

Figure 1. Amplification of chemiluminescence by double energy transfer in a polymer system. The "native" chemiluminescence of **1** in the polymer is weak fluorescence and phosphorescence. Chemiluminescence can be amplified by energy transfer to DBA ($\phi_F \sim 0.1$)⁹ but the transfer step is inefficient if diffusional triplet-triplet energy transfer occurs (path 3). Transfer from ³A to the efficient emitter DPEA ($\phi_F \sim 1$)¹¹ is inefficient by all mechanisms. The long range energy transfer from ³A to ¹DBA in a polymer (path 1) removes the inefficiency of path 3 and the tandem energy transfer from ¹DBA to ¹DPEA (path 2) occurs resulting in a potential increase in chemiluminescence efficiency above and beyond that of **1** alone or the **1**-DBA and **1**-DPEA systems.

luminescence, all three probabilities, ϕ_* , ϕ_{ET} , and ϕ_F must be high. It has been shown⁷ that **1** (in analogy to other dioxetanes)^{6a,8} thermolyzes into ³A with a high efficiency ($\phi_* \sim 1$). Thus for high overall efficiency, $\phi_{ET}\phi_F$ must now correspond to an efficient triplet-singlet (TS) energy transfer followed by efficient fluorescence. Such a situation is extremely difficult to obtain in fluid solution because (a) all triplet-singlet acceptors also will be triplet-triplet acceptors (thereby causing a competitive nonluminescent path for deactivation of ³A and a low value of ϕ_{ET}) and (b) the most effective triplet-singlet acceptors (e.g., DBA) have inherently low fluorescence yields ($\phi_F < 0.1$).⁹

From our previous results,¹ it is clear that *the inefficiency in ϕ_{ET} can be circumvented by employing DBA as a triplet-singlet acceptor in a polymer matrix, since the competitive triplet-triplet energy transfer from ³A to DBA is severely inhibited under these conditions.* Furthermore, if ¹DBA can be made to efficiently transfer to an acceptor which possesses a high ϕ_F , the product $\phi_{ET}\phi_F$ may approach a much higher value than that obtained in fluid solution (since the second acceptor cannot compete *via* triplet-triplet energy transfer). This strategy would thus allow for a highly efficient chemiluminescent system to be based on *two* spin forbidden steps (Figure 1)!

Experimentally, we find that the limiting intensity of DBA *vs.* DPA chemiluminescence (which equals $\phi_{ET}^{TS}\phi_{ET}^{SS}\phi_F^{DPA}$)^{2,10} is two to three times as great in a polymer matrix than in fluid solution. This observation is consistent with our expectations that the inhibition of diffusion in the polymer would lead to an enhanced value of ϕ_{ET}^{TS} for DBA, since we do not expect the fluorescence yield ratio or the singlet-singlet

transfer efficiency to DPA to change upon proceeding from benzene solution to a polymer system. A more dramatic effect was observed when 9,10-dichloroanthracene (DCA) was employed as acceptor. In fluid solution, ϕ_{ET}^{TS} for this acceptor is much lower than for DBA. In the polymer the chemiluminescence limiting emission from DCA excited by decomposition of **1** is nearly ten times greater than it is for benzene solutions!

Even a more impressive and convincing experimental confirmation of the general idea proposed on Figure 1 is possible. The tertiary system, **1**, DBA, and DPEA (9,10-diphenylethylanthracene),¹¹ in polystyrene was employed. The strategy of this chemiluminescence system is that **1** will yield ³A with good efficiency, that the latter will transfer *via* a long range efficient mechanism to ¹DBA, and finally that ¹DBA will transfer to the strongly fluorescent DPEA *via* a long range singlet-singlet energy transfer.^{3,4} Note again that the polymer system inhibits the nonlight producing triplet-triplet transfers to *both* DBA and DPEA.

