posite charge as the ionic strength is decreased.[14] Using this theory and our value for k_f at low ionic strength, the value calculated at 0.1 M ionic strength is $0.8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. Consistency in this respect is also observed for the samarium anthranilate system measured in 0.2 M ionic strength.[9] Only the oxalate complexation of samarium[15] fails to correspond with the above ionic strength dependence which places further doubt on the resultant rate constants for the entire series of rare earth oxalates. By contrast the rate constants for the rate-determining step in a multistep mechanism show little dependence on the ionic strength[16] as expected since this step does not involve the collision of ions of opposite sign but only the desolvation of the cation in the complex. If one correlates the overall forward rate constant k_f with the rate-determining stepwise rate constant k_{ij}, according to $k_f = K_o k_{ij}$, where K_o is the outer ion-pair formation constant, then the decrease in k_f with increasing ionic strength is reflected entirely in a concomitant decrease in K_o.

The activation enthalpy change for the forward process $\Delta H_f^{\ddagger} \simeq 5$ kcal mol^{-1} is in good agreement with that observed for other closely related systems, *e.g.*, 2-4 kcal mol^{-1} for water exchange[17] on Gd^{3+} measured by ^{17}O nmr, 2-4 kcal mol^{-1} for samarium sulfate measured acoustically,[18] and 4.4 kcal mol^{-1} for dysprosium anthranilate measured by temperature jump.[19] Therefore, the value of $k_f = 8.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ at 25° and low ionic strength appears to conform well with the general scheme of the results for rare earth complexation reactions. With this figure for k_f measured at the experimental conditions of the acoustic experiments it should be possible to make a more realistic correlation between rate data from different relaxation techniques.[16]

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Registry No. Samarium, 7440-19-9; murexide, 134-02-1.

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Reaction of Molecular Oxygen and Titanium Trichloride in Anhydrous Pyridine

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Molecular oxygen and titanium trichloride react in anhydrous pyridine to give the oxo-bridged titanium(IV) complex $Cl_3TiOTiCl_3 \cdot 4C_5H_5N$ in quantitative yield. The rate law $-d[O_2]/dt = k_{\text{exptl}} P_{O_2} [TiCl_3]$ was observed. Values for the specific rate constant of the homogeneous reaction ($k_1^{25°}$), $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are 7.1×10^{-2} l mol^{-1} sec^{-1}, 10 kcal mol^{-1}, and −31 eu, respectively. A direct electron-transfer mechanism is proposed. Spectral evidence is presented for the existence of a dimeric titanium(III) species in solution. An initial rapid uptake of oxygen by titanium trichloride solutions is accounted for in terms of a $Ti_2Cl_9^{3-}$ dimer, whose concentration diminishes as the reaction progresses.

Introduction

Because of the assiduous care taken to exclude molecular oxygen in studies of nonaqueous solutions of titanium compounds in low oxidation states, little is known of the products and mechanisms of reactions involving titanium(III) and molecular oxygen in nonaqueous solvents. In the absence of solvent, titanium trichloride and molecular oxygen combine at elevated temperatures to give a 1:1 mole ratio mixture of titanium(III) oxychloride and titanium tetrachloride.[1] In moist air or basic to slightly acid aqueous solution, titanium trichloride is rapidly and irreversibly oxidized to hydrated titanium dioxide.[2] Bis(cyclopentadienyl)titanium(III) chloride,[3] bromide,[4] cyanide, cyanate, and thiocyanate[5] yield oxo-bridged dimers of the type $(Cp)_2(X)Ti\text{-}O\text{-}Ti(X)(Cp)_2$ when exposed to molecular oxygen in anhydrous solvents. Despite the detrimental effect of the irreversible oxidation by molecular oxygen upon the chemical, catalytic, and physical properties of compounds of titanium in low oxidation states, analyses of the products and mechanisms of these oxidations are useful in the formulation of chemical synthesis, the definition of solute species, and the empirical differentiation of the chemistry of titanium(III), a d^1 system, from the more thoroughly investigated chemistry of the low-spin d^7 Co(II) systems which also contain a single unpaired electron.

Results and Discussion

The chemistry of titanium(III) in this system is markedly different from that of low-spin cobalt(II) systems. When oxygen is passed through an aqueous solution of cobalt(II) chloride or nitrate and potassium cyanide, a μ-peroxo complex anion $[(NC)_5CoO_2Co(CN)_5{}^{6-}]$ is rapidly formed.[6] Reduction of oxygen by cobalt(II) stops at the peroxide state in the presence of ammonia with the formation of $[(NH_3)_5CoO_2Co(NH_3)_5]^{4+}$ salts.[7] With titanium trichloride as the

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reducing agent in pyridine, molecular oxygen is reduced completely to the oxide.

