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Magnetic Resonance Study of Titanium(III) Chloride in Acetonitrile[1]

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Recently, Hinckley[2] reported the chemical shift of the solvent acetonitrile protons as a function of temperature for a 0.01 M solution of $TiCl_3$ in acetonitrile between about -5 and $+80°$. He pointed out that his observations would be consistent with slow exchange between complexed acetonitrile and bulk solvent. Since other workers[3-5] have demonstrated that in solutions of $TiCl_3$ in CH_3CN at room temperature, the Ti(III) is essentially all in the form of the neutral species $TiCl_3(CH_3CN)_3$, we felt it might be possible to study the rate of solvent exchange by measuring proton nmr line widths as a function of temperature. However, we found that in the temperature interval between -44 and $+80°$ the variation of line width with temperature strongly suggested more than one exchanging Ti(III)–CH_3CN species. In an effort to confirm this conclusion, we measured the nmr shift of the CH_3CN proton as a function of temperature and examined the epr spectrum of $TiCl_3$–CH_3CN solutions at several temperatures.

Experimental Section

Acetonitrile was purified by refluxing with P_2O_5 followed by distillation. The $TiCl_3$ solution was prepared on a vacuum line by distilling CH_3CN onto solid $TiCl_3$ (Stauffer Chemical Co.) and, after stirring for several hours to dissolve some of the $TiCl_3$, filtering the solution directly into an evacuated 5-mm o.d. nmr sample tube. With the solution cooled, the nmr sample tube was sealed off under vacuum. After the nmr measurements were made, the sample tube was broken under a solution of ferric ion and the concentration of Ti(III) in the original sample was determined by titrating the resulting ferrous ion with Ce(IV) using ferroin as indicator. Total titanium was determined on the same sample using the H_2O_2 colorimetric method. The results showed that the nmr sample was 98.3% Ti(III) and 1.7% Ti(IV). Nmr spectra of prepared solutions of $TiCl_4$ in CH_3CN showed that Ti(IV) has a negligible effect on the acetonitrile proton resonance; hence the presence of a small amount of Ti(IV) in the Ti(III) solution was ignored.

Nmr measurements were made on a Varian DA-60A spectometer equipped with a variable-temperature probe. TMS was used as an internal standard for shift measurements. The epr measurements were carried out on a homemade superheterodyne spectrometer which has been described previously.[6] All g value measurements were carried out relative to DPPH. The microwave frequency was measured with a Hewlitt-Packard Model 540A transfer oscillator and the magnetic field was calibrated with an LFE Model 101 nmr gaussmeter.

Results and Discussion

Figure 1 displays the dependence upon temperature of the line width of the solvent acetonitrile proton resonance in our 0.11 M solution of $TiCl_3$ in CH_3CN over the temperature range of -44 to $+82°$. The plot, in the form of log (T_{2p}^{-1}) (where T_{2p}^{-1} is the line width at half-height multiplied by π) *vs.* $10^3/T$ is clearly characteristic of a system in which two important CH_3CN-exchange processes are present, one determining the line width at low temperatures and the second becoming increasingly important at higher temperatures. As the low-temperature exchange process reaches the fast-exchange region, at about $(10^3/T) < 3.6$, the second exchange process begins to dominate the line width. At the highest temperature studied, 82°, this second process is just getting into the fast-exchange region.

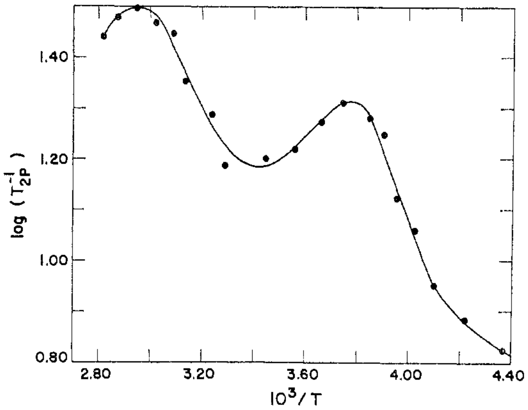

Figure 1.—Temperature dependence of solvent acetonitrile proton resonance line width in a 0.11 M solution of $TiCl_3$ in CH_3CN.

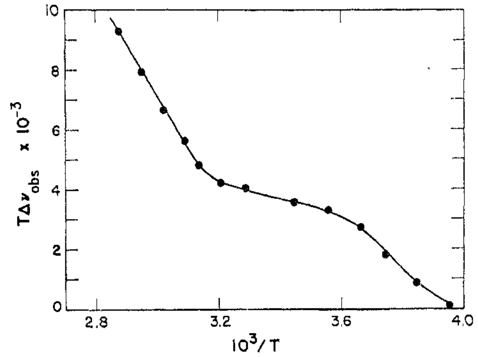

Figure 2.—Temperature dependence of solvent acetonitrile proton resonance chemical shift in a 0.11 M solution of $TiCl_3$ in CH_3CN.

Figure 2 shows the variation with temperature of the shift, due to chemical exchange, of the solvent acetonitrile proton resonance over roughly the same temperature interval in the same solution. The temperature dependence of the shift agrees completely with that of the line width. In the fast-exchange region, $T\Delta\nu_{obsd}$ should attain a constant value. In the range $3.2 < (10^3/T) < 3.6$, this appears to be happening. However, at about $10^3/T = 3.2$ a new species begins to dominate the shift. The behavior

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(1) Work supported by the U. S. Atomic Energy Commission.

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(3) R. J. H. Clark, J. Lewis, D. J. Machin, and R. S. Nyholm, *J. Chem. Soc.*, 379 (1963).

