It is doubtful that additional force constant adjustments could be devised which would force the A_Q and A_f factors much below the values shown in Table III, without extending the models so far beyond what could be considered mechanistically reasonable as to make them meaningless. Our models, which were constructed not for mechanistic reasonableness, but specifically to produce low Arrhenius preexponential factors, did not result in values of A_Q less than ~0.7 nor values of A_f less than ~0.5.

Conclusions

There is probably no strictly defined lower limit to the value of the kinetic isotope effect Arrhenius preexponential factor, A_Q, that can result, in the harmonic approximation, solely from force constant changes, at the isotopic position, between reactant and transition state. The present study indicates that, for sizable magnitude primary hydrogen kinetic isotope effects,

increase in A_Q with increasing temperature does not occur until temperatures as high as ~200°K (for the simple acid ionization model) to ~650°K (for the decarboxylation model) are attained. We are indebted to Professor Jacob Bigeleisen for pointing out to us a significant error in our original analysis of the temperature variation of A_Q.

(24) M. J. Stern, W. Spindel, and E. U. Monse, *J. Chem. Phys.*, **48**, 2908 (1968).

the *effective* lower limit to such A_Q values is ~0.7. A more conservative estimate, $A_Q \gtrsim 0.5$, is obtained by considering the lowest value found for the Arrhenius preexponential factor of the purely quantum mechanical contribution to a kinetic isotope effect (A_f) to be the lower limit to the preexponential factor of the entire isotope effect (A_Q). This conclusion is in excellent agreement with a prediction made by Bell on the basis of a less rigorous theoretical treatment[3] and lends support to the common practice of interpreting experimental values of A_Q significantly lower than 0.5 as due to the operation of quantum mechanical tunneling.

We wish to stress, however, that we have considered, and our conclusions are meant to apply to, only primary hydrogen kinetic isotope effects of sufficiently large magnitudes to be characterized by regular temperature dependences. We have estimated[16,25] that, in order for a pure primary or mixed primary–secondary hydrogen kinetic isotope effect to be assuredly associated with a regular temperature dependence, the value of k_H/k_D at 300°K must be greater than ~2.7 (regular at all temperatures) or less than ~0.5 (regular at least at room temperature and above).

(25) These estimates[16] were based, in part, on the results of the isotope effect temperature-dependence plotting procedure carried out in conjunction with the present investigation.

Electrogenerated Chemiluminescence. VIII. The Thianthrene–2,5-Diphenyl-1,3,4-oxadiazole System. A Mixed Energy-Sufficient System

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Abstract: Electrogenerated chemiluminescence (ecl) resulting from reaction of the thianthrene (TH) cation radical and the 2,5-diphenyl-1,3,4-oxadiazole (PPD) anion radical in acetonitrile solutions is characterized by emission at wavelengths of both TH and PPD fluorescence. A consideration of the enthalpy of the reaction shows the process to be energy sufficient with respect to formation of excited singlet TH (430 nm) and to be energy deficient with respect to formation of excited singlet PPD (340 nm). The absence of a magnetic field effect on ecl emission at 430 nm also suggests the direct formation of singlet TH* on radical-ion annihilation. Emission at 340 nm probably arises from triplet–triplet annihilation of triplet PPD, formed either in the radical annihilation reaction or by energy transfer from triplet TH. Variations in the spectral distribution and the intensity of the ecl emission with the frequency of the applied potential steps were also investigated.

