by about a factor of two in the presence of 4 *M* tetramethylethylene (Figure 2), *i.e.*, $\Phi_f = 0.03$. The multiplicity of the excited state responsible for trans → cis isomerization in the direct irradiation is still a topic of active debate.[5] It is known, however, that the decay ratio in the direct irradiation and the triplet-sensitized isomerization are the same.[13] Values for the triplet decay ratio are available.[13,14] The probability (α) of decay of the excited state to *cis*-stilbene is 0.55.[14] The quantum yield (Φ_x) for formation of the excited state which produces *cis*-stilbene is given by Φ_c/α. The sum ($\Phi_{total} = 0.92$) of the quantum yields for fluorescence ($\Phi_f = 0.03$), photocycloaddition ($\Phi_a = 0.54$), and formation of the excited state leading to *cis*-stilbene ($\Phi_x = 0.35$) shows that these three processes account for virtually all of the quanta absorbed by *trans*-stilbene.

The conclusions concerning the photocycloaddition of *trans*-stilbene to tetramethylethylene which can be reached at this time are (1) the initial step in the cycloaddition involves addition of S_1 *trans*-stilbene to tetramethylethylene to give an exciplex, (2) the rate constant for exciplex formation is greater than or equal to 1.4×10^8 l. mol^{-1} sec^{-1}, (3) the chemistry of the exciplex is limited to dissociation to singlet (S_1) excited *trans*-stilbene and tetramethylethylene and demotion to adduct, and (4) decay of exciplex to ground-state *trans*-stilbene and tetramethylethylene is negligible in comparison to demotion to adduct.

A warning is in order concerning rate constants based on mechanisms which ignore exciplex dissociation. This process is almost universally ignored in mechanisms for photocycloaddition because it complicates the kinetic analysis. The present work shows that rate constants based on this assumption can be seriously in error.

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Proton Hyperfine Structure from Water Ligands in the Electron Spin Resonance Spectra of Aqueous Titanium(III) Complexes with Alcohols[1]

Sir:

Although Ti(III) contains one unpaired electron, no esr spectrum is observed for this ion when the crystal-field environment has octahedral symmetry. This is due to the fact that the residual orbital angular momentum in the $^2T_{2g}$ ground state virtually cancels the spin angular momentum; thus it is predicted that $g \approx 0$.[2] A small axial or rhombic distortion will partially quench the orbital angular momentum; however, a very short spin–lattice relaxation time is expected. Thus, it is not surprising that no esr spectrum is observed for aqueous solutions of Ti^{3+}, where the ion is believed to exist as the $Ti(H_2O)_6{}^{3+}$ species.

If the crystal-field symmetry is reduced to tetragonal or lower, the orbital angular momentum is almost completely quenched, and a narrow-line esr spectrum with $g \sim 2$ is expected. This was first demonstrated by Waters and Maki for the $Ti(CH_3O)^{2+}$ and $TiF_2{}^+$ complexes in methanol solutions.[3] Other workers have found similar results for aqueous and alcoholic systems.[4–6]

In a similar manner, we have observed the appearance of a narrow esr line as various alcohols are added to aqueous solutions of $TiCl_3$. A study is being carried out on the equilibria involved in this system. These results will be reported in a later paper. The novel observation of interest here is the appearance of hyperfine structure on the main esr line of Ti^{3+} (see Figure 1a). We believe that this arises from water molecules in the primary coordination sphere of the Ti^{3+} ion and represents the first observation of proton hyperfine structure from water ligands of a transition metal complex.

Standard aqueous solutions of $TiCl_3$ were prepared by dissolving Ti sponge (Alfa Inorganics) in $\sim$1 *N* HCl. Solutions were prepared in a glove bag under nitrogen to minimize the oxidation of Ti(III) to Ti(IV). Esr spectra were run on a Varian E3 esr spectrometer in an aqueous solution quartz sample cell.

In the series methyl, ethyl, isopropyl, and *tert*-butyl alcohols, *tert*-butyl alcohol gave the strongest (*i.e.*, most intense) esr spectrum for the same alcohol concentration with the others getting steadily weaker in the series from *tert*-butyl alcohol to methyl alcohol. Furthermore, the line width is observed to *decrease* from methyl alcohol to *tert*-butyl alcohol. In every case but the latter a single structureless line is observed. (Some satellite lines are observed due to ^{47}Ti and ^{49}Ti hyperfine splitting; see below). The esr spectrum shown in Figure 1a is that of 10^{-2} *M* $TiCl_3$ in a 20% (v/v) *tert*-butyl alcohol–water solution at pH 2.0.

The proof that the hyperfine structure is due to water protons was obtained when D_2O was substituted for H_2O. The magnetogyric ratio of D is only about $^1/_7$th that of H: hence, a narrowing of the line and loss of hyperfine structure are expected when D substitutes for H. This is exactly what was observed.

It is of interest to know how many water molecules are in the complex. To ascertain this we simulated spectra of variable hyperfine splitting, line width, and number of protons until a good fit was obtained. Parts b, c, and d of Figure 1 are the simulated spectra for six, eight, and ten protons, respectively, with a hyperfine splitting of 1.80 G and line width of 1.96 G.