Experimentally, a system of $4 \times 10^{-2} M$ **1**, $2 \times 10^{-3} M$ DBA, and varying concentrations of DPEA was studied at 49°. At $2 \times 10^{-3} M$ DPEA, the chemiluminescence (essentially pure DPEA fluorescence) is twice that of DBA as acceptor alone and more than *ten times* that of DPEA as acceptor alone. Extrapolation to a limiting concentration of DPEA (with appropriate substitution of DPEA chemiluminescence on the absence of DBA) allows determination of a value of DPEA chemiluminescence which is *10-15 times* the value of DBA alone. Indeed, the ratio of fluorescence yields of DPEA to DBA is ~ 14 (at 49°), so that the product $\phi_{ET}^{TS}(^3A \rightarrow ^1DBA) \times \phi_{ET}^{SS}(^1DBA \rightarrow ^1DPEA) \times \phi_F^{DPEA}$ must be approaching a value of unity in the limit!

In conclusion, we provide evidence that the efficiency of indirect chemiluminescence on polymer systems can be made to greatly exceed that for fluid solutions and furthermore that, in principle, a highly efficient chemiluminescent system based on *two* spin forbidden steps (**1** \rightarrow ³A and ³A \rightarrow ¹DBA) and one long range spin allowed step (¹DBA \rightarrow ¹DPEA) can be designed by employing a double energy transfer and a rigid medium.

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(11) The sample of DEPA employed in this work was the kind gift of Dr. Arthur Mohan, American Cyanamid Co., Bound Brook, N. J. The quantum yield of fluorescence of DEPA is comparable to that of DPA, which is reported⁹ to be close to 1.0.

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(7) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(8) E. H. White, P. D. Wiles, J. Wiecko, H. Doshan, and C. C. Wei, *J. Amer. Chem. Soc.*, **95**, 7050 (1973); E. H. White, J. Wiecko, and C. C. Wei, *ibid.*, **92**, 2167 (1970).

(9) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970.

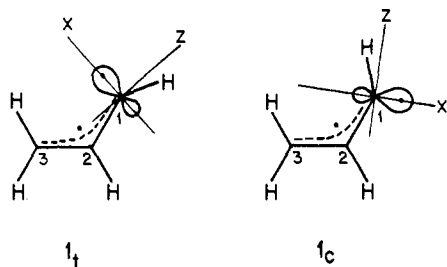
(10) This follows from eq 1 since the comparison of I_{CL} values is made under conditions of identical rates of decomposition and since the extrapolated value of ϕ_{ET} for singlet-singlet transfer to DPA must, by definition, equal unity.

Geometric Isomers of Vinylmethylene

Sir:

We have observed the electron paramagnetic resonance spectrum of the ground state triplet vinylmethylene

lene (**1**) after photolysis of vinyl diazomethane in a rigid matrix. The spectrum indicates the presence of two similar but nonidentical triplets which are assigned to the geometrical isomers **1_c** and **1_t**. The vinylmethylene pair provides a particularly simple case of geometric isomerism, previously observed for 1- and 2-naphthylmethylenes.¹ The distribution of unpaired electrons, derived by an analysis of the zero-field parameters, supports a description in which the π -system closely resembles an allyl radical, and the " σ "-unpaired electron is largely localized at the divalent carbon atom. The observation of geometric isomers excludes a linear structure at C₁ and indicates a geometry around C₁ and C₂ similar to that of the vinyl radical.² The triplets have unusually high reactivity as indicated by the irreversible disappearance of the spectra in the temperature range 20–35°K. This behavior points to thermal excitation to a nearby reactive state.



When we irradiated solid solutions of vinyl diazomethane³ in several matrices (methyltetrahydrofuran (MTHF), hexafluorobenzene, perfluorokerosene (PKF)) at 6°K with light of $\lambda > 3300 \text{ \AA}$, we observed triplet epr spectra for two distinct species⁴ (Figure 1). Under comparable irradiation conditions solutions containing benzophenone gave signals an order of magnitude more intense than those without a photosensitizer. Triplet sensitization combined with increased absorption of light may be involved in this more efficient production of the triplet methylenes. The variation of signal intensity with temperature in the range of 6–15°K indicated that **1_c** and **1_t** are each ground state triplets or within a few calories of the ground state.

