bridges. The Cu(1)–O(5) and Cu(1)–O(5)′ bond distances within this arrangement are 1.95 (1) and 2.31 (1) Å, respectively. The resulting metal–metal separation is 3.271 (6) Å. (c) The Cu(2)–Cu(2)′ linkage is similar to that between Cu(1) and Cu(1)′, but with a considerably longer copper–apical oxygen bond (Cu(2)–O(7)′ = 2.46 (1) Å) and a copper–copper distance of 3.341 (6) Å. Interactions b and c join square-pyramidal copper polyhedra along common apical edges. In view of the long Cu(2)–O(7)′ distance, the linear polymer might also be regarded as comprised of tetrameric units.

Because of the long metal–metal distances and of the low symmetry of the individual metal pairs in this complex, any magnetic interaction would most probably arise through a superexchange mechanism. Spin coupling could, in principle, occur within any of the three types of copper–copper pairs, within an infinite one-dimensional lattice or in some combination of interactions. Further investigations of these points and of the relationship of the compound to the aniline adducts prepared by Kokot and Martin[9] are in progress.

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The Mechanism of Photochemical Addition of *trans*-Stilbene to Tetramethylethylene[1]

Sir:

Photoaddition of *trans*-stilbene to tetramethylethylene gives *trans*-1,2-diphenyl-3,3,4,4-tetramethylcyclobutane in high yield.[2] The quantum yield for adduct formation (Φ_a) is 0.54 at 313 nm with 4 *M* tetramethylethylene (TME) in hexane. The quantum yield is constant to at least 20% conversion. Conversions were kept to 5% or less in the experiments reported. A plot of $1/\Phi_a$ *vs.* 1/[TME] is linear (Figure 1, intercept 1.0, slope 4.2) in accord with expectation for a process in which electronically excited *trans*-stilbene adds to ground-state tetramethylethylene. The quantum yield (4 *M* olefin) is temperature dependent and increases by a factor of almost three as the temperature is lowered from 65 ($\Phi = 0.24$) to 5° ($\Phi = 0.69$).[3] The addition is not sensitized by sensitizers (thioxanthone, Michler's ketone) which sensitize the trans to cis isomerization of *trans*-stilbene. This result suggests that the addition involves singlet-excited *trans*-stilbene. Direct evidence that the addition involves the low lying singlet excited state (S_1) of *trans*-stilbene is provided by tetramethylethylene quenching of *trans*-stilbene fluorescence. A plot of the ratio of the quantum efficiency of fluorescence in the absence of olefin to that in the presence of olefin, $\Phi_f/(\Phi_f)_{\text{olefin}}$, *vs.* tetramethylethylene concentration is linear (slope 0.20, intercept 1.0, Figure 2).

If one considers the simplest possible mechanism for photochemical cycloaddition of *trans*-stilbene (S_t) to tetramethylethylene (O), it is possible to derive an

$$S_t + h\nu \longrightarrow {}^1S_t$$

$${}^1S_t \xrightarrow{k_d} S_t$$

$${}^1S_t \xrightarrow{k_f} S_t + h\nu_f$$

$${}^1S_t \xrightarrow{k_{ic}} {}^3S_t$$

$${}^1S_t \xrightarrow{k_c} S_c \text{ (trans} \longrightarrow \text{cis isomerization)}^{5}$$

$${}^1S_t + O \xrightarrow{k_{add}} \text{adduct}$$

expression for $1/\Phi_a$ as a function of olefin concentration [$\tau = 1/(k_d + k_{ic} + k_c + k_f)$]. It should be possible

$$\frac{1}{\Phi_a} = \frac{1}{\tau k_{add}[O]} + 1$$

then to determine k_{add} from the slope of the $1/\Phi_a$ *vs.* 1/[O] plot since the lifetime (τ) of the low lying singlet excited state of stilbene is known. The rate constant (k_{add}) so determined is not a true rate constant for it shows a negative temperature dependence (Figure 3). It is clear that a more sophisticated mechanism is required. The negative temperature dependence of the observed rate constant (k_{add}) suggests the presence of a prior equilibrium.