Careful measurements of the amount of oxygen consumed per mole of titanium(III) chloride gave a $TiCl_3$:O_2 mole ratio of 4:1. The yield of crystalline product was essentially quantitative (98-99%) for a reaction stoichiometry

$$4TiCl_3 + O_2 + 8C_5H_5N \xrightarrow{py} 2[Ti_2Cl_6O \cdot 4C_5H_5N] \qquad (1)$$

The infrared spectrum of the product contains medium-intensity bands at 625 and 435 cm^{-1} due to the complexed pyridine ring in-plane stretching vibration (ν 6a, 6b)[8] and out-of-plane deformation (ν 16b), respectively, and a very strong band at 830 cm^{-1} which has been assigned to the Ti-O-Ti stretching vibration.[9] The compounds Cl_3Ti-O-$TiCl_3 \cdot 4CH_3CN$ and Cl_3Ti-O-$TiCl_3 \cdot$4(dioxane) had been prepared previously by the partial hydrolysis of the appropriate $TiCl_4 \cdot nD$ adduct.[10] In the acetonitrile adduct a strong band at 800 cm^{-1} and a shoulder at 740 cm^{-1} were assigned to the Ti-O-Ti moiety. These appear at 820 and 763 cm^{-1} in the dioxane adduct. A broad strong band at 720 cm^{-1}, which appears in the infrared spectra of the $(Cp)_2(X)Ti$-O-$Ti(X)(Cp)_2$ compounds, was assigned to a Ti-O-Ti stretching vibration.[3,5] The infrared spectrum of our product contains the following additional bands below 2000 cm^{-1}: 1632 (w); 1600 (s), pyridine ring deformation (ν 8a); 1450 (vs), ring deformation (ν 19b); 1220 (m), C-H in-plane deformation (ν 3); 1200 (w, sh); 1155 (m), C-H in-plane vibrations (ν 9a, ν 15); 1070 (m), C-H in-plane vibration (ν 18b); 1042 (m), in-plane ring vibration (ν 12); 1012 (m), in-plane ring vibration (ν 1); 755 (s) (ν 10b), 695 (s) (ν 11), C-H out-of-plane deformations; 680 (w, sh); 452 (w); 385 (m, sh), 370 (s), 350 (m), 315 (s), Ti-Cl vibrations.

The infrared spectrum of the product is not a composite of the spectra of $TiCl_4 \cdot 2C_5H_5N$ and $TiCl_2 \cdot 2C_5H_5N$.[11] The possibility that the product contains a peroxo-bridged titanium linkage was also eliminated by the negative test for peroxide with cerium(IV) in acid solution.[12] The total results outlined above indicate that the product is a unique compound containing a Ti-O-Ti linkage.

Within the first 5 min after oxygen was admitted to the reaction vessel containing the pyridine solution of titanium trichloride, there always occurred a rapid uptake of oxygen accompanied by a change in color of the solution from brown to green. Thereafter the oxygen uptake was markedly slower. Kinetic data were taken over the time span of the slower reaction. Rates were obtained from plots of oxygen pressure *vs.* time at constant known volume. These are given in Table I. Plots of initial rate *vs.* initial oxygen pressure at a fixed titanium trichloride concentration and of initial rate *vs.* initial titanium trichloride concentration at a fixed oxygen pressure are both linear as shown in Figure 1. The reaction is first order with respect to each component

$$-d[O_2]/dt = k_{exptl}P_{O_2}[TiCl_3] \qquad (2)$$

Table I. Rate Data for the Reaction of $TiCl_3$ and O_2 in Pyridine at 25.0°

$10^2[TiCl_3]$,[a] M	P_{O_2},[a] atm	$10^4 \times$ rate,[a] $M\ min^{-1}$	$10^2[TiCl_3]$,[a] M	P_{O_2},[a] atm	$10^4 \times$ rate,[a] $M\ min^{-1}$
7.64	0.0408	0.28[b]	1.93	0.179	0.57[b]
7.66	0.122	1.53	3.72	0.190	1.11
7.64	0.128	1.72	5.70	0.190	1.76
7.66	0.187	2.67	9.54	0.193	2.90
7.65	0.194	2.70	7.64	0.411	2.95[c]
7.64	0.265	3.82	7.63	0.396	1.89[d]
7.64	0.396	5.93			

[a] Initial values, $-d[O_2]/dt$. [b] Approximate solution surface area at the gas–liquid interface was 58 cm^2. For all other measurements the surface area was approximately 25 cm^2. [c] Rate at 14.7°. [d] Rate at 5.3°.

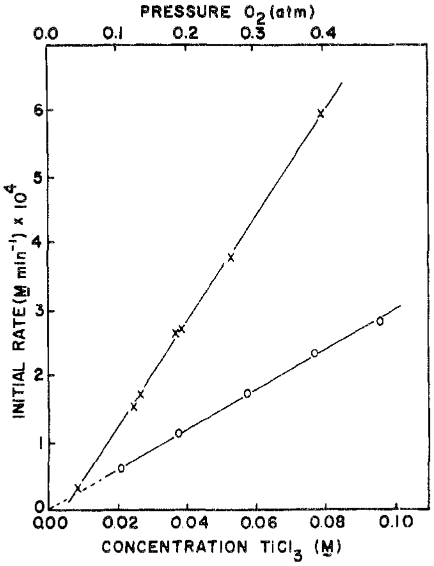

Figure 1. Initial reaction rate as a function of $TiCl_3$ concentration (○) and of O_2 pressure (×).

