₂ H ₅ O/Ti goes from 3 to 1. Saddle observed between the end-member and mixed-species resonances
(CH ₃) ₂ CHO	(CH ₃) ₂ N	0.5, 1.0	Doublet-septuplet pattern at -0.65 and -3.92 p.p.m. corresponding, respectively, to the methyl and methine groups of the (CH ₃) ₂ CHO. Same pattern for pure [(CH ₃) ₂ CHO] ₄ Ti and all mixtures, with no appreciable shifting or broadening with changes in over-all composition	Resonance for [(CH ₃) ₂ N] ₄ Ti, either pure or in mixtures, at -2.48 p.p.m. Single peak (width = 0.5 c.p.s.) for all mixed species shifting from -2.60 to -2.53 p.p.m. at [(CH ₃) ₂ CHO]/Ti = 3 and 1, respectively
(CH ₃) ₂ CO	(CH ₃) ₂ N	2, 1	Two or more very sharp, closely spaced singlets (width ≈ 0.3 c.p.s.), with exact number obscured by ringing. Resonance for [(CH ₃) ₂ CO] ₄ Ti at -0.72 p.p.m., with peak(s) for mixed species slightly upfield	Separate sharp resonances (width ≈ 0.3 c.p.s.) for all four dimethylamino-containing species, with inappreciable changes in the shifts with varying composition. Resonance at -2.50, -2.56, -2.59, and -2.62 p.p.m. for <i>i</i> = 4, 3, 2, and 1, respectively, in [(CH ₃) ₂ CO] _{4-i} Ti[(CH ₃) ₂ N] _{<i>i</i>}
CH ₃ O	(CH ₃) ₃ CO	0.5, 1	The 3:2:2:1 spectrum of (CH ₃ O) ₄ Ti retained the same shape in mixtures as when pure. However, line broadening in mixtures, presumably due to faster exchange. Singlet at -3.88 p.p.m. (width ≈ 4.5 c.p.s.) attributable to methoxyl group of all of mixed species. Sharp methyl resonance (width ≈ 0.3 c.p.s.) at -0.72 p.p.m. of <i>t</i> -butyl group of pure [(CH ₃) ₃ CO] ₄ Ti widens (4-5 c.p.s.) and becomes difficult to interpret owing to combined effects of different chemical shifts for the various mixed species and broadening due to increased rate of exchange (run in toluene)	
CH ₃ O	Cl	0.5	See Figure 3 (run in HCCl ₃)	
CH ₃ CH ₂ O	Cl	0.5	Single, sharp triplet-quadruplet pattern. The methyl triplet (width ≈ 1 c.p.s.) shifts from -0.78 to -0.40 p.p.m. as A/T decreases from 4 to 1. The methylene quadruplet (width ≈ 1 c.p.s.) shifts downfield from -3.97 to -4.05 p.p.m. as A/Ti decreases from 4 to 3. It then shifts upfield to -3.53 p.p.m. at A/Ti = 1	
(CH ₃) ₂ CHO	Cl	0.5	Single sharp doublet-septuplet pattern. The methyl doublet (width ≈ 1 c.p.s.) shifts from -0.58 to -0.26 p.p.m. as A/Ti decreases from 4 to 1. The methine septuplet shifts (width ≈ 1 c.p.s.) downfield from -3.67 to -3.80 p.p.m. as A/T decreases from 4 to 3; then shifts upfield to -3.4 p.p.m. at A/Ti = 1	
(CH ₃) ₂ N	Cl	0.25, 0.1		Single rather sharp peak for methyl hydrogen in pure or mixed compounds. Singlet (width ≈ 0.4 c.p.s.) shifts from -2.50 to 2.34 p.p.m. as A/Ti decreases from 4 to 1

^a Samples run in benzene unless otherwise noted.

The *t*-butyl titanate was prepared by the method of Bradley,⁵ and the methyl titanate was made from the

(5) D. C. Bradley, R. C. Mehrotand, and W. Wardlaw, *J. Chem. Soc.*, 4204 (1952).

t-butyl titanate by the alcoholysis procedure of Adkins.⁶ Tetrakisdimethylaminotitanium was prepared according

(6) H. Adkins and F. Bischoff, *J. Am. Chem. Soc.*, 46, 256 (1924).

to Bradley.⁷ The above reagents were carefully purified until they gave sharp, unambiguous n.m.r. spectra. Titanium tetrachloride (99.5%) was purchased from Matheson Coleman and Bell and used directly. The titanium tetrabromide came from K and K Laboratories and was distilled before use. The solvents were purified by standard methods and stored in an inert-atmosphere drybox. The toluene had <20 p.p.m. water by Karl Fischer analysis, the benzene <50 p.p.m., and the chloroform <30 p.p.m. All subsequent manipulations involving solvents or reagents were carried out in an inert-atmosphere drybox.