It has been convenient to classify reactions in electrogenerated chemiluminescence (ecl) as "energy sufficient" when the energy of the light produced is equal to or smaller than the enthalpy of the redox reaction for a single pair of reacting species producing ground-state molecules. For example, the reversible peak potentials for the oxidation (E_{p_a}) and reduction (E_{p_c}) of 9,10-diphenylanthracene (DPA) in *N,N*-dimethylformamide (DMF) solution (V *vs.* sce) are +1.35 and −1.89, respectively, and the energy of the first excited singlet (E_s) is 3.0 eV, so that, correcting for the difference between E_p and E^0 and estimating a small contribution for the entropy term, DPA ecl is an "en-

ergy-sufficient" system.[1] Ecl is also observed in mixed systems, that is, systems in which the electrogenerated oxidant and reductant are produced from different species. Typical examples of mixed-system chemiluminescence involve Wurster's Blue cation radical (TMPD·+) and chrysene anion radical,[2] TMPD·+ and DPA·−, and a number of other systems recently studied by Freed and Faulkner.[3] In all cases these were "energy-deficient" systems where the energy of

(1) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 209 (1969).
(2) A. Weller and K. Zachariassse, *J. Chem. Phys.*, **46**, 4984 (1967).
(3) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).

the emitted photon was greater than the enthalpy calculated from E_{p_a} and E_{p_c}. Studies of magnetic field effects,[1] critical enthalpy,[3] and quenching of the ecl[3,4] have led to an explanation of energy-deficient ecl in terms of initial production of triplets followed by triplet–triplet annihilation. We describe here ecl in the mixed system composed of thianthrene (TH) and 2,5-diphenyl-1,3,4-oxadiazole (PPD), which provides the first example of a mixed energy-sufficient system.
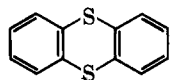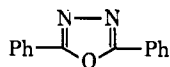
thianthrene (TH)   2,5-diphenyl-1,3,4-oxadiazole
                                    (PPD)

Experimental Section

Chemicals. Acetonitrile (AN), reagent grade, Matheson Coleman and Bell, was purified using the method given by Osa and Kuwana[5] and was stored under vacuum; the amount necessary for individual experiments was vapor transferred directly into the ecl cell on the vacuum line. The ethanol used in phosphorescence studies was dried by the magnesium metal process and was distilled. Tetra-*n*-butylammonium perchlorate (TBAP) (Polarographic grade), obtained from Southwestern Analytical Chemical Co., was dried for 48 hr in a vacuum oven at 80° and was stored in a desiccator over anhydrone. The melting point was 217–218°. Thianthrene (TH) was obtained from Aldrich Chemical Co. Samples recrystallized from spectrograde benzene had melting point (154–156°) and fluorescence, electrochemical, and ecl properties undistinguishable from those of unrecrystallized TH, so that most ecl and other experiments were conducted using the latter. However, to eliminate any doubts about the effects of possible impurities in TH, a sample was purified by chromatography on an alumina column followed by three recrystallizations from spectroscopic grade methanol.[6] The fluorescence and ecl behavior for this high-purity sample were essentially the same as those of unrecrystallized TH. Similarly, 2,5-diphenyl-1,3,4-oxadiazole (PPD) obtained from Aldrich Chemical Co. was used as received, because recrystallization from benzene resulted in no detectable change in the melting point (140–141°) or the electrochemical, fluorescence, and ecl properties.