Because as much as 30% (based on eq 1) of the titanium trichloride is consumed during the initial rapid process, it was necessary to correct the initial concentration of the titanium trichloride in order to compute specific rate constants for the slower reaction. The initial linear segment of the oxygen pressure *vs.* time plot, corresponding to the fast process, was extended to intersect the extrapolated linear portion of the curve corresponding to the slow reaction. (See curve B of Figure 3 for the general appearance of P_{O_2} *vs.* time plots.) The initial oxygen pressure, obtained from the intersection of the two extrapolated lines, never differed from the oxygen pressure at time zero by more than 2.5%. The initial titanium trichloride concentration for the slow reaction was then computed by applying a correction based on the amount of oxygen consumed in the rapid initial reaction according to the stoichiometry of eq 1. Plots of reaction rates *vs.* the corrected oxygen pressures and titanium trichloride concentrations show some scatter but are consistent with an overall second-order rate law (eq 2). The observed second-order rate constant, $k_{exptl}^{25°}$ (eq 2), is $(1.88 \pm 0.18) \times 10^{-2}$ atm^{-1} min^{-1}. The error is given as the standard deviation. An approximate value of 7.1×10^{-2} l. mol^{-1} sec^{-1} for the specific rate constant of the homogeneous reaction (k_1 in eq 3) was estimated from the solubility of oxygen in pyridine.[13] The enthalpy and entropy of activation are compared to those of other reactions of metal complexes with molecular oxygen in Table II.[14,15]

The rate of oxidation of titanium trichloride in pyridine is much slower than the corresponding reactions of cobalt(II) complexes in aqueous medium where values of $k \geqslant 10^3$ l. mol^{-1} sec^{-1} are the rule.[14] It compares to the rate of molecular oxygen uptake by *trans*-$IrX(CO)(PPh_3)_2$ in benzene.

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Table II. Activation Parameters for Reactions of Metal Complexes with Molecular Oxygen at 25°

Reactant	Solvent	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$TiCl_3$	Pyridine	10	−31
Co(dien)$^{2+}$ [14]	Water	10	−12
Co(hist)$_3{}^{2+}$ [14]	Water	8	−8
trans-IrCl(CO)(PPh$_3$)$_2$ [15]	Benzene	13.1	−21
trans-IrBr(CO)(PPh$_3$)$_2$ [15]	Benzene	11.8	−24
trans-IrI(CO)(PPh$_3$)$_2$ [15]	Benzene	10.9	−24

Second-order rate constants of 3.36×10^{-2}, 7.4×10^{-2}, and 30×10^{-2} l. mol^{-1} sec^{-1} were reported for the chloro, bromo, and iodo derivatives, respectively.[15] The rate of oxidation of titanium(III) to titanium(IV) by molecular oxygen is, like that of V(III) to V(IV),[16] a slow reaction.

A slow reaction rate would be expected for a mechanism that involves electron transfer in the rate-determining step accompanied by an appreciable reorganization in bond angles and bond distances during formation of the activated complex. The large $\Delta S^{\ddagger}$ is greater than that usually observed for reactions involving uncharged reactants and products. This suggests a highly polar transition state or unusually stringent stereochemical requirements associated with the combination of reactants in forming the activated complex. A straightforward mechanism which involves direct electron transfer in the rate-determining step is given by eq 3-5. A negative

$$O_2(C_5H_5N)_n + TiCl_3 \xrightarrow{k_1} Cl_3Ti^{IV}(O_2\cdot^-) + nC_5H_5N \qquad (3)$$

$$Cl_3Ti(O_2\cdot^-) + TiCl_3 \xrightarrow{k_2} 2TiCl_3O\cdot \qquad (4)$$

$$Cl_3TiO\cdot + TiCl_3 \xrightarrow{k_3} \text{product} \qquad (5)$$

entropy change would also accompany a mechanism involving the formation of an activated complex of molecular oxygen strongly bound to titanium(III). If the molecular oxygen is only weakly complexed by pyridine, the magnitude of the entropy decrease would be large. The suggestion that a superoxide ion is produced in pyridine as an intermediate in oxygen reduction is not without precedent. Peover and White observed a reversible one-electron reduction wave in the polarogram of molecular oxygen in pyridine and an epr signal of the superoxide ion.[17] Since d^1 ions are characteristically labile[18] and a pseudo-first-order rate constant of *ca.* 10^4 has been reported for the replacement of water molecules in the first coordination sphere of aqueous Ti(III),[19] slow electron transfer rather than Ti-O_2 bond formation controls the rate.