Reagents and solvent were weighed into precision-bore, thin-walled n.m.r. tubes and sealed. Equilibration took place immediately except in the cases involving methyl titanate, which was found to dissolve slowly, and the system based on *t*-butyl titanate and tetrakisdimethylaminotitanium, which required *ca.* 50 hr. at 80° to reach equilibrium as indicated by pilot runs.

Nuclear Magnetic Resonance. Proton n.m.r. spectra were obtained from a Varian Model A-60 spectrometer, at a frequency of 60,000 Mc., generally using a sweep width of 50 cycles for full scan. Quantitative determinations of individual n.m.r. peaks were made with an Ott compensating planimeter. Low-temperature spectra were produced on the same type of spectrometer equipped with a variable-temperature probe. A methanol standard was used to calibrate for temperature.

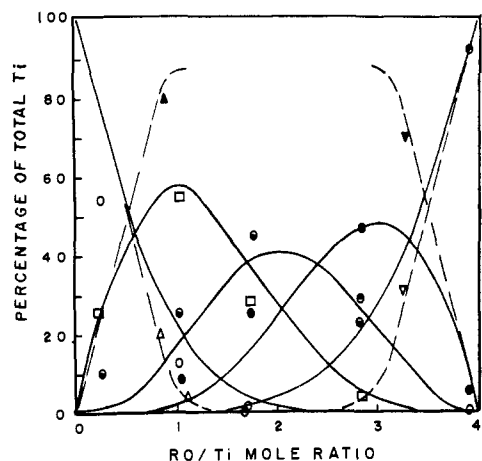


Figure 1. Distribution of products (solid lines) from equilibrating tetra-*t*-butyl titanate with tetrakisdimethylaminotitanium at 80°. The solid-line curves are calculated¹¹ on the basis of $K_1 = 0.24$, $K_2 = 0.11$. Some data are also shown (dotted lines) for equilibration of tetraethyl titanate with tetrakisdimethylaminotitanium at 25°. The dotted lines correspond to K_1 and $K_3 = 5 \times 10^{-3}$ with a similarly small value of K_2 : Δ and \circ , $[(CH_3)_2N]_4Ti$; \square , $[(CH_3)_2N]_3Ti[OC(CH_3)_3]$; \ominus , $[(CH_3)_2N]_2Ti[OC(CH_3)_3]_2$; \bullet , $[(CH_3)_2N]Ti[OC(CH_3)_3]_3$; \odot , $[(CH_3)_3CO]_4Ti$; \blacktriangle , $[(CH_3)_2N]_3Ti(OCH_2)$; ∇ , $(CH_3O)_4Ti$.

The n.m.r. findings are summarized in Table I, from which it can be seen that the scrambling equilibria could be measured by this technique only for the system $[(CH_3)_3CO]_4Ti$ vs. $[(CH_3)_2N]_4Ti$. In all other cases, the exchange was sufficiently rapid so that the minimum total of four quantitatively measurable

(7) D. C. Bradley and T. M. Thomas, *J. Chem. Soc.*, 3857 (1960).

species required to evaluate the three equilibrium constants of eq. 1 was not available. However, since the calorimetrically measured enthalpy for the related reaction between $(C_2H_5O)_4Ti$ and $[(CH_3)_2N]_4Ti$ was a rather large negative value, it was assumed that the species for which $i = 1$ and 3 in $(CH_3O)_{4-i}Ti[N(CH_3)_2]_i$ would not be present simultaneously except in a small range of composition near that corresponding to equimolar proportions of the methyl titanate and tetrakisdimethylaminotitanium so that an estimate could be obtained for K_1 and K_3 (see eq. 1 below). The experimental results for these two systems are presented in Figure 1, in which the experimental points are compared with calculated curves based on the best experimental values for the equilibrium constants.