The zero-field parameters (cm^{-1}) of the two species are:⁴ $D_c = 0.4578$, $E_c = 0.0193$, $D_t = 0.4093$, $E_t = 0.0224$, in MTHF. The values in other matrices are the same for either species within $4 \times 10^{-3} \text{ cm}^{-1}$ for D and $8 \times 10^{-4} \text{ cm}^{-1}$ for E , typical of the variations occurring for a given triplet in different environments.⁵ The small but consistent differences indicate closely related but nonidentical systems. This observation is readily explained by a pair of geometric isomers.

The assignment of the zero-field parameters to the two isomers follows from an analysis of the unpaired spin

(1) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **87**, 129 (1965).

(2) E. L. Cochran, E. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964).

(3) Vinyl diazomethane was prepared from α -nitroso- α -allylurea in a 10% solution of KOH in 2-(2-methoxyethoxy)ethanol similar to the preparation of diazomethane (F. Arndt, "Organic Syntheses," Collect. Vol. 2, Wiley, New York, N. Y., 1943, p 165). α -Nitroso- α -allylurea was prepared from allylamine following the procedure of F. Arndt ("Organic Syntheses," Collect. Vol. 3, Wiley, New York, N. Y., 1943, p 943) for nitrosomethylurea.

(4) E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

(5) A. M. Trozzolo, E. Wasserman, and W. A. Yager, *J. Chim. Phys. Physicochim. Biol.*, **61**, 1663 (1964).

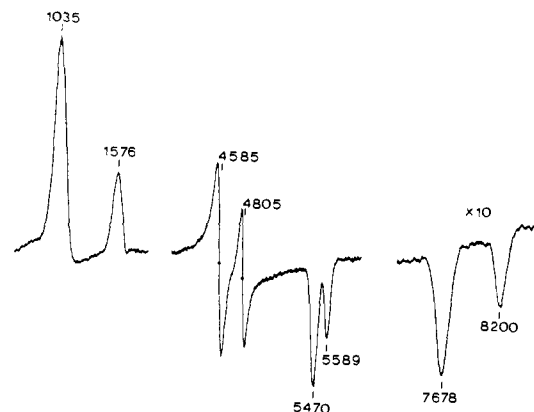


Figure 1. Epr spectrum of vinylmethylene in MTHF at 6°K. Fields are given in gauss: $h\nu/g\beta = 3304.4 \text{ G}$.

density distribution in these species. We note that

$$D \propto \left\langle \frac{r^2 - 3z^2}{r^5} \right\rangle \approx \left\langle \frac{1}{r^3} \right\rangle$$

where r is the distance between the two unpaired electrons. Since one electron is largely localized in the σ -orbital at the divalent carbon atom (C₁), the main contribution to D is due to the spin density of the delocalized π -electron at that carbon (ρ_1). An analog which also has localized " σ " and delocalized π -spins is diphenylmethylene. Its D value of 0.4054 cm^{-1} corresponds to a spin density of $\rho_1 = 0.55$.⁶ The average D value of **1_c** and **1_t** (0.434 cm^{-1}) indicates $\rho_1 = 0.58$. This value corresponds to the ρ 's at the terminal carbon atoms of the allyl radical.⁷ Therefore, we approximate the π -spin distribution in **1** with $\rho_1 = \rho_3 = 0.58$ and $\rho_2 = -0.16$. The angle at the divalent carbon atom is approximately determined by the ratio E/D . For the two isomers, **1_c** and **1_t**, these ratios are similar to those of most aromatic methylenes and would correspond to an angle of $\sim 140^\circ$.⁶ To approximate the interactions about the divalent carbon atom, we represent each unpaired electron by a pair of fractional spins in a geometric arrangement which reproduces the zero-field parameters of triplet CH_2 .⁸ The unpaired densities at C₂ and C₃ are each treated as two point spins above and below the molecular plane. With these assumptions one calculates $D_c = 0.468 \text{ cm}^{-1}$ and $D_t = 0.395 \text{ cm}^{-1}$, in reasonable agreement with the experimental values. D_t is lower because r_{13}^2 is approximately parallel to z in **1_t** and ρ_3 gives a substantial negative contribution (since $z_{13} \approx r_{13}$, $\langle (r^2 - 3z^2)/r^5 \rangle \approx \langle -2z^2/r^5 \rangle$). The corresponding contribution to D_c is close to zero, since in **1_c** $r^2 - 3z^2 \approx 0$.