The nature of the solute species responsible for the initial rapid uptake of oxygen, which is accompanied by a change in color of the solution from brown to green, was investigated by electronic and epr spectroscopy. The initial rapid pressure drop was first shown not to be the result of dissolution of oxygen, since the oxygen pressure above pure pyridine stabilized within 10 sec after the gas had been admitted to the reaction vessel. The brown color of the titanium trichloride solutions was found to correspond to the presence of a small concentration of a highly reactive binuclear titanium(II) species and the green coloration to its absence. Pecsok and Fletcher[20] reported earlier that unidentified polynuclear titanium(III) species in aqueous solutions are much more reactive to oxidation than either Ti^{3+} or $TiOH^{2+}$. More recently, the existence in very low concentration of titanium(III) dimer in aqueous HCl solutions was proposed to account for kinetic data.[21]

Others have used epr spectroscopy to determine the presence and structures of binuclear copper(II) and binuclear vanadyl complexes in solution.[22-26] If titanium(III) dimers are formed in solution, a coupling of spins (S_1 and $S_2 = {}^1/_2$) will result in a triplet state ($S = S_1 + S_2 = 1$) and a singlet state ($S = S_1 - S_2 = 0$). A magnetic field splits the triplet state into states with $M_s = 1, 0$, and -1. Allowed transitions will occur between states of $\Delta M_s = \pm 1$ at about 3300 G at 10,000 MHz. The forbidden $\Delta M_s = \pm 2$ transition may occur if the exchange coupling constant J is small because of mixing of states. This transition will appear around $H_0/2$ (1650 G or "half-field") at 10,000 MHz. Although exchange broadening, short spin-lattice relaxation time, or other effects may sufficiently broaden a low-field signal so that it may not be detected, the observation of a half-field signal is definite proof of a dimeric structure. The appearance of a weak, complex epr signal at half-field centering around $g = 4.03$, in frozen solutions of titanium(III) chloride in pyridine, gives diagnostic evidence for the presence of titanium(III) dimers. The presence of a single intense singlet at $g = 1.957$ in the room-temperature epr spectrum is consistent with a single monomeric species or with the presence of multiple monomeric species undergoing rapid geometrical or ligand exchange to produce a time-averaged signal. An apparent molecular weight of 152 ± 12 for solutions of titanium(III) chloride indicates that the dominant species is the monomer (mol wt 154) and that the equilibrium constant of dimerization is very small.

Enough oxygen was admitted to a solution of 0.03 *M* titanium trichloride in pyridine to give a $TiCl_3:O_2$ mole ratio of 11:1. In approximately 4 min the solution color was changed from brown to green and the epr signal at $g = 4.03$ disappeared.

The electronic spectrum of a brown solution contained a highly asymmetric change-transfer (CT) band at λ_{max} 24.0×10^3 cm^{-1} (apparent ϵ *ca.* 1.1×10^3) (Figure 2) and d-d transition at λ_{max} 16.3×10^3 cm^{-1} (apparent ϵ *ca.* 31) (not shown in the figure). Introduction of molecular oxygen to

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(13) The solubility of oxygen at 18° in pyridine is 0.099 cm^3 (STP)/(ml of pyridine)(atm of oxygen) as reported by A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. II, 4th ed, American Chemical Society, Washington, D. C., 1965, pp 1234-1235. In the absence of the temperature coefficient of solubility, the coefficient is taken as zero. Based on the temperature coefficients of oxygen solubility in other nonaqueous solvents, this approximation would not alter the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ by more than 10%. Because the solubility of oxygen at 25° is somewhat greater than at 18°, the computed rate constant will be slightly higher than the true value.

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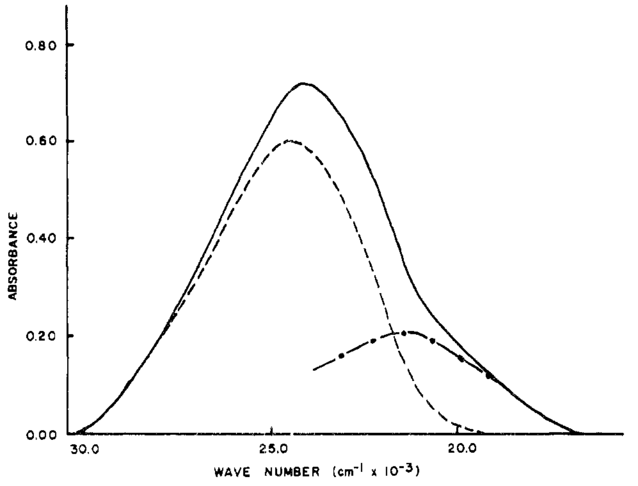

Figure 2. Electronic spectra: 6.5×10^{-4} *F* $TiCl_3$ in pyridine, ——; 6.5×10^{-4} *F* $TiCl_3$ plus 6×10^{-5} *F* O_2, - - - -; charge-transfer band assigned to a titanium trichloride dimer, — • — •.

give a $TiCl_3$:O_2 mole ratio of 11:1 caused no change in the d-d transition band but produced a shift in the CT band to λ_{max} 24.5×10^3 cm^{-1} (apparent ϵ *ca.* 9.2×10^2) and an increase in symmetry of this band. Subtracting the near-symmetrical CT band of the green solution from the total absorbance of the brown solution gave a resolved band with λ_{max} *ca.* 21.7×10^3 cm^{-1} (Figure 2). A very weak band centering near 11.4×10^3 cm^{-1} was also present in the spectrum of brown solutions but absent in the oxygen-containing solutions. These bands are assigned to a CT band and d-d transition band, respectively, of titanium(III) dimers present in unknown but low concentration. Assignment of these bands to dimers is supported by the reflectance spectrum of the cesium salt of the dimeric ion $Ti_2Cl_9^{3-}$, which contains a d-d transition at 13.4×10^3 cm^{-1} and a CT band at 21.5×10^3 cm^{-1}.[27] The reflectance spectra of the diethylammonium and tetra-*n*-propylammonium salts contain the d-d transition at 12.4×10^3 and 11.8×10^3 cm^{-1}, respectively.[28]

A somewhat more detailed description of the dimeric species may be inferred from the following data. The brown-green color transition was found to be reversible and highly sensitive to chloride ion concentration. The addition of strong Lewis acids such as $AlCl_3$, $TiCl_4$, and $Cl_3TiOTiCl_3$, which are capable of complexing chloride ion, caused brown solutions to turn green. The addition of chloride ion reversed the color change. The addition of aluminum chloride to a pyridine solution of titanium(III) chloride to give a 20:1 $TiCl_3$:$AlCl_3$ mole ratio caused the brown solution to turn green. Simultaneously, the visible bands at 21.7×10^3 and 11.4×10^3 cm^{-1} due to dimers and the epr signals of the dimers at $g = 4.03$ disappeared. The d-d transition of the monomer at 16.5×10^3 cm^{-1} remained unaltered, but in a large excess of aluminum chloride[3] (13:1 $AlCl_3$:$TiCl_3$) the d-d transition band was shifted slightly to 16.9×10^3 cm^{-1}. A similar behavior was observed when titanium(IV) chloride was added in an amount to give a 3:1 $TiCl_3$:$TiCl_4$ mole ratio. The product $Ti_2Cl_6O \cdot 4C_5H_5N$ when added in small quantities to the brown solution also turned the solution green. The addition of lithium chloride or pyridinium chloride to the green solutions containing aluminum chloride restored the brown coloration of the solution as well as the electronic bands and epr spectrum of the titanium(III) dimers. Equilibria which are strongly chloride dependent and involve titanium dimeric species are indicated. The self-ionization of titanium trichloride in eq 6 is just such an equilibrium. The addition of a strong Lewis acid would increase the $TiCl_2^+$ concentration (eq 7) and suppress the dimeric anion concentration. Equilibria giving other dimeric species are also possible.

$$5TiCl_3 \rightleftharpoons [(TiCl_2^+)_3, (Ti_2Cl_9^{3-})] \rightleftharpoons 3TiCl_2^+ + 3TiCl_9^{3-} \qquad (6)$$

$$TiCl_3 + AlCl_3 \rightleftharpoons [TiCl_2^+, AlCl_4^-] \rightleftharpoons TiCl_2^+ + AlCl_4^- \qquad (7)$$

The epr data are consistent with structures for the dimers which have Ti-Ti bond distances approximately equal to that found in $Ti_2Cl_9^{3-}$. The X-ray powder pattern of $Cs_3Ti_2Cl_9$, which is isomorphous with $Cs_3Cr_2Cl_9$,[29,30] indicates that in the solid state the Ti-Ti distance would be around 3.12 Å. If only crystal radii are considered, the internuclear distances for the face-shared, edge-shared, and corner-shared octahedra complexes would be 3.00, 3.62, and 5.12 Å, respectively. To a first approximation, these values should give us a good estimate of the internuclear titanium-titanium distances in the solute titanium(III) complex dimers.

All of the observed low-field epr spectra are composed of two lines at 1627 and 1670 G (ν 9320 MHz). At low gain, strong high-field signals due to monomers are observed in the epr spectra, with g inflection points at 1.946, 1.906, 1.888, and 1.866 and maxima at 2850, 2970, 3070, 3950, and 4020 G (ν 9320 MHz). At high gain, however, broad (2400-2600 G) high-field lines that are due to the dimers are observed beneath the strong signals. High-field and half-field δ function spectra were computed as a function of the frequency ν, exchange coupling constant J, internuclear distance r, $g_{\parallel}$, and $g_{\perp}$. Frequency is an experimental parameter and was held constant at 9320 MHz, a typical experimental value. Appropriate g values (Table III), consistent with observed g inflection points, were used in the calculations. Both J and r were varied in the calculation to determine the effect of these parameters on the spectra. There is no noticeable effect upon the lines for values of $J \leqslant 50$ cm^{-1}. Changes in r from 3.0 to 5.0 Å have a dramatic effect upon the low- and high-field lines. High-field lines are broad (*ca.* 2.0 kG) at r = 3.0 Å but become narrow and intensify rapidly as r increases. At r = 5.12 Å high-field absorptions are only 200 G wide. Half-field absorptions decrease rapidly in intensity and shift upfield in position as r increases. At r = 3.0 Å the line is centered around 1670 G. At 3.62 Å it shifts to 1725 G and decreases to about 50% intensity, while at 5.12 Å it is at 1760 G and its intensity is only $^1/_{60}$th of the value at r = 3.0 Å.

Table III contains parameter values and calculated low- and high-field maxima. The computed maxima are consistent with the observed spectra. Comparison of the observed and calculated spectra suggests that the dimeric species present in the solution have relatively short (3.0 Å) Ti-Ti distances and face-shared octahedral structures.