Calorimetry. The heats of reaction were measured in a calorimeter constructed from a 1-l. dewar flask with electrical heating for calibration. The reagents were weighed into thin glass bulbs which were sealed and placed in the calorimeter. A weighed sample of toluene was then added since a solvent was needed when the mixed compounds were solids. When the system had reached a constant temperature, the bulbs were cracked, and the resulting increase in temperature (0.1 to 0.5°) of the calorimeter water was read on a Beckmann thermometer. Heats of solution of the various liquid compounds in toluene were also measured and proved to be negligible (≤ 0.1 kcal./mole of solute).

The calorimetric results are presented in Table II, from which it can be seen that large exothermic effects were observed on mixing tetrakisdimethylaminotitanium or alkyl titanates with titanium tetrachloride.

Table II. Calorimetric Data at 25° for the Various Systems TiA_4 vs. TiZ_4 in Toluene Solvent

Substituents	Z	Compn. ratio A/Ti	Concn. in toluene, g.-atoms of Ti/l. of solvent	Heat of combining TiA_4 with TiZ_4 , kcal./g.-atom Ti
C_2H_5O	$(CH_3)_2N$	2	3.3	-3.9
$(CH_3)_2CHO$	$(CH_3)_2N$	2	No solv.	-0.3
C_2H_5O	$(CH_3)_2CHO$	2	No solv.	-4.5
C_2H_5O	$(CH_3)_3CO$	2	No solv.	-1.6
C_2H_5O	Cl	3	1.7	-12.
		2	1.7	-14.
		1	1.7	-5.7
$(CH_3)_2CHO$	Cl	2	1.8	-12.
		1	1.7	-8.6
$(CH_3)_2N$	Cl	3	0.31	-17.
		2	0.34	-19.
		2	0.15	-22. ^a

^a Precipitate observed so that reported value is affected by the heat of solution which appears to be positive (endothermic by several kilocalories) as would be expected for a higher degree of association in the solid than in the liquid.

Cryoscopy. The classical Beckmann technique for determining molecular weight by freezing-point depression was used. The apparatus was a Bender and Hobein automatic freezing-point device. The molal freezing-point-depression constant for benzene was taken⁸ to be 5.12.

(8) N. A. Lange and G. M. Forker, "Handbook of Chemistry," 8th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1952.

The cryoscopic data involving tetraethyl titanate are summarized in Figure 2. In addition, it was found that tetramethyl titanate was tetrameric over a concentration range of 0.02 to 0.06 g.-atom of Ti/l. of solvent, whereas isopropyl and *t*-butyl titanates as well as tetrakisdimethylaminotitanium were monomeric. Other cryoscopic data are reported in the final section of this paper dealing with the associated molecules.

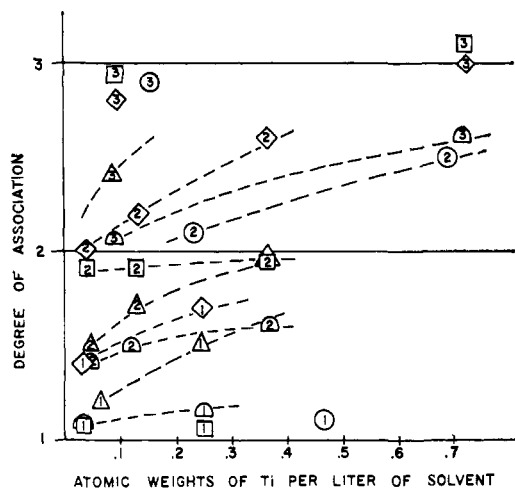


Figure 2. Cryoscopic data on various titanium compounds in which the ethoxyl group is a substituent: O, $(\text{CH}_3\text{CH}_2\text{O})_{4-t}\text{TiCl}_t$; □, $(\text{CH}_3\text{CH}_2\text{O})_{4-t}\text{TiBr}_t$; Δ, $(\text{CH}_3\text{CH}_2\text{O})_{4-t}\text{Ti}[(\text{CH}_3)_2\text{N}]_t$; ◇, $(\text{CH}_3\text{CH}_2\text{O})_{4-t}\text{Ti}[(\text{CH}_3)_2\text{CHO}]_t$; and ○, $(\text{CH}_3\text{CH}_2\text{O})_{4-t}\text{Ti}[(\text{CH}_3)_2\text{CO}]_t$; the numbers inside the symbols refer to the over-all $\text{CH}_2\text{O}/\text{Ti}$ mole ratio.