Apparatus. The basic ecl cell used in this work is shown in Figure 1. Not shown in Figure 1 is the silver wire reference electrode, which is similar in size and placement to the two platinum electrodes. For preliminary experiments a comparable cell with detachable and exchangeable electrodes, and also equipped with fritted glass chambers for the reference and auxiliary electrodes, was used without permanently sealing off the top. We have previously discussed[7] the feasibility of using a silver wire as reference electrode in DMF solutions containing tetra-*n*-butylammonium iodide (TBAI) as supporting electrolyte. In our mixed systems the potential of the silver wire was about 0.02 V more negative than that of an aqueous sce, so that $E(vs. Ag) = E(vs. sce) + 0.02$ V. The Ag wire potential is somewhat dependent upon the solvent and depolarizer. In addition, if a silver wire is not shielded in a fritted reference compartment, the electrogenerated species may shift the reference potential during long-duration controlled-potential experiments. The silver wire reference electrode has several advantages, however. It does not introduce water to the nonaqueous system. It allows oxygen to be excluded more rigorously, since freeze–pump–thaw cycles can be carried out and the cell maintained under vacuum without the need to open to insert an sce. Possible quenching by inert gases which need to be added when an sce is introduced into the vacuum cell is avoided. The joint necessary for the introduction of the sce is replaced by the graded glass seal used for the silver wire. Finally, a much larger temperature range can be covered with the silver wire reference electrode, as demonstrated by recent experiments on ecl in molten systems.[8]
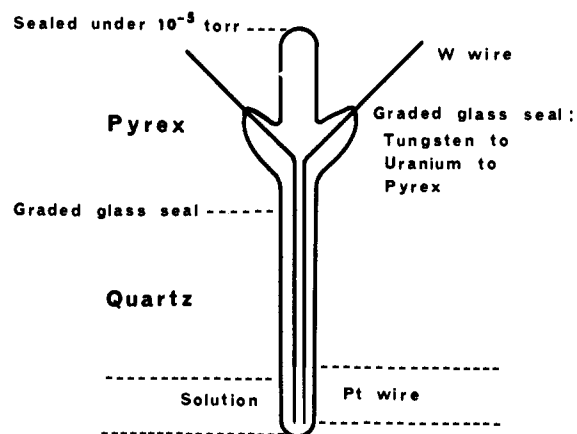

Figure 1. Ecl cell (silver wire reference electrode is not shown).

The sealed cell containing platinum working and auxiliary electrodes and a silver wire reference electrode thus offers many advantages in the preparation and investigation of systems with rigorous exclusion of oxygen and minimization of water contamination. Preliminary cyclic voltammetric experiments are used to choose oxidation and reduction potentials for ecl experiments. A McKenna Model No. 35-11 ultrasonic stirrer was used to facilitate dissolution and mixing of the solutions in the ecl cell and also provided stirring between electrochemical and ecl measurements. Electrochemical experiments were performed with a Princeton Applied Research Corp. Model 170 electrochemistry system (PAR). For fast electrogeneration the "external input" terminal of the PAR was linked to a Wavetek Model 114-G function generator. Fluorescence and ecl data were taken using an Aminco Bowman spectrophotofluorometer (SPF) in conjunction with a Hamamatsu TV Corp. R456 photomultiplier tube having uv-improved S-20 spectral response. The phosphorescence spectrum of TH was obtained with a phosphorimeter designed by Dr. S. Webber of this department, which contained a McPherson Model 218 monochromator and a low-pressure mercury lamp. An excitation wavelength of 3130 Å was employed. The solution for phosphorescence measurements was prepared in a quartz cell, degassed on a vacuum line, and sealed under helium at about 0.33 atm. Magnetic field effects on ecl were performed as previously described.[1,9] The electrode potentials were controlled with a Wenking Model 61RH potentiostat programmed with a Wavetek Model 114-G function generator operating in the square-wave mode at 10 Hz.

Procedure. In a typical experiment the clean ecl cell (Figure 1) and an adaptor consisting of ground glass joints and an evacuable high-vacuum stopcock are pumped down to a pressure of approximately 5×10^{-6} Torr. The TBAP and other solids are placed in the ecl cell, which is evacuated to a pressure below 10^{-5} Torr. Acetonitrile is transferred from a storage flask on the vacuum line under a temperature gradient to the ecl cell. After several freeze–pump–thaw cycles, the pressure over the frozen (liquid N_2) solution drops below 10^{-5} Torr, at which time the cell is permanently sealed with a natural gas–oxygen torch. The ecl and electrochemical properties of solutions in such cells have shown no change over weeks and months, depending on the number of experiments one performs.

Most of the ecl experiments were performed in the two-electrode mode, with the voltage span adjusted to the peak-to-peak separation found from cyclic voltammetry. In this mode the auxiliary and reference electrode leads of the PAR were connected to one platinum electrode and the working electrode lead was connected to the other platinum electrode. The results obtained by this technique compared closely to those obtained using a three-electrode mode.