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(5) G. D. McDonald, M. Thompson, and E. A. Larsen, *Inorg. Chem.*, **7**, 648 (1968).

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here is exactly what one expects for exchange of CH_3CN between bulk solvent and two paramagnetic species with significantly different exchange rates and/or coupling constants for first-sphere acetonitrile. Thus the nmr line-width and shift data are both consistent with CH_3CN exchange between bulk solvent and two different Ti(III)–CH_3CN species. Hinckley[2] reported no line-width measurements and his shifts, measured at roughly one-tenth our Ti(III) concentration, are too small to show any significant departure from a linear dependence of shift on $1/T$. (His largest shift was less than 2.5 Hz while our maximum shift was 26.7 Hz.)

As mentioned earlier, the dominant species in $TiCl_3$–CH_3CN solutions at room temperature appears to be the electrically neutral species $TiCl_3(CH_3CN)_3$. Conductivity measurements as a function of $TiCl_3$ concentration indicate that a small amount of ionization takes place according to the equation

$$TiCl_3(CH_3CN)_3 + CH_3CN \rightleftharpoons TiCl_2(CH_3CN)_4{}^+ + Cl^-$$

with an estimated equilibrium constant of 1.39×10^{-4} at room temperature.[6] It thus appears that the two Ti(III)–CH_3CN species required for interpretation of the nmr results could conceivably be either (1) the *cis* and *trans* forms of the neutral $TiCl_3(CH_3CN)_3$ or (2) the ionic species $TiCl_2(CH_3CN)_4{}^+$ and the neutral species $TiCl_3(CH_3CN)_3$. In the first instance, *cis* and *trans* forms with different exchange rates and/or coupling constants for CH_3CN could account for the nmr observations, either with both forms present over the entire temperature range or with a conversion from one form to the other with change in temperature. With regard to the ionic species $TiCl_2(CH_3CN)_4{}^+$, it seems unlikely that it could play a significant role at room temperature but since the temperature dependence of the ionization is not known, the possibility that it may become an important species at higher temperatures cannot be entirely ruled out.

In an effort to learn more about the solution species as a function of temperature, we undertook an epr study of $TiCl_3$–CH_3CN solutions. Unfortunately, no epr spectrum was obtained from solution species between the solution freezing point (about −40°) and +80°. This indicates that both Ti(III) species detected by the nmr measurements have short electronic spin–lattice relaxation times.[7] We were able to observe the epr spectrum of the solid compound $TiCl_3(CH_3CN)_3$ prepared by evaporating solutions of $TiCl_3$ in CH_3CN. At room temperature the spectrum of this compound consists of a single line about 250 G wide. However at −140°, the spectrum of solid $TiCl_3(CH_3CN)_3$ is characteristic of that obtained from axially symmetric complexes. The value of $g_{\parallel}$ is 1.881 and that of $g_{\perp}$ is 1.919. Thus the epr data indicate that this compound is in the axially symmetric *cis* configuration at least at low temperature. These general conclusions are in agreement with those of Giggenbach and Brubaker[8] but our g values are significantly different from the values which they report. In an acetonitrile glass at −150° prepared by cooling a $TiCl_3$–CH_3CN solution until it solidified, we observed an epr spectrum which strongly indicates that the axial symmetry observed in solid $TiCl_3(CH_3CN)_3$ is beginning to break down, probably due to interaction of the solvent with the $TiCl_3(CH_3CN)_3$ complex.

Though the epr results are of interest in themselves, they do not serve to discriminate between possible solution species. Unless the compositions and relative amounts of all solution species are known at each temperature, one cannot derive reliable rate parameters from the nmr data.

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Octahedral Metal Carbonyls. XV.[1] Estimates of Ligand–Chromium Bond Strengths from Kinetic Data

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The nature of metal–ligand bonding in octahedral metal carbonyls is incompletely understood. In particular, recent studies have demonstrated a poor correlation between carbonyl stretching frequencies and reactivities of derivatives.[3] Several investigations have attempted more fully to define the nature of metal–ligand bonding. Graziani, Zingales, and Belluco studied the kinetics of replacement of various Lewis bases (L) from $(L)_2M(CO)_4$ complexes (M = Mo, W) by 2,2′-bipyridyl.[4] Since kinetic data indicated the reactions to proceed *via* a dissociative mechanism, relative rates were taken as a rough measure of M–L bond strengths. It was stressed, however, that since the postulated intermediates in these systems are $LM(CO)_4$ species, the effect of the various L on the energy of the activated complexes must be reflected in the M–L bond strength data obtained. Angelici and Ingemanson have studied equilibria between (amine)-$W(CO)_5$ and other $LW(CO)_5$ complexes and have obtained comparisons of the relative ground-state energies of the species.[5] However, the derived values of $\Delta H°$ and $\Delta S°$ appear to be anomalously high.

Angelici and Graham have also reported studies of the reaction of $(phen)Cr(CO)_4$ (phen = *o*-phenanthroline) with L ($=P(OCH_2)_3CCH_3$) to give (phen)Cr-

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[1] The two previous papers in this series: XIII, G. C. Faber and G. R. Dobson, *Inorg. Chim. Acta*, in press; XIV, E. P. Ross and G. R. Dobson, *J. Chem. Soc., D*, 1229 (1969).

[2] To whom correspondence concerning this paper should be addressed at the Department of Chemistry, North Texas State University, Denton, Texas 76203.

[3] See, *e.g.*, R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).

[4] M. Graziani, F. Zingales, and U. Belluco, *Inorg. Chem.*, **6**, 1582 (1967).

[5] R. J. Angelici and C. M. Ingemanson, *ibid.*, **8**, 83 (1969).