Although it would have been desirable to obtain all of the physical data in the same concentration range this could not readily be done. In all but one case, high concentrations in the range of 2 to 3 g.-atoms of Ti/l. of solvent were employed for the calorimetric measurements in order to obtain maximum precision. Similarly, the n.m.r. measurements were carried out in a range of 0.1 to 2 g.-atoms of Ti/l. of solvent in order to avoid too much background noise, while cryoscopic measurements were made in the range of 0.03–0.7 g.-atom of Ti/l. of solvent so as to avoid complications with activity coefficients, etc. At the low end of this range, below 0.1 g.-atom of Ti/l., it is possible that errors are introduced by trace water in the benzene⁹ (found to have <50 p.p.m. water by Karl Fischer analysis). The sole exception to these generalizations was the $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ vs. TiCl_4 system in which all measurements were carried out between 0.10 and 0.34 g.-atom of Ti/l. of solvent in order to avoid precipitation of the rather insoluble mixed species.

Scrambling Reactions

Exchange Rates.¹⁰ Line broadening of the n.m.r. spectrum of tetramethyl titanate, see line 1 of Figure 3, leads to a calculated lifetime of *ca.* 0.1 sec., with respect to exchange of a methyl group from one chemically different site to another. This numerical value for

(9) D. C. Bradley and C. E. Holloway, *Inorg. Chem.*, **3**, 1163 (1964).

(10) The interpretative technique employed in this study is described by K. Moedritzer and J. R. Van Wazer, *ibid.*, **3**, 139 (1964), eq. 1–3.

the lifetime was obtained for the spectra taken in chloroform from interpretation of two broadened resonances (each treated as a single, uncoalesced peak) and one saddle between peaks. The individual lifetimes from these measurements ranged from 0.13 to 0.16 sec. When benzene was used as a solvent, two broadened resonances and three saddles were used in the estimation of lifetimes, the individual values for which ranged from 0.08 to 0.14 sec. In the exchange reactions, the rates of which could be measured by interpretation of n.m.r. line widths, it is thought that the transfer of an alkyl group from one site to another probably involves transfer of the RO or $(\text{CH}_3)_2\text{N}$ moiety without rupture of the C–O or C–N bonds, since these steps would be expected to be reasonably slow (lifetimes > *ca.* 1 sec.) at room temperature in these moderately dilute solutions in organic solvents. The relatively long lifetimes measured for exchange of methyl groups between chemically different sites in tetramethyl titanate is probably attributable to the utilization of all available orbitals of titanium in the associated structure, in which the titanium is thought (see structure I below) to have a coordination number of 6.

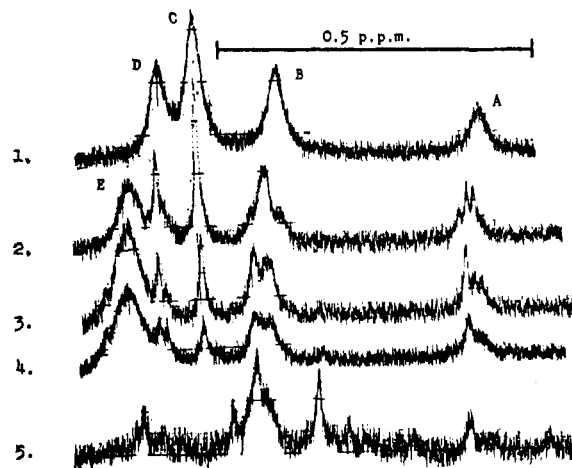


Figure 3. Proton n.m.r. spectra corresponding to the system $(\text{CH}_2\text{O})_4\text{Ti}$ vs. TiCl_4 at 0.5 g.-atom of Ti/l. of solvent in chloroform at 25°. The average number of chlorine atoms per tetrameric molecule varies as follows, reading from the top spectrum down: 0, 0.4, 1.1, 1.7, and 3.0.

For the $(\text{CH}_3\text{O})_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ system, a value of *ca.* 10^{-3} sec. was estimated for exchange of substituents between the various mixed species $(\text{CH}_3\text{O})_{4-t}\text{Ti}[(\text{CH}_3)_2\text{N}]_t$. This value came from the width of each coalesced n.m.r. peak and its shift with composition in both the CH_3O and $(\text{CH}_3)_2\text{N}$ regions of the spectra. Exchange between the $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ molecule and the mixed species is considerably slower, corresponding to a lifetime of *ca.* 0.1 sec. as estimated from the shape of the saddle between the resonance for pure tetrakisdimethylaminotitanium and that for the mixed species. Similar approximations for the system $(\text{C}_2\text{H}_5\text{O})_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ led to *ca.* 10^{-3} sec. for the lifetime for exchange of substituents between the various mixed species and 0.05 sec. for exchange of dimethylamino groups between the tetrakisdimethylaminotitanium molecule and the mixed species. For the system

$[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$, data on the $(\text{CH}_3)_2\text{N}$ region of the n.m.r. spectrum indicated a lifetime of $<ca. 10^{-3}$ for exchange of dimethylamino groups between the tetrakisdimethylaminotitanium molecule and the mixed species.

In the $(\text{RO})_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ system, the slower rate of substituent interchange of the tetrakisdimethylamino compound with the mixed species as compared to interchanges between the various mixed species is probably due to steric shielding of the titanium atom by the four bulky dimethylamino groups. Likewise, slow exchanges involving the other end member, tetramethyl titanate, are probably attributable to its tetrameric structure in which the titanium is hexacoordinate.

The substitution of a *t*-butyl for either a methyl, ethyl, or isopropyl group in the system $(\text{RO})_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ causes a ten-millionfold reduction in the exchange rates—a reduction which conventionally would be attributable to steric hindrance. As expected, the n.m.r. resonances in the system $[(\text{CH}_3)_3\text{CO}]_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ correspond to the limiting narrow line width of 0.3 c.p.s. found for the Varian A-60 spectrometer. In agreement with this, a series of kinetic runs at 80° led to lifetimes of 10–15 hr. for several different ratios of the starting materials.

Exchange of *t*-butyl for methyl groups in the system $(\text{CH}_3\text{O})_4\text{Ti}$ vs. $[(\text{CH}_3)_3\text{CO}]_4\text{Ti}$ was considerably slower than the values measured for exchange in the systems $(\text{RO})_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ for all R's except *t*-butyl. However, an estimation for the lifetimes for exchange could still be obtained from the n.m.r. data. Thus, from the methoxyl region of the spectrum, we find that the lifetime for exchange of the mixed species with each other or with the tetramethyl titanate is in the range of 2 to 8×10^{-2} sec. Exchange of alkoxy or dimethylamino groups for chlorine atoms was too rapid to estimate with any accuracy from the n.m.r. data, which merely showed that the lifetimes were definitely less than 10^{-3} sec.

Equilibria. The only system which exhibited a sufficiently low rate of exchange so that n.m.r. could be employed for measuring the amounts of the various species was the $[(\text{CH}_3)_3\text{CO}]_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$. From the data given in Figure 1, it was possible to evaluate¹¹ the three equilibrium constants of the form

$$K_1 = \frac{[\text{TiA}_{5-t}\text{Z}_{t-1}][\text{TiA}_{3-t}\text{Z}_{t+1}]}{[\text{TiA}_{4-t}\text{Z}_t]^2} \quad (1)$$

where, in this particular case, A = $(\text{CH}_3)_3\text{CO}$ and Z = $(\text{CH}_3)_2\text{N}$.

The constants of the form of eq. 1 were found for this system to be $K_1 = 0.24$, $K_2 = 0.40$, and $K_3 = 0.11$, with a standard error computed from the weighted distribution of values for each constant = *ca.* 0.09. These constants are very close to those expected for random sorting of the substituents, in which case $K_1 = K_3 = 0.375$, and $K_2 = 0.441$. This nearly random behavior is in accord with the nature of the substituents and the fact that the end-member and mixed species in this system were all found to be unassociated.

An indirect measure¹⁻³ of the value of the equilibrium constants may be obtained from the heats evolved upon

(11) L. C. D. Groenweghe, J. R. Van Wazer, and A. W. Dickinson, *Anal. Chem.*, **36**, 303 (1964).

combining the end-member compounds, *i.e.*, from the data of Table II. From these data, it can be seen that the system $[(\text{CH}_3)_2\text{CHO}]_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ is close to random (*i.e.*, the ΔH is small). This system is also monomeric throughout so that the equilibrium constant is a "normal" one unaffected by association.