Additional support for the assignment comes from the line widths. As seen in Figure 1, the absorptions of **1_t** are consistently wider than those of **1_c**. In analogy to the vinyl radical,² the difference is ascribed to the larger unresolved hyperfine interaction of the 2-hydrogen with the σ -unpaired electron in a trans arrangement (**1_t**).

(6) (a) E. Wasserman, A. M. Trozzolo, W. A. Yager, and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964); (b) R. W. Brandon, G. L. Closs, C. E. Devoust, C. A. Hutchison, Jr., B. E. Kohler, and R. Silbey, *ibid.*, **43**, 2006 (1965).

(7) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(8) E. Wasserman, R. S. Hutton, V. J. Kuck, and W. A. Yager, *J. Chem. Phys.*, **55**, 2593 (1971).

The cis/trans ratio of the vinylmethylene isomers, as indicated by their signal intensities, can vary between 0.65 and 0.05, depending on the experimental conditions. The lowest ratio is found in the PFK matrix; the highest relative intensity of the cis isomer is observed when vinyl diazomethane is irradiated for short periods (seconds) in an MTHF matrix in the presence of benzophenone. Here continued irradiation increases the intensities of both species but decreases the cis/trans ratio. After reaching an intensity maximum at a ratio of ~ 0.4 , both isomers decay on further illumination. One possible explanation for the change in intensity ratios involves interconversion of 1_c and 1_t . This process is of interest in view of the wide range of inversion rates ($>10^{10}$) reported for the structurally related vinyl radical, depending on matrix and site.⁹

In the dark, the vinylmethylenes are stable between 6 and 15°K and their ratios remain unchanged; at 77°K, both isomers disappear within 1 min. At temperatures between 20 and 35°K, 1_c and 1_t decay with energies of activation <200 cal/mol, the cis isomer at somewhat faster rates than the trans isomer. Accordingly, the vinylmethylenes are considerably more reactive than phenylmethylene^{6a} or the naphthylmethylenes¹ in similar environments. At these low temperatures, far below the melting points of the matrices employed, second-order diffusion-controlled processes are not expected. Therefore, we assume an intramolecular conversion of the vinylmethylenes to a more reactive state, probably a singlet, which can then undergo intra- or intermolecular reactions. These transformations are currently under investigation. In several cases substituted vinylmethylenes, presumably in their singlet states, have been invoked as intermediates in the thermal racemization of chiral cyclopropenes and in the photodecomposition of various 3*H*-pyrazoles leading to cyclopropenes (ring closure) or dienes (hydrogen migration).¹⁰ Closs and coworkers have previously observed esr spectra of several 1,2-benzvinylmethylenes in the photolysis of the corresponding 3*H*-indazoles.^{11,11a}

Acknowledgment. We would like to thank Z. Wasserman for the computer calculations of the zero-field tensors.

(9) This remarkable conclusion follows from the work of P. H. Kasai and E. B. Whipple, *J. Amer. Chem. Soc.*, **89**, 1033 (1967); cf. e.g., ref. 2.

(10) (a) E. J. York, W. Dittmar, J. R. Stevenson, and R. G. Bergman, *J. Amer. Chem. Soc.*, **95**, 5680 (1973), and references quoted therein; (b) J. A. Pincock, R. Morchat, and D. R. Arnold, *ibid.*, **95**, 7536 (1973).

(11) G. L. Closs, L. R. Kaplan, and V. I. Bendall, *J. Amer. Chem. Soc.*, **89**, 3376 (1967); G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *ibid.*, **90**, 173 (1968).