If equilibria of the type shown in eq 6 and 7 exist, the addition of the titanium(IV) product of the reaction would decrease the dimer concentration. Furthermore, if the initial rapid uptake of oxygen is due to the reaction of molecular oxygen with a *dimeric* titanium(III) species, addition of $Ti_2Cl_6O \cdot 4C_5H_5N$ would be expected to suppress the initial rate.

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Table III. Calculated Epr Dimer Spectra Lines

$g_{\parallel}$	$g_{\perp}$	*r*, Å	Half-field[a] max, G	High-field[a] max, G	
1.90	1.88	3.0	1670	2975	4025
1.91	1.86			3025	4060
1.92	1.85			3035	4075
1.95	1.91	3.0	1625	2925	3975
1.94	1.92		1622	2900	3950

[a] ν 9320 MHz.

Such behavior is observed. The rapid initial uptake of oxygen by a solution of 7.64×10^{-2} *M* $TiCl_3$ containing 1.46×10^{-3} *M* $Ti_2Cl_6O{\cdot}4C_5H_5N$ is completely suppressed as shown in Figure 3. Lithium chloride increases slightly the rate of initial oxygen uptake and prolongs the rapid uptake until approximately 42% of the stoichiometric oxygen is consumed as compared to *ca.* 30% in its absence (curve C, Figure 3). We conclude that the initial rapid uptake of oxygen is due to the reaction of molecular oxygen with *dimeric* titanium(III) species. The titanium(IV) product suppresses the dimer concentration, whereupon the remainder of the reaction involves a relatively slow interaction of oxygen with a titanium trichloride monomer.

Experimental Section

Stoichiometry and Product Characterization. In a typical experiment, about 40 ml of pyridine, which had been dried over sodium metal and degassed, was condensed into a flask containing 2.73 g (17.7 mmol) of titanium trichloride (K & K) chilled to liquid nitrogen temperature. Upon warming to room temperature, the solid dissolved to give a brown solution. Introduction of 1 atm of oxygen caused the solution to turn green rapidly. After 48 hr with constant stirring, the solution became amber. Removal of pyridine under vacuum gave 5.6 g (98% yield) of a pale yellow to tan solid with a stoichiometry of $Ti_2Cl_6O{\cdot}4C_5H_5N$. Recrystallization of the solid from anhydrous acetonitrile gave pale yellow prismatic crystals, mp 83–100° dec. The infrared spectrum of the recrystallized product was identical with that of the original solid. *Anal.* Calcd for $Ti_2Cl_6O{\cdot}4(C_5H_5N)$: C, 37.48; H, 3.14; N, 8.74; Cl, 33.19; Ti, 14.95. Found for unrecrystallized sample: C, 38.89; H, 4.13; N, 8.66; Cl, 31.10; Ti, 14.55.

For a second sample recrystallized from acetonitrile a similar analysis was obtained. *Anal.* Found: C, 38.49; H, 4.00; N, 8.38; Cl, 30.92, 30.83*, 30.90*; Ti, 14.13; 14.31*. Asterisks signify values measured in our laboratory.

A detailed examination of the elemental analysis became necessary to account for carbon and hydrogen analyses which were consistently higher and nitrogen, chlorine, and titanium analyses which were lower than the theoretical values. It was noted that these results were reproducible and could not be improved upon by analysis of the product recrystallized from acetonitrile. The Cl:Ti mole ratio for three analyses on two samples was 2.84, 2.91, 2.92 (3.00 theory); N:Ti, 2.03, 2.03, 2.00 (2.00 theory); and Cl:N, 1.46, 1.42, 1.45 (1.50 theory). At the same time the C:N ratio was 5.36 and 5.24. This suggested to us that picolines, which were initially present in our pyridine to the extent of approximately 0.5% and which gas chromatography showed were still present after purification, were concentrated and preferentially complexed to the titanium in the final step of our synthesis during the removal of the solvent. The proton nmr spectrum of the compound in deuteriopyridine contained a small band at −2.09 ppm (reference TMS) which could be assigned to the methyl group of γ-picoline (−2.07 ppm). The γ-picoline represented 6% of the N-containing ligand in the complex. Despite the somewhat unfavorable elemental analyses, the stoichiometry of the reaction product can only be that of a $Cl_3TiOTiCl_3$ molecular unit bound to four pyridine or picoline ligands. No other composition conforms to the observed Cl:Ti, Cl:N, and N:Ti ratios.

The oxygen consumed in the reaction was metered and found to be 4.32 mmol, equivalent to an experimental $TiCl_3$:O_2 mole ratio of 4.1:1.0. In subsequent experiments this ratio was found to be 4.1:1.0 and 4.0:1.0.

Kinetic Measurements. Kinetic studies were carried out in a single-neck, round-bottomed flask, attached to a high-vacuum line and immersed in a constant-temperature bath held at 25.0 ± 0.02°. The measurements at 14.7 and 5.3° required a Lauda Type KB-20 circulator for temperature control. The free volume of the system was computed for each rate measurement. After the titanium trichloride had completely dissolved to give a brown solution and the solution was given an opportunity to achieve thermal equilibrium, oxygen was admitted to the reaction vessel with rapid stirring. Pressure readings were taken within 15 sec after the reagents were mixed and at intervals of 2–10 min thereafter for periods of about 60 min. There is sharp curvature in plots of oxygen pressure *vs.* time in the first 1–5 min and the solution turns from brown to green. The plot is then linear over the next 20–40 min. It is over this linear region that the initial rates were measured.