Cyclic voltammetric experiments were performed with a cell consisting of an 0.018-in. platinum wire working electrode (geometric area 0.17 cm²), a 1.5 × 4.5 cm platinum foil auxiliary electrode, and an sce reference positioned so that the capillary tip of the sce was less than 0.5 mm from the working electrode.

(4) J. Chang, D. M. Hercules, and D. K. Roe, *Electrochim. Acta*, **13**, 1197 (1969).

(5) T. Osa and T. Kuwana, *J. Electroanal. Chem.*, **22**, 389 (1969).

(6) J. M. Bonnier and R. Jardon, *J. Chim. Phys. Physicochim. Biol.*, **68**, 428 (1971).

(7) W. V. Childs, J. T. Maloy, C. P. Keszthelyi, and A. J. Bard, *J. Electrochem. Soc.*, **118**, 874 (1971).

(8) C. P. Keszthelyi and A. J. Bard, manuscript in preparation.

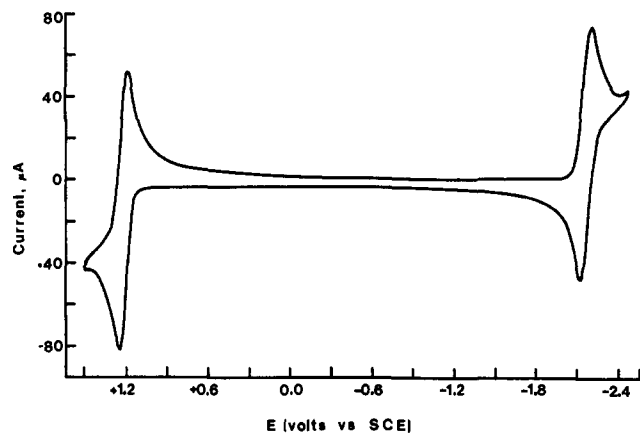(9) L. F. Faulkner and A. J. Bard, *Chem. Instrum.*, **2**, 337 (1970).

Figure 2. Cyclic voltammogram of the thianthrene-2,5-diphenyl-1,3,4-oxadiazole mixed system. The area of the platinum wire electrode = 0.17 cm^2, [TH] = 1.00 mM, [PPD] = 0.94 mM, [TBAP] = 0.10 M, scan rate = 100 mV/sec.

Results

Electrochemical Data. A cyclic voltammogram of a solution 1 mM each in TH and PPD in 0.1 M TBAP–acetonitrile (AN) at a platinum electrode is shown in Figure 2. TH oxidizes to a stable cation radical with $E_{p_a} = +1.25$ V vs. sce. The relevant cyclic voltammetric criteria, $E_p - E_{p/2}$, $E_{p_a} - E_{p_c}$, and i_{p_a}/i_{p_c}, are characteristic of a Nernstian oxidation to a stable oxidation product. The diffusion coefficient, calculated from the $i_p/v^{1/2}C$ value of 8.0 (μA sec$^{1/2}$)/(V$^{1/2}$ mM) was about 2.9 $\times$ 10^{-5} cm^2/sec. Shine and coworkers[10] previously demonstrated the electrochemical formation of the TH radical cation and its stability in a nitromethane–magnesium perchlorate medium. TH is not reducibled in the TBAP–AN medium at a platinum electrode to potentials of -2.4 V; however, reduction of TH at -2.59 V vs. sce in DMF solutions has been reported.[11] PPD reduces to a stable anion radical, with $E_{p_c} = -2.17$ V vs. sce. The voltammetric results are again consistent with a Nernstian reaction to a stable reduction product. The calculated diffusion coefficient of PPD was about 2.8 $\times$ 10^{-5} cm^2/sec. Shimanskaya and Bezuglyi[12] found that PPD is reduced in a 92% methanolic medium at -1.97 V vs. sce in a two-electron step. However, Grieg and Rogers[13] found that a related compound, 2,5-diphenyloxazole (PPