constant (K_{app}). Plots of log k_{obsd} vs. pH in the presence of Co^{2+} or Ni^{2+} and for the OH^- catalyzed reaction in the absence of metal ($k_{OH} = 1.63$ min^{-1} M^{-1}) are shown in Figure 2. The metal ion data were fit to eq 6 using $k = 0.98$ min^{-1}, $pK_3' = 8.4$ for Co^{2+}, and $k = 0.4$ min^{-1}, $pK_3' = 9.1$ for Ni^{2+}.

$$k_{obsd} = k\frac{K_3'}{K_3' + a_H} \quad (6)$$

The fact that pK_3' is less than pK_3 allows distinction to be made between attack of the substrate bound metal-hydroxide (Scheme I) and the apparently identical kinetic mechanism which involves attack of external OH^- on the carbonyl group activated by the bound metal.[6]

A stable tetrahedral intermediate along the reaction path (Scheme I) could account for the fact that pK_3' determined kinetically is significantly different from the thermodynamic constant pK_3. The nonrate determining formation of an additional intermediate after ionization of the $M(OH_2)$ moiety would result in the apparent ionization constant (pK_3') of the $M-OH_2$ moiety of the complex being less than pK_3.[7,8] On the basis of Scheme I, k_{obsd} is given by eq 7.

$$k_{obsd} = \frac{k_r K_{eq}}{(1 + K_{eq})}\left[\frac{K_3(1 + K_{eq})}{a_H + K_3(1 + K_{eq})}\right] \quad (7)$$

From eq 7 it can be seen that K_3' of the complexed $M(OH_2)$ moiety is provided by $K_3(1 + K_{eq})$ and that $k = k_r K_{eq}/(1 + K_{eq})$. The data in Figure 2 can be fitted to eq 7 using the thermodynamic pK_3 and $k_r = 1.05$ min^{-1}, $K_{eq} = 14.5$ for Co^{2+}, and $k_r = 0.6$ min^{-1}, $K_{eq} = 2.5$ for Ni^{2+}.

According to Scheme I the value of K_{app} determined kinetically is given by eq 8 which may be compared to eq 5 which provides the value of K_{app} determined from the titrimetric data.

$$\log K_{app} = \log K_m - pH + \log\left(1 + \frac{a_H}{K_1} + \frac{K_2}{a_H}\right) + \log\left(1 + \frac{K_x}{a_H}\right) - \log\left[1 + \frac{K_3(1 + K_{eq})}{a_H}\right] \quad (8)$$

The fit of the experimental data to eq 8 is shown in Figure 2; $K_{eq} = 13.5$ for Co^{2+} and 1.5 for Ni^{2+}. The agreement between K_{eq} determined from eq 7 and 8 is reasonable. Examination of Stuardt and Breigleb models of metal complexes of I reveal that once complexation with the imidazole nitrogen and phenolic hydroxyl occurs, it is not possible for the metal to coordinate with the ester carbonyl. This taken in conjunction with the observed pH-rate profile which shows that ionization of the $M-OH_2$ moiety is associated with catalysis eliminates metal ion activation of the carbonyl to intermolecular attack by OH^- as a contributing factor in this model system. Catalysis and complexation both exhibit a degree of specificity for the metal ion. No detectable complexation or catalysis was observed with Mg^{2+}, Ca^{2+}, or Mn^{2+}. Zn^{2+} forms a catalytically inactive dimeric complex $(I)_2Zn$, whereas, the 1:1 Cd^{2+} complex is catalytically inactive, perhaps due to steric requirements.

At pH values below pK_3, intramolecular M-OH hydrolysis of I exceeds that for OH^- mediated hydrolysis by 2×10^5 (Co^{2+} complex) and 1.2×10^4 (Ni^{2+} complex). The specific rate constants for intramolecular catalysis by the M-OH moiety ($K_{eq}k_r = 14.7$ and 1.2 min^{-1} for Co^{2+} and Ni^{2+}, respectively) are ca. 10^3 less than the reported values of k_{cat} for the hydrolysis of a good ester substrate by carboxypeptidase.[9] This rate ratio of 10^3 (ca. 4 kcal M^{-1}) is not large when taken with the fact that some distortion of the metal ion geometry is required in the model system[10] in order to effect the formation of the tetrahedral intermediate. Without this requirement the intramolecular catalysis by M-OH may be expected to approach that of carboxypeptidase.

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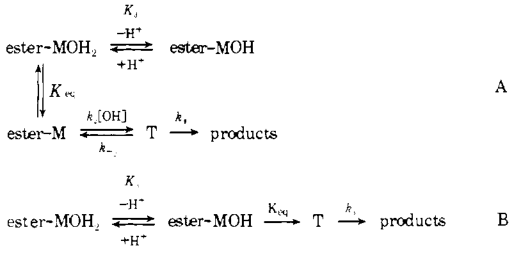
(6) Thus, mechanisms A and B (where T = tetrahedral intermediate) both provide the kinetic expression of eq 6. For A, where ester–M is the carbonyl



activated intermediate, two cases can be considered. (1) k_2 is rate determining, thus k of eq 6 = $k_2K_wK_{eq}/K_a$ and $K_3' = K_3/(1 + K_{eq})$. (2) k_3 is rate determining and steady state in T is assumed. $k = k_2k_3K_wK_{eq}/(k_3 + k_2)K_a$ and $K_3' = K_3/(1 + K_{eq})$. Assumption of steady state in ester–M shows that $K_3' = K_3$. For B assuming k_3 is rate determining eq 7 is derived. Assumption of steady state in T shows $K_3' = K_3$. Therefore, only mechanism B can account for the observation that pK_3' is less than pK_3. In addition only mechanism B can account for the observation that the kinetically determined metal substrate dissociation constant is less than the thermodynamically determined constant (see eq 8). More importantly, mechanism A is eliminated by observations that metal Ion does not accelerate the reaction of NH_2OH with the ester. For a fuller discussion of the influence of preequilibria on kinetically pK_a's see ref 7.

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Michael A. Wells,[11] Gary A. Rogers, Thomas C. Bruice*
Department of Chemistry, University of California
Santa Barbara, California 93106

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The Diphenylvinylene Carbonate–Diene Exciplex. Solvent Dependence of Radiative and Nonradiative Decay Processes

Sir:

There is growing evidence that excited state π complexes or exciplexes are intermediates in numerous photochemical cycloaddition reactions.[1-4] Previous investigations of the stereospecific ${}_{\pi}2_s + {}_{\pi}2_s$ cycloaddition reactions of singlet *trans*-stilbene and diphenylvinylene carbonate (V) with electron rich alkenes[5] and dienes[6] provided indirect evidence for exciplex intermediates. The high quantum yields (~1.0) for adduct formation in nonpolar solvents[5a,b,6c,e] seemed to preclude the observation of exciplex fluorescence. We now wish to report the observation of solvent sensitive exciplex fluorescence from singlet V and 2,5-dimethyl-2,4-hexadiene (D). The effect of solvent upon exciplex fluorescence, cycloaddition, and nonradiative decay pathways provides important insights into the behavior of the exciplex intermediate.

Quenching of the fluorescence of V[7] is accompanied by the appearance of a new structureless emission at longer wave-

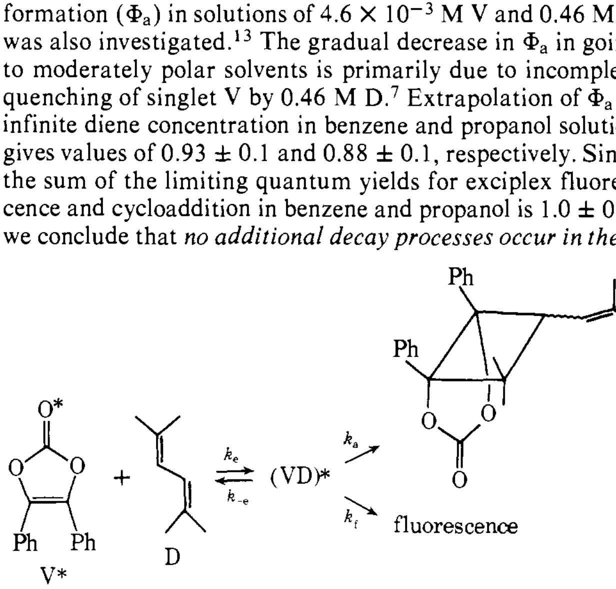
Table I. Diphenylvinylene Carbonate–2,5-Dimethyl-2,4-hexadiene Exciplex Fluorescence and Cycloadduct Formation