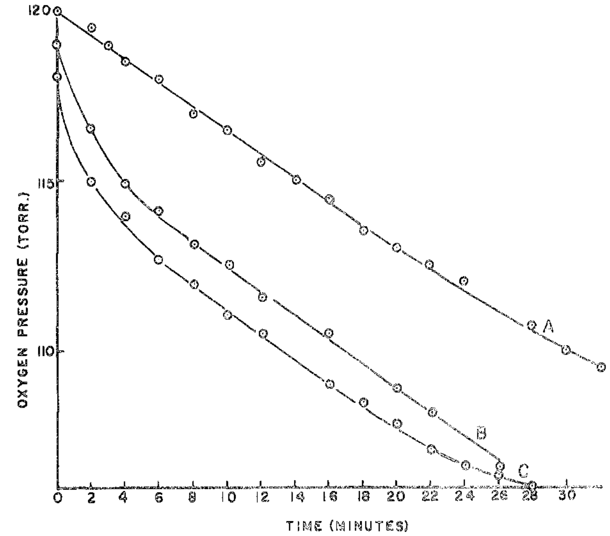

Figure 3. Effect of $Ti_2Cl_6O{\cdot}4C_5H_5N$ and LiCl on initial uptake of oxygen by pyridine solutions of titanium trichloride: A, $[TiCl_3] = 7.64 \times 10^{-2}$ *M*, $[Ti_2Cl_6O{\cdot}4C_5H_5N] = 1.46 \times 10^{-3}$ *M*; B, $[TiCl_3] = 7.64 \times 10^{-2}$ *M*; C, $[TiCl_3] = 7.64 \times 10^{-2}$ *M*, $[LiCl] = 0.173$ *M*.

The purity of titanium trichloride was determined by the standard potentiometric dichromate titration[31] and found to be 95.5% Ti(III). All titanium trichloride concentrations were corrected accordingly.

Epr Studies. Aluminum trichloride (MCB) was twice sublimed under vacuum and stored under nitrogen. Titanium(IV) chloride was distilled once and degassed on the vacuum line. Lithium chloride (Fisher reagent grade) was dried in an oven at 130° for 24 hr and then stored under nitrogen. Pyridinium chloride was produced on a vacuum line by adding an excess amount of dry HCl to pyridine. The white solid was stored under nitrogen.

All epr spectra were recorded on a Varian V-4502-15 spectrometer, equipped with a 100-kc field modulation unit. The field was calibrated using a dual cavity with DPPH in one cavity and a Hewlett-Packard Model X532B frequency meter. The Varian E-4557-9 variable-temperature controller, set at −100°, was used for frozen solution spectra.

All solutions were approximately 0.02–0.05 *M* in Ti(III) and epr spectra were obtained in 3-mm quartz sample tubes. All transfers of solution were made in a closed apparatus.

Computations of δ function lines for the titanium dimer were carried out on an IBM 360/50 computer at Washington University, St. Louis, Mo., and at Southern Illinois University. Titanium hyperfine coupling was ignored. Using a FORTRAN program, the 3 × 3 matrix given by Smith[23] produced δ function spectra in terms of the variables *r* (internuclear distance), $g_{\parallel}$, $g_{\perp}$, the exchange coupling constant *J*, and the frequency ν. δ function lines, instead of actual absorbances, were computed because our interest was only in line centers and estimated line widths. No effort was made to reproduce the observed spectra.

Physical Measurements. Infrared spectra were taken on a Beckman IR10 spectrophotometer and calibrated with polystyrene film. Band assignments are considered accurate to ±5 cm^{-1}. Solids were examined as mineral oil (Nujol) mulls between cesium bromide plates. Mulls were prepared in a drybag under nitrogen.

Electronic spectra were recorded on a Beckman DK-1A spectrophotometer. A special all-glass vessel was used for obtaining spectra of the air-sensitive samples prepared on the vacuum line. This apparatus was a 50-ml, round-bottomed reaction flask fitted with a side arm containing a 1.0-cm path length Pyrex cell for visible spectra, a sec-

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(31) A. I. Vogel, "Quantitative Inorganic Analysis," 3rd ed, Longmans, Green and Co., London, 1969, pp 329–331.

ond side arm equipped with a quartz epr tube, and a third side arm with a glass break-seal to allow the introduction of oxygen. The Pyrex visible cells were fabricated from square tubing supplied by Ace Glass Co. and had a cutoff near 30 × 10^3 cm^{-1}.

A freezing point depression method with a modified apparatus described by Choi, Firth, and Brown[32] was used for molecular weight measurements. A Leeds and Northrup Model 8163 platinum-resistence thermometer and Leeds and Northrup Model 8069 ER thermometer bridge and Model 9838 nanovolt detector were used for temperature measurements. The molal freezing point constant 4.75[33] was used.