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Clearly the best fit is obtained for eight protons or four water molecules. Further confirmation is provided by the fact that a simulated spectrum for eight deuterons, where only the magnetogyric ratio was changed, matched the experimental spectrum in D_2O almost exactly.

Since proton hyperfine structure is observed, it is evident that some delocalization of the d electron onto the water ligands occurs. In other words the interaction of Ti^{3+} with H_2O molecules is *not purely ionic.* The question is whether the magnitude of the proton hyperfine coupling can give some insight as to the extent of covalency in this complex.

The d electron is undoubtedly stabilized in the d_{xy} orbital, and thus only π bonding with the water molecules in the equatorial plane is possible. The highest bonding molecular orbital in H_2O is a pure $2p_z$ oxygen orbital perpendicular to the plane of the H_2O molecule.[7] It can participate in π bonding with Ti(III) if the plane of the H_2O molecule is oriented perpendicular to the equatorial plane of the complex. This type of π bonding would allow some spin density in the $2p_z$ oxygen orbital on H_2O, but to zero order there would be no spin density in the hydrogen 1s orbitals, and thus no proton hyperfine splitting should be seen. However, it is well known that higher-order calculations will allow some hydrogen spin density through the mechanism of spin polarization.[8] These calculations show that for a fragment of the type XH where X has a π spin density ρ_X^{π} one may write

$$a^H = Q_{XH}{}^H \rho_X{}^{\pi}$$

A number of radicals of the type ROH, where R is generally a conjugated system, have been studied. From these studies[9] it is concluded that $Q_{OH}{}^H \sim 33$ G. Although the bonding situation is not exactly analogous, $Q_{OH}{}^H$ should not be too different in H_2O. If we take the above value of $Q_{OH}{}^H$ with the observed $a^H = 1.80$ G, we obtain a *total* spin density of ~0.22 on all four water molecules.

There is additional evidence that a significant degree of covalency with water ligands is present. The $^{47,49}Ti$ hyperfine coupling in our complex is 14.2×10^{-4} cm^{-1}, whereas the hyperfine coupling for Ti^{3+} in a tetragonal site in MgO is 15.7×10^{-4} cm^{-1}.[10] The bonding in the latter case would be expected to be closer to purely ionic. It has been found that the magnitude of the central-ion hyperfine coupling is closely related to the spin density on the central ion.[11] Thus from the two lines of argument presented above, one may conclude that between 10 and 20% of the spin density is delocalized onto the water ligands in our complex. The actual figure is probably closer to the upper limit, as even in MgO some covalency is probably present.[10]

We are not yet ready to say what the exact nature of the complex is except that it contains four water molecules and at least one *tert*-butyl alcohol molecule. Since all protons are observed to be equivalent, we propose that the *tert*-butyl alcohol molecule attaches in an axial position with the four water molecules in equatorial positions. The nature of the other axial ligand is not known.

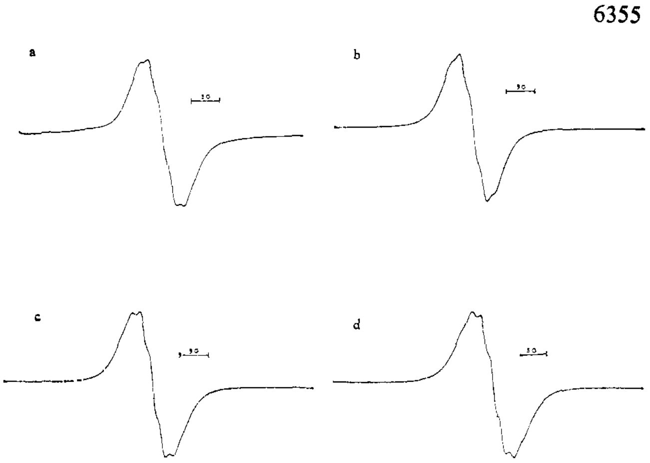

Figure 1. (a) First-derivative esr spectrum of 10^{-2} *M* $TiCl_3$ in a 20% (v/v) *tert*-butyl alcohol-water solution at pH 2.0. (b) Computer simulation based on *six* equivalent protons with a hyperfine splitting of 1.80 G and a Lorentzian line shape with a peak-to-peak width of 1.96 G. (c) Same as part b, except for *eight* equivalent protons. (d) Same as part b, except for *ten* equivalent protons. The ranges marked on the figure are 5 G.

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Energy-Volume Coefficients of Alcohol-Water Mixtures

Sir:

The energy-volume coefficient (or "internal pressure"), $(\partial U/\partial V)_T$, is one of the most fundamental thermodynamic properties of a liquid system and relates the susceptibility of the internal energy to isothermal volume change. Since both the internal energy and volume are sensitive to intermolecular interaction, it can be argued that this parameter will reflect changes in the "structure" and state of intercomponent interaction present in liquid mixtures. If this simple hypothesis is valid, the energy-volume coefficient should prove to be a valuable probe in the investigation of binary liquid systems. A few previous investigations of nonaqueous mixtures[1,2] support this claim. However, no studies of this type have been reported for aqueous-organic mixtures despite the fact that these systems often exhibit unusual properties[3] and have been used extensively in physicochemical investigations. We have investigated three aqueous alcohol systems which exhibit positive deviations from Raoult's law.[3] This behavior is determined by large negative excess entropies, suggesting considerable "structural" changes on mixing. Further, by comparing different

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