Solvent	ϵ^a	$\nu_{\max}$, cm$^{-1\,b}$	τ^{obsd}, ns^c	$\Phi_f{}^d$	$10^{-7}k_f$, s$^{-1\,f}$	$\Phi_a{}^g$	$10^{-8}k_a$, s$^{-1\,h}$
Hexane	2.0	23 300	<0.5	0.006	>1.2	0.50	>10
Benzene	2.3	23 200	<0.5	0.008	>1.6	0.59 (0.93)^e	>12
Diethyl ether	3.9	22 200	~0.5	0.015	3.0	0.50	10
Ethyl acetate	5.3	21 700	3.5	0.046	1.3	0.39	1.1
Dimethoxy ethane	5.9	21 500	5.7	0.071	1.2	0.22	0.39
tert-Butyl alcohol	10.5	21 100	4.6	0.059	1.3	0.28	0.61
n-Propyl alcohol	16.7	20 800	4.7	0.070 (0.12)^e	1.5	0.17 (0.88)^e	0.36
Ethanol	19.6	20 400	5.0	0.044	0.88	0.12	0.24
Methanol	26.7	20 000	2.6	0.019	0.73	0.014	0.054
Acetonitrile	31.5	19 400	1.5	0.004	0.2	<0.001	<0.01

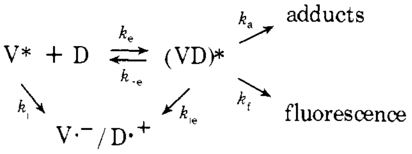
[a] Dielectric constant of 1.45 M diene solutions calculated assuming $\epsilon = \sum_i \epsilon_i V_i$, where V_i is the volume fraction of component i. [b] Maximum of exciplex fluorescence spectrum corrected for spectrometer response, accuracy ±500 cm^{-1}. [c] Exciplex fluorescence lifetime obtained from single exponential decay plots, accuracy ±0.5 ns. [d] Corrected quantum yield for exciplex fluorescence in 1.45 M diene solutions, relative accuracy ±20%, absolute accuracy ±50%. [e] Value extrapolated to infinite diene concentration. [f] $k_f = \Phi_f \tau^{\text{obsd}}$. [g] Quantum yield for cycloadduct formation in 0.46 M diene solution, accuracy ±10%. [h] $k_a = \Phi_a \tau_{\text{obsd}}$.

lengths. The red-shift of this new emission with increasing solvent polarity (Table I) is consistent with previous observations of exciplex fluorescence.[8] The corrected quantum yields for exciplex fluorescence (Φ_f) in solutions containing 2×10^{-3} M V and 1.45 M D increase in going from nonpolar to moderately polar solvents, but decrease in highly polar solvents. Quenching of the fluorescence of V by 1.45 M D is more efficient in nonpolar (>95%) than highly polar solvents (>80%) due to the decrease in the singlet lifetime of V with increased solvent polarity.[7] Extrapolation of the exciplex fluorescence quantum yield in propanol solution to infinite diene concentration provides a limiting quantum yield of 0.12. The values of Φ_f in Table I are lower than the limiting quantum yields by as much as 50% in the most polar solvents. Single exponential decay was observed for the exciplex emission in diethyl ether and solvents of higher polarity.[9] The observed lifetimes given in Table I are not true exciplex lifetimes due to the reversible nature of exciplex formation as well as incomplete quenching of singlet V by 1.45 M D.[10] It is interesting to note that both the exciplex fluorescence quantum yield and observed lifetime increase, pass through a maximum, and then decrease with increasing solvent polarity. Similar behavior has been reported without explanation for an intramolecular anthracene-*N*,*N*-dimethylaniline exciplex.[11] Rate constants for exciplex fluorescence (k_f) can be calculated from the quantum yield and lifetime data. The values of k_f given in Table I are independent of solvent polarity in all but the most polar solvents.[12]

The effect of solvent on the quantum yield for cycloadduct formation (Φ_a) in solutions of 4.6×10^{-3} M V and 0.46 M D was also investigated.[13] The gradual decrease in Φ_a in going to moderately polar solvents is primarily due to incomplete quenching of singlet V by 0.46 M D.[7] Extrapolation of Φ_a to infinite diene concentration in benzene and propanol solution gives values of 0.93 ± 0.1 and 0.88 ± 0.1, respectively. Since the sum of the limiting quantum yields for exciplex fluorescence and cycloaddition in benzene and propanol is 1.0 ± 0.1, we conclude that *no additional decay processes occur in these solvents* (eq 1). Rate constants for adduct formation (k_a) can be estimated from the quantum yields for adduct formation and observed lifetimes. Unlike k_f, which is relatively insensitive to solvent polarity in all but the most polar solvents, values of k_a decrease with increasing solvent polarity. The decrease in k_a is particularly large in going from hexane to ethyl acetate. *The decrease in k_a and resulting increase in τ^{obsd} in moderately polar solvents can be attributed to greater solvent stabilization of the polar exciplex than the transition state leading to cycloadducts.* This hypothesis is supported by the theoretical prediction of Michl[14] that exciplex cycloaddition requires a surface crossing from the polar exciplex state to the nonpolar pericyclic minimum followed by vertical deactivation to the ground state energy surface.



(1)



(2)

In highly polar solvents, the quantum yields for exciplex fluorescence and cycloadduct formation decrease more rapidly than the singlet lifetime (Table I). Similar observations for the solvent dependence of exciplex τ and Φ_f values have been reported by Weller[15] and Mataga.[12,16] Weller's proposal that solvated radical ions can be formed both upon encounter of excited and ground state molecules (k_i) and from the exciplex (k_{ie}, eq 2) has been experimentally verified by Mataga.[16b] The behavior of the V*-D system in methanol and acetonitrile is consistent with both direct (k_i) and indirect (k_{ie}) solvated radical ion formation.[17] It is interesting to note that the more polar pyrene-*N*,*N*-dimethylaniline exciplex (12.4 D)[18] requires a solvent dielectric constant of 12–15 for significant radical ion formation[16c] whereas the less polar V*–D exciplex (9.1 D)[19] requires a solvent dielectric constant >20.

In conclusion, we find that solvent polarity can exert a pronounced effect on the photochemical as well as photophysical behavior of an exciplex. By appropriate choice of solvent, quantum yields for cycloaddition, radical ion formation, and exciplex fluorescence can be optimized.

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Frederick D. Lewis,[20a]* Charles E. Hoyle[20b]

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received March 16, 1976

Synthesis of Ternary Metal Sulfide Arrays

Sir:

Metal-sulfur aggregates are currently of interest because of their unusual structural and bonding features,[1] and because of possible relevance to biological electron transfer processes[2-4] and fixation of atmospheric gases.[5,6] We report here the synthesis, by a novel deoxygenation reaction of dithiotungstates, $WO_2S_2^{2-}$, of a new class of neutral ternary metal sulfur arrays containing tungsten and a group 1b metal and the structural characterization of a representative member of this class, $(Ph_2PCH_3)_2Au_2WS_4$.

Formerly,[7] it was thought that reactions of transition metal ions with MoS_4^{2-} or WS_2^{2-} in water led to MoS_2 or WS_2 and metal sulfide. Müller and co-workers[8] showed that, by careful attention to reaction conditions, anionic complexes of the type $M(M'S_4)_2^{2-}$ (M = Co, Ni, Zn; M′ = Mo, W) could be prepared and we[9] found that similar reactions involving $WO_2S_2^{2-}$ and rare earth ions produced metal tungstates by hydrolysis processes. To extend our previous work, metathetic reactions of $WO_2S_2^{2-}$ in nonaqueous solvents were carried out.

In certain cases, such reactions proceeded cleanly to give the expected product. Thus, orange (diphos)$NiWO_2S_2$ (**1**) was prepared in 42% yield from (diphos)$NiCl_2$ and $(Ph_3PCH_3)_2WO_2S_2$ (**2**) in dichloromethane.[10] The infrared spectrum of **1** showed ν_{WO} at 928, 918, 910, and 890 cm^{-1} and ν_{WS} at 457(sh) and 452 cm^{-1}; it may be a mixture of isomers. In systems containing labile, nonchelating phosphines, however, deoxygenation of $WO_2S_2^{2-}$ occurred. Reation of **2,** copper(I) chloride, and diphenylmethylphosphine in dichloromethane at room temperature afforded, after chromatography on silica gel, a 22% yield (based on tungsten) of diamagnetic, yellow crystalline $[(Ph_2PCH_3)_2Cu]_2WS_4$ (**3**):[11] mp 175–176°, ν_{WS} 451, 438 cm^{-1}, $\Delta\nu$ (Raman) 470, 458, 246 cm^{-1}, λ_{max} (1,2-$C_2H_4Cl_2$, log ϵ) 410 (3.42), $\delta^{31}P$ 129.3 ppm,[12] $\delta^1H - 1.70$ (d, $^2J_{PCH} = 4.2$ Hz), $\chi_g - 0.38 \times 10^6$ cgs. A similar synthesis employing silver hexafluorophosphate produced yellow $[(Ph_2PCH_3)_2Ag]_2WS_4$[11] (**4**) in 25% yield: mp 145–146° dec, ν_{WS} 463, 447, λ_{max} 392 (3.04), $\delta^{31}P$ 134.0, $\delta^1H - 1.85$ ppm (d, 3.5), Λ_M 7.57 $ohm^{-1}\ cm^2\ mol^{-1}$ (CH_3NO_2). The absence of ^{31}P–$^{107,109}Ag$ coupling at ambient temperatures indicates the occurrence of rapid ligand exchange.[13] This has been substantiated by molecular weight determinations: calcd, 1328; found, 502 ($CHCl_3$), 676 (C_6H_6).

Solutions of **4** in donor solvents such as acetone or acetonitrile were unstable and deposited large orange crystals of $[(Ph_2PCH_3)Ag]_2WS_4$ (**5**) on standing at room temperature:[11] mp 149° dec; ν_{WS} 447, 432 cm^{-1}; λ_{max} 383 (3.16); $\delta^1H - 1.98$ (d,6), along with diphenylmethylphosphine. An analogous gold complex,[11] **6,** $[(Ph_2PCH_3)Au]_2WS_4$, was synthesized from **2** and $(Ph_2PCH_3)AuCl$: mp 175° dec; ν_{WS} 445, 438 cm^{-1}; $\Delta\nu$ 460(s), 449, 441, 272 cm^{-1}; λ_{max} 402 (3.76); $\delta^{31}P$ 88.0 ppm; $\chi_g - 0.38 \times 10^6$ cgs. Associative ligand exchange in **6** was observed. The ^1H NMR spectrum in acetone-d_6 contained a doublet at −2.57 ppm which collapsed to a singlet upon addition of excess diphenylmethylphosphine.

Crystals of the gold–tungsten sulfide **6** were grown from dichloromethane–cyclohexane. They are monoclinic, $P2_1$ (No. 4, C_2^2) with $a = 16.542$ (7) Å, $b = 13.504$ (4) Å, $c = 6.647$ (2) Å, $\beta = 96.18$ (2)° $d_{calcd} = 2.494$ g cm^{-3} for $z = 2$, and d_{found} (flotation) = 2.51. Data were collected at −160 °C on a diffractometer equipped with a highly oriented graphite monochromator and molybdenum tube source and using a standard θ–2θ scan technique. A total of 2709 unique intensities were collected, corrected for absorption, and reduced in the usual manner. The metal atoms were located by direct methods and Patterson techniques, and all remaining nonhydrogen atoms were located in three successive Fourier syntheses. Full matrix anisotropic least-squares refinement converged at $R(F) = 0.0265$. The structure shown in Figure 1, consists of a tetrahedral WS_4 core with S–W–S angles ranging from 108.54 to 111.55° and $d(W\text{–}S)_{av} = 2.22$ Å. The gold atoms are bound to opposite pairs of sulfur atoms with $d(Au\text{–}S)_{av} = 2.53$ Å, $\angle S\text{–}Au\text{–}S_{av} = 98°$, and ∠W–S–Au (av) = 75.15°. The phosphorus lies in the S–Au–S plane with $d(Au\text{–}P)_{av} = 2.27$ Å and $\angle P\text{–}Au\text{–}S = 131°_{av}$.

Structurally characterized materials containing trigonally coordinated Au(I) are rare, but the geometry about gold in **6** approximates that found in the salt $[(Ph_3P)_3Au]B_9H_{12}S$.[14] The tungsten–sulfur bond distance is 0.05 Å greater than in $(NH_4)_2WS_4$,[15] indicating the expected decrease in W–S bond order. A singular feature of the structure is the sharply acute Au–S–W angles. The 2.84 Å gold–tungsten distance is 0.06 Å longer than the sum of the atomic radii for these two metals. More significantly, the observed distortion of the $AuWS_2$ rhombus may imply a direct, transannular gold–tungsten bonding interaction[16] and, indeed, the importance in less constrained systems of the angles about bridging atoms as a measure of interactions between the atoms being bridged has been pointed out many times.[19-21] Metal–metal bonding might appear to be a logical consequence of placing two metals of