The efficient, endothermic quenching of the S_1 state of *trans*-stilbene by tetramethylethylene suggests that an exciplex is formed.[8,9] If exciplex formation is reversible, the negative temperature dependence of the observed rate constant and the other known facts are consistent with the mechanism shown below. Expressions can be derived for $1/\Phi_a$ as a function of 1/[O]

$$S_t + h\nu \longrightarrow {}^1S_t$$

$${}^1S_t \xrightarrow{k_d} S_t$$

$${}^1S_t \xrightarrow{k_f} S_t + h\nu_f$$

$${}^1S_t \xrightarrow{k_{ic}} {}^3S_t$$

$${}^1S_t \xrightarrow{k_c} S_c$$

$${}^1S_t + O \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} \text{exciplex } [{}^1S_t \cdots O]$$

$$\text{exciplex} \xrightarrow{k_a} \text{adduct}$$

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[1] Photochemical Transformations. XXXIX.

[2] O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **90**, 2333 (1968).

[3] The increased efficiency of cycloadditions at low temperature has been reported by de Mayo, *et al.*[4]

[4] R. O. Loutfy, P. de Mayo, and M. R. Tchir, *J. Amer. Chem. Soc.*, **91**, 3984 (1969).

[5] Saltiel[6] has argued that isomerization of *trans*-stilbene involves isomerization of singlet-excited stilbene while Fischer[7] maintains that the isomerization involves triplet-excited stilbene. The singlet isomerization step is included in our mechanism to cover all possibilities. Our arguments would not change if $k_c = 0$.

[6] J. Saltiel, *J. Amer. Chem. Soc.*, **90**, 6394 (1968); J. Saltiel, E. D. Megarity, and K. G. Kneipp, *ibid.*, **88**, 2336 (1966).

[7] D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, **90**, 3907 (1968), and references therein cited.

[8] S. L. Murov, R. S. Cole, and G. S. Hammond, *ibid.*, **90**, 2957 (1968).

[9] Singlet exciplexes are widely accepted while triplet exciplexes are still a matter of debate.[10]

[10] Th. Förster, *Angew. Chem., Int. Ed. Engl.*, **8**, 333 (1969).

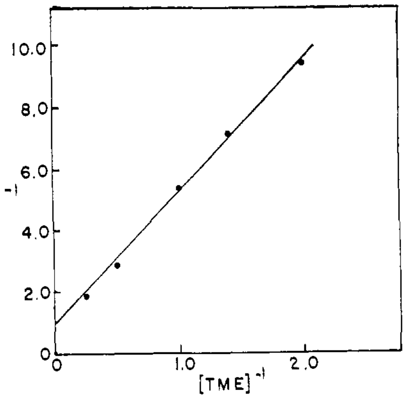


Figure 1. Plot of the reciprocal of the quantum yield for cycloaddition *vs.* the reciprocal of the tetramethylethylene concentration.

$$(\text{exciplex} \xrightarrow{k_{ed}} S_t + O) \text{ negligible}$$

$$\frac{1}{\Phi_a} = \frac{k_a + k_{ed}}{k_a} + \frac{k_{-e} + k_a + k_{ed}}{\tau k_a k_e[O]}$$

$$\frac{\Phi_f}{(\Phi_f)_{\text{olefin}}} = 1 + \frac{k_e(k_a + k_{ed})[O]\tau}{(k_{-e} + k_a + k_{ed})}$$

and $\Phi_f/(\Phi_f)_{\text{olefin}}$ *vs.* [O]. The intercept of the $1/\Phi_a$ *vs.* 1/[O] plot (Figure 1) is given by $(k_a + k_{ed})/k_a$. The observed intercept (1.0) can only mean that $k_a \gg k_{ed}$, *i.e.*, that deactivation of the exciplex to ground-state stilbene and olefin is negligible. The slope is given by

$$\frac{k_{-e} + k_a + k_{ed}}{\tau k_a k_e}$$

This expression can be simplified ($k_a \gg k_{ed}$), and a

$$\text{slope} = \frac{k_{-e} + k_a}{\tau k_a k_e} = 4.2$$

$$\frac{k_a k_e}{k_{-e} + k_a} = 1.4 \times 10^8 \text{ l. mol}^{-1} \text{ sec}^{-1}$$

value is obtained for the quantity $k_a k_e/(k_{-e} + k_a)$.[11] It is possible to interpret this expression in terms of the minimum and maximum values of the rate constant (k_e) for exciplex formation.