The degree of association measured across the full range of composition ratios in the system $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ vs. TiCl_4 was always close to unity so that the measured ΔH of *ca.* -18 kcal. is also unaffected by association. The equivalent equilibrium constants are $K_i \approx 10^{-8}$. Since no association is found for tetraisopropyl titanate and titanium chloride, as well as for the mixed compound $[(\text{CH}_3)_2\text{CHO}]_4\text{TiCl}_3$, the ΔH of -8.6 kcal. obtained for this composition should also be free of complicating effects owing to association so that the respective equilibrium constant is $K_3 \approx 2 \times 10^{-5}$. All of the other calorimetric data presented in Table II correspond to equilibria in which the normal relationships for scrambled systems^{1,3} are complicated by association. This is also true of the system $(\text{CH}_3\text{O})_4\text{Ti}$ vs. $[(\text{CH}_3)_2\text{N}]_4\text{Ti}$ for which some data are shown in Figure 1. These data indicate that, for this system, $K_1 < ca. 10^{-3} > K_3$. These two values correspond to ΔH_1 and $\Delta H_3 \approx -5.4$ kcal./mole.

As expected from studies on other systems,¹⁻³ the greatest deviation from randomness in the unassociated systems is found on exchanging an amino group with chlorine. The next corresponds to exchange of an alkoxy group with chlorine, with very little deviation from randomness for exchange of alkoxy with amino. It is expected that the deviations from randomness in exchange of different alkoxy groups will be small so that the heats of several kilocalories reported in Table II for such reactions must be nearly completely attributable to the effects of association.

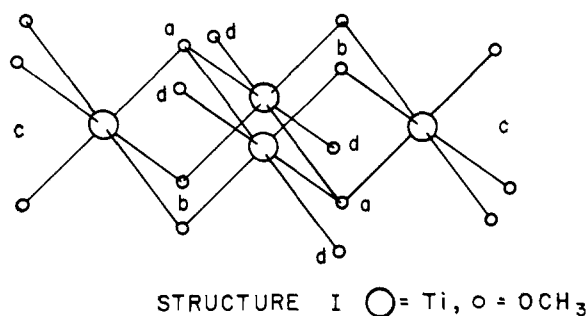
Associated Molecules

Thermodynamics of Ethoxyl Bridges. The enthalpy data of Table II offer several routes to an estimation of the heat of formation of an ethoxyl bridge in an association complex. Thus, in the reaction between trimeric tetraethyl titanate and monomeric tetrakisdimethylaminotitanium to give dimeric bis-ethoxylbisdimethylaminotitanium, we estimate the energy for formation of an ethoxyl bridge is $2(-3.9) = -7.8$ kcal./mole. Likewise, in the reaction between trimeric tetraethyl titanate and monomeric tetraisopropyl titanate to give diethyl diisopropyl titanate, the heat of formation of an ethoxyl bridge is approximately equal to $2(-4.5) = -9.0$ kcal./mole. These calculations are based on the conclusion in the preceding section that enthalpies in these systems are due primarily to association effects.

Similarly, if we conclude the enthalpy (-8.6 kcal./mole) found for the reaction of monomeric tetraisopropyl titanate with monomeric titanium tetrachloride to form monomeric $[(\text{CH}_3)_2\text{CHO}]_4\text{TiCl}_3$ is due only to nonassociation effects such as back-coordination, we can calculate the heat of formation of ethoxyl bridges in the following way. When the trimeric tetraethyl titanate and the monomeric titanium tetrachloride react to form monomeric $(\text{C}_2\text{H}_5\text{O})_4\text{TiCl}_3$, there is a loss of ethoxyl bridges so the measured enthalpy (-5.7 kcal./mole) is lower than obtained for

the completely monomeric isopropyl system (-8.6 kcal./mole). The heat of formation of an ethoxyl bridge calculated from these data is $4(+5.7 - 8.6) = -11.6$ kcal./mole. Likewise, for the reactions in which the trimeric compounds $(C_2H_5O)_3TiCl$ and $(C_2H_5O)_2TiCl_2$ are formed, similar calculations can be made. For $(C_2H_5O)_3TiCl$, the heat of formation of an ethoxyl bridge is $2(-14 + 8.6) = -11$ kcal./mole, and for $(C_2H_5O)_2TiCl_2$, the value is $4(-12 + 8.6) = -14$ kcal./mole. The latter two calculations are somewhat doubtful since we do not know how chlorine substitution influences the energy of association. In summary, we obtain an average value of -11 kcal./mole for the formation of an ethoxyl bridge—a value which is close to the ones reported in the literature, *i.e.*, -9.8 kcal./mole¹² and -10 kcal./mole.¹³

Structure of the Associated Species. The data reported here suggest that the structure of methyl titanate may be the same as that proposed¹⁴ for crystalline ethyl titanate on the basis of X-ray diffraction. The n.m.r.