(11a) NOTE ADDED IN PROOF. O. L. Chapman, M. Chedekel, J. Pacansky, N. Rosenquist, R. Roth, and R. S. Sheridan have observed the ir and esr of vinylmethylene in matrix-deposited argon and nitrogen. Their experiments and our more limited matrix isolation studies show substantial differences from the frozen solutions discussed above. For example, we find 1_t and 1_c in frozen pentane solutions, whereas vinyl diazomethane and pentane, deposited at 8°K from the vapor phase, give only 1_t . Also, E was 10% lower than observed in solution.

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Synthesis and Structural Characterization of the Nickel(II) and Copper(III) Complexes of the 1,1-Dicarboethoxy-2,2-ethylenedithiolate Ligand

Sir:

The ability of dithiocarbamate ligands to stabilize metal ions in unusually high oxidation states is well documented.¹ A less well-known ligand capable of stabilizing metal ions in high oxidation states is the 1,1-dicarboethoxy-2,2-ethylenedithiolate dianion² (DED²⁻). In our studies of the chemistry of this ligand we have isolated and characterized complexes which formally contain Fe(IV)³ and Cu(III) ions.

Galactose oxidase, a copper-containing enzyme for which Cu-S coordination has been implicated,⁴ catalyzes the oxidation of D-galactose to the corresponding aldehyde. In a recently proposed mechanism for the action of this enzyme, Hamilton, *et al.*, suggested that the two-electron oxidation of the substrate proceeds after the enzyme-bound copper is oxidized to the +3 state.⁵ We have undertaken the present study to explore the nature of the Cu-S bonding in oxidized copper complexes and possibly design models for copper-containing metalloenzymes.

The water insoluble (BzPh₃P)₂Cu(DED)₂ (I) is precipitated from brown-red dilute aqueous solutions of K₂Cu(DED)₂, upon addition of benzyltriphenylphosphonium chloride. This compound is recrystallized from dichloromethane-pentane mixtures, and its physical properties are similar to those reported for other bis-1,1-dithiolate-copper complexes.⁶ It is X-ray isomorphous to the (BzPh₃P)₂Ni(DED)₂ complex and has similar infrared spectra.

In the presence of a 10–15% excess of Cu(II) ions or H₂O₂, aqueous solutions of K₂Cu(DED)₂ afforded a water insoluble⁷ green complex of the stoichiometry KCu(DED)₂ (II), which can be recrystallized from acetonitrile-chloroform mixtures. Replacement of the potassium ions by BzPh₃P⁺ is readily accomplished in acetonitrile giving BzPh₃PCu(DED)₂ (III). This compound also is obtained by iodine oxidation of the corresponding parent complex, I, in acetonitrile.

Consistent with its chemically determined redox behavior, I undergoes a reversible one-electron electrochemical oxidation at -0.50 V in CH₂Cl₂ vs. Ag|AgI with Bu₄NClO₄ as the supporting electrolyte. The K⁺ and BzPh₃P⁺ salts of [Au^{III}(DED)₂]⁻ were found X-ray isomorphous to II and III, respectively. Furthermore the energies of the bands in the electronic spectra of II and III were similar to those of the corresponding Ni(II) complexes. On the basis of these data it appeared that the anions in II and III could best be described as Cu(III) complexes.

(1) (a) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Aust. J. Chem.*, **26**, 2533 (1973); (b) J. P. Fackler, Jr., A. Avdeef, and R. G. Fischer, Jr., *J. Amer. Chem. Soc.*, **95**, 774 (1973); (c) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(2) D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967.

(3) F. J. Hollander, R. Pedelty, and D. Coucouvanis, *J. Amer. Chem. Soc.*, **96**, 4032 (1974).

(4) R. S. Giordano, R. D. Bereman, D. J. Kosman, and M. J. Ettinger, *J. Amer. Chem. Soc.*, **96**, 1023 (1974).

(5) G. A. Hamilton, R. D. Libby, and C. R. Hartzell, *Biochem. Biophys. Res. Commun.*, **55**, 333 (1973).

(6) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

(7) It is noteworthy that even the sodium salt of this compound is insoluble in water indicating an unusually strong interaction between the complex anion and the alkali metal cation.