The expression $k_e[k_a/(k_a + k_{-e})]$ is really the product of the rate constant for exciplex formation (k_e) and the fraction of exciplex which goes to adduct $[k_a/(k_a + k_{-e})]$. The fraction can have values between zero and one. If the fraction were unity, the value of k_e would be 1.4×10^8 l. mol^{-1} sec^{-1}. This is the minimum value for k_e. The maximum value for k_e will be the diffusion-controlled rate constant which is estimated from the Debye equation to be 2.3×10^{10} l. mol^{-1} sec^{-1}. The slope of the $\Phi_f/(\Phi_f)_{\text{olefin}}$ *vs.* [O] plot (Figure 2) is given by $\tau k_e(k_a + k_{ed})/(k_{-e} + k_a + k_{ed})$ which can be simplified ($k_a \gg k_{ed}$) to $\tau k_e k_a/(k_{-e} + k_a)$. The slope is 0.2 and this gives an independent value for $k_e[k_a/(k_{-e} + k_a)]$ of 1.2×10^8 l. mol^{-1} sec^{-1} in excellent agreement with the value obtained from the $1/\Phi_a$ *vs.* 1/[O] plot.

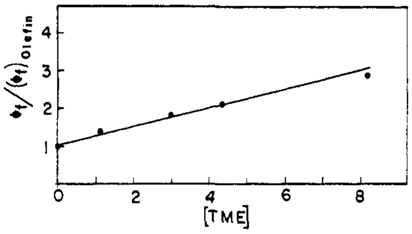


Figure 2. Plot of the ratio of quantum yield for fluorescence in the absence of olefin to that in the presence of olefin as a function of tetramethylethylene concentration.

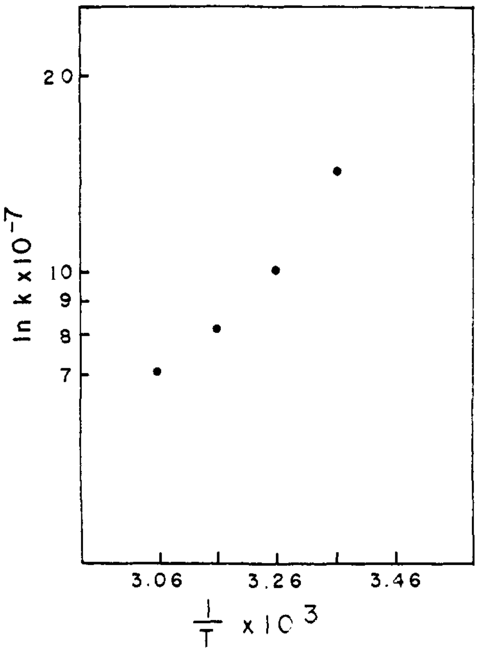
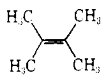
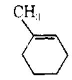


Figure 3. Plot of ln k_{add} as a function of reciprocal temperature.

Values of $k_e k_a/(k_{-e} + k_a)$ (minimum values for k_e) for 1-methylcyclohexene and cyclohexene have been measured (Table I). The decrease in the values of $k_e k_a/(k_{-e} + k_a)$ with decreasing alkyl substitution on the olefin shows that the reactivity of S_1 *trans*-stilbene toward olefins falls off rapidly with decreasing alkyl substitution on the olefin.

Table I. Minimum Rate Constants for Exciplex Formation

	$k_e[k_a/(k_a + k_{-e})]$, l. mol^{-1} sec^{-1}		
T, °C			
25	1.4×10^8	6.7×10^6	7.1×10^5
34	1.0×10^8		
44	8.4×10^7		
54	7.3×10^7		

Isomerization of *trans*-stilbene to *cis*-stilbene competes with photocycloaddition. The quantum yield for formation of *cis*-stilbene (Φ_c) is 0.19 at 313 nm in *n*-hexane with 4 *M* tetramethylethylene at 25°. The quantum yield (Φ_a) for photocycloaddition under these conditions is 0.54. The quantum yield for fluorescence (Φ_f) of *trans*-stilbene in hydrocarbon solvents at 25° is 0.06.[7] The quantum yield of fluorescence is reduced

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(11) The value used for τ is 1.7×10^{-9} sec.[12]

(12) V. R. Priimachek and A. N. Faidysh, *Izv. Vyssh. Ucheb. Zaved., Fiz.*, 10 (5), 32 (1967); *Chem. Abstr.*, 68, 73790w (1968).

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.

Acknowledgment. This research was supported in part by a grant (AM 14624) from the National Institute of Arthritis and Metabolic Disease, U. S. Public Health Service.

[13] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).

[14] S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).

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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 ∼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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[1] This research was supported in part by Grant No. GP-8416 from the National Science Foundation, and by the Undergraduate Research Participation Program of the National Science Foundation, Grant No. NSF-GY-6004.

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[5] S. Fujiwara and M. Codell, *Bull. Chem. Soc. Jap.*, 37, 49 (1964).

[6] S. Fujiwara, K. Nagashima, and M. Codell, *ibid.*, 37, 773 (1964).