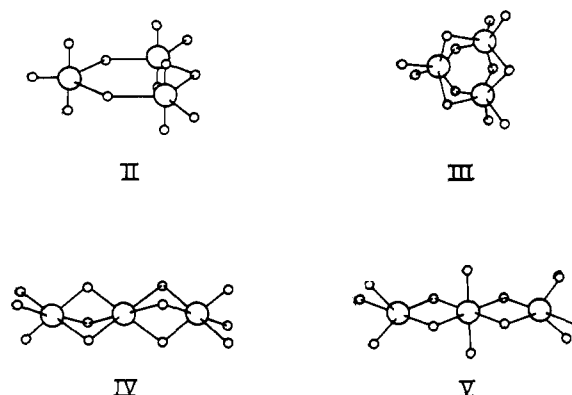
spectra of methyl titanate in benzene or chloroform are consistent with this structure, as are the cryoscopic data which show this compound to be tetrameric within the limit of error permitted by its low solubility. On the top line of Figure 3, the n.m.r. spectrum of tetramethyl titanate in chloroform is reproduced. The relative areas of the four peaks labeled A through D are 1:2:3:2. These four different resonances have been assigned to the methoxyl positions which have been labeled in structure I with the same letters in lower case. It should be noted that the positions labeled c in this structure are not all identical, but it is assumed that they are indistinguishable by n.m.r. at the resolution employed. In benzene solution, the same 1:2:3:2 spectrum is seen, but peak D is shifted so as to lie between peaks A and B. A spectrum similar to the benzene one is seen for toluene except that peaks B and D are almost wholly coalesced.

The mixed compound, $(CH_3O)_3TiCl$, in the system $(CH_3O)_4Ti$ vs. $TiCl_4$ was also found to be tetrameric while a higher proportion of chlorine caused a decrease in complexity. Figure 3 shows the effect on the n.m.r. spectra of increasing chlorine substitution when going from tetrameric $(CH_3O)_4Ti$ to a composition having somewhat less chlorine than the tetrameric $(CH_3O)_3TiCl$, *i.e.*, from 0 to 3 chlorine atoms per tetramer. Since $TiCl_4$ is unassociated, we expect chlorine substitution to occur in the peripheral positions c and d, thereby altering the methoxyl resonances. If we as-

sume that substitution of one chlorine in a c position causes the two other c methoxyl groups on the same titanium plus the four d methoxyls to produce the resonance labeled E, or alternatively, if we assume that the substitution of a chlorine in a d position causes the other d methoxyl on the same titanium as well as the six c methoxyl groups to show up as the E resonance, the first three spectra of Figure 3 can be accounted for semiquantitatively, with qualitative fit for the latter two spectra. This assumes the idea that the methoxyl groups bridging between only two titaniums (position b) transmit essentially all of the effects determining the n.m.r. chemical shifts, with the methoxyls bridging between three titaniums (position a) and hence having no unshared electron pairs being ineffective.

Presumably all of the spectra except the top one in Figure 3 correspond to mixtures of molecules in which the basic structure of the tetramer (see structure I) is maintained intact until the average number of chlorines per tetramer exceeds *ca.* 2. Beyond this point, further structural modification is presumed to include the conversion of an a-type methoxyl group (bonded to three titaniums) to a bifunctional methoxyl of the type labeled b, by the opening of one of the Ti-O bonds. This would thereby reduce the coordination number of the titanium from 6 to 5.

Although, as was mentioned above, the solid ethyl titanate is tetrameric,¹⁴ the liquid or dissolved specie is apparently trimeric,^{9,15} A number of structures have been proposed for this trimer (see II,¹² III,¹² IV,¹⁶ V). Ordinarily, proton n.m.r. would be ideally suited to distinguish the possibilities. However, be-



cause of rapid exchange, only a simple methylene quartet is visible at room temperature. At lower temperatures some peak separation is observed, as shown in Figure 4. While interpretation of this low-temperature spectrum is not clear-cut, it apparently excludes configurations having two different methoxyls in a 1:1 ratio as expected for structures III and IV. Although structure V is not excluded by the n.m.r. data, one would have to rationalize the poor cryoscopic representation of linear tetramer or higher homologs. Structure II appears to fit the available data. Thus, upon cooling, the methylene quartet of the ethoxyl group is partially split into a superimposed double pattern which could have peak areas in the ratio 3:1, as seen in Figure 4. The upfield peak in this spectra

(12) R. L. Martin and G. Winter, *J. Chem. Soc.*, 2947 (1961).