Commerical elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn., and by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach uber Engelskirchen, West Germany. Laboratory chloride analyses were by the Volhard method and titanium was determined gravimetrically as TiO_2.[34]

Acknowledgment. Support of National Science Foundation Grant GP-11526 is gratefully acknowledged.

Registry No. C_5H_5N, 110-86-1; $TiCl_3$, 7705-07-9; O_2, 7782-44-7; $Ti_2Cl_6O \cdot 4C_5H_5N$, 51364-53-5.

[32] S. U. Choi, W. C. Frith, and H. C. Brown, *J. Amer. Chem. Soc.*, 88, 4128 (1966).

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Notes

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Quadrupole-Induced ^{1}H-^{10,11}B Spin Decoupling in Carboranes. Correlation of Decoupling Efficiency with Molecular Volume

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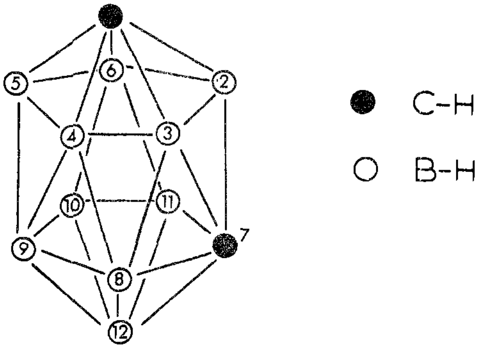
In applying dynamic nuclear magnetic resonance (dnmr) spectroscopy to elucidation of the structure and molecular dynamics of boron hydrides, two fundamentally different types of rate process may effect changes in the spectrum.[2] One process involves intramolecular or intermolecular chemical exchange and the other interconversion between ^{10}B $(I = 3)$ and ^{11}B $(I = {}^3/_2)$ spin states induced principally by boron quadrupolar relaxation.[3] Previous investigations of the ambient temperature ^{11}B nmr spectra of carboranes and carborane derivatives indicate clearly that the hydrogens are not scrambling.[2] This report concerns a variable-temperature ^{1}H nmr study of carboranes and halocarboranes in which ^{1}H-^{10,11}B spin decoupling is observed at low temperatures. Although the decoupling efficiency correlates well with molecular volume, *i.e.*, the greater the molecular volume the higher the temperature at which decoupling occurs,[3] increasing molecular dipole moment also accompanied increasing molecular volume for the compounds studied and may provide additional mechanisms for ^{10,11}B nuclear spin relaxation.

Examination of the ^{1}H dnmr spectrum (60 MHz) of *m*-carborane [**1**; 1,7-dicarba-*closo*-dodecaborane(12)] in 50% CD_3OD-50% CD_3COCD_3 (v/v) at −21° (Figure 1) revealed a spectrum similar to that observed at room temperature with a sharp C-H resonance superimposed on the diffuse B-H peaks. Upon lowering the temperature, the B-H spectrum coalesced and then sharpened into a broad singlet resonance of approximate lorentzian line shape (Figure 1). This spectral behavior is very analogous to that reported for *o*-carborane [**2**; 1,2-dicarba-*closo*-dodecaborane(12)][4] and is best rationalized in terms of increasing viscosity and lower temperatures rendering boron quadrupole-induced ^{1}H-^{10,11}B spin decoupling more efficient.[2] It is evident at −134° (Figure 1) that all of the ^{1}H chemical shifts in **1** are very similar and much smaller than the ^{1}H-^{11}B spin-spin coupling constants [$J(^1\text{H}, ^{11}\text{B}) = 148\text{-}177$ Hz].[5] Indeed, successive irradiation at the nmr resonant frequencies of the various boron atoms in **2** at room temperature produced respective decoupled ^{1}H resonances all having very similar chemical shifts. In addition to the B-H resonances in **1**, the C-H peak also sharpens markedly at lower temperatures (Figure 1) indicating the loss of small coupling of ^{11}B to the C-1 and C-7 protons at low temperatures.



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Examination of the ^{1}H dnmr spectra (60 MHz) of 9,12-dibromo-1,2-dicarba-*closo*-dodecaborane(12) or **3** in 50% CD_3OD-50% CD_3COCD_3(v/v) at −20° (Figure 2) revealed a typical spectrum. Lowering the temperature resulted in the expected spectral sharpening due to quadrupole-induced ^{1}H-^{10,11}B spin decoupling (Figure 2). Very similar behavior was observed for 9,10-dibromo-1,7-dicarba-*closo*-dodecaborane(12) and 8,9,10,12-tetrabromo-1,2-dicarba-*closo*-dodecaborane(12) in 50% CD_3OD-50% CD_3COCD_3 as illustrated respectively in Figures 3 and 4.

Although the solvent impurity peaks (*e.g.*, CHD_2COCD_3) have been subtracted from Figures 1-4, it was observed that the CHD_2 ^{1}H dnmr pentet of either solvent impurity coalesced at about the same temperature (∼−110°) in all four

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[1] Alfred P. Sloan Research Fellow, 1971-1974; Camille and Henry Dreyfus Teacher-Scholar, 1972-present.

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