(13) D. C. Bradley, R. C. Hehrota, J. D. Swanwick, and W. Wardlaw, *ibid.*, 2025 (1953).

(14) J. A. Ibers, *Nature*, 197, 686 (1963).

(15) R. L. Martin and G. Winter, *ibid.*, 197, 687 (1963).

(16) C. N. Coughlan, H. S. Smith, W. Katz, W. Hodgson, and R. W. Crowe, *J. Am. Chem. Soc.*, 73, 5652 (1951).

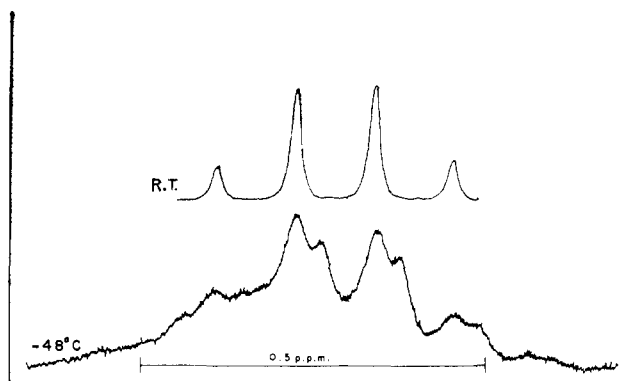
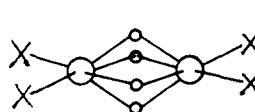


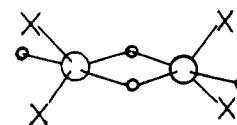
Figure 4. Proton n.m.r. spectra at room temperature (R.T.) and at -48° of tetraethyl titanate at a concentration of 1.5 g.-atoms of Ti/l. of solvent in toluene.

is thought to correspond to the bridging ethoxyl groups of structure II, with all of the remaining ethoxyls producing the downfield part of the doubled quartet.

Although the compound $(\text{CH}_3\text{O})_3\text{TiCl}$ was found to be tetrameric in benzene solution, the ethyl analog $(\text{CH}_3\text{CH}_2\text{O})_3\text{TiCl}$ is apparently trimeric. The most likely structure for this trimer is again II, with the more bulky chlorine atoms filling the relatively uncrowded equatorial positions. An increasing proportion of chlorine atoms in the trimer would force the chlorine atoms to occupy the more crowded axial positions. Such a trimer would be less favored and, indeed, the compound $(\text{CH}_3\text{CH}_2\text{O})_2\text{TiCl}_2$ exhibits a degree of association between 2.2 and 2.6, up to concentrations of 0.7 *M* in benzene. Also the compounds $[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{TiCl}_2$ ¹² and $(\text{CH}_3\text{CH}_2\text{O})_2\text{TiBr}_2$ are dimeric in this range. Martin and Winter¹² have suggested structure VI for $[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{TiCl}_2$, but we feel this would



VI



VII

be prohibitively strained and suggest structure VII for the *n*-butoxyl compound as well as for $(\text{CH}_3\text{CH}_2\text{O})_2\text{TiBr}_2$. This structure permits energy lowering through back-coordination as well as through bridging. Additional support for structure VII was obtained from dipole moment measurements¹⁷ of $[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{TiCl}_2$ in benzene at concentrations where it is known to be dimeric.¹² A value of 4.6 D. was obtained (calculated on the basis of dimer) ruling out structure VI which would be expected to have a dipole moment near zero. Structure VII could easily represent these data if the molecule occasionally assumed conformations where the Ti-Cl bond moments did not cancel.

The cryoscopic results for mixed compounds containing the ethoxyl substituent, which are summarized in Figure 2, can be explained as follows: (1) the only atom involved in bridging to more than a minor extent is the ethoxyl oxygen; (2) the preferred structure is II unless steric pressures make it less favored relative to a dimer such as VII or the monomer; and (3) $(\text{CH}_3\text{CH}_2\text{O})\text{Ti}[(\text{CH}_3)_2\text{CHO}]_3$ and $(\text{CH}_3\text{CH}_2\text{O})\text{Ti}[(\text{CH}_3)_2\text{N}]_3$ have an average degree of association between 1 and 2 because the only available way to achieve additional energy lowering is through association.

(17) The dipole moment measurements were made by Carl E. Vogler of the Monsanto Company using the capacity bridge method described in "Physical Methods of Organic Chemistry," Vol. II, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1946, part 2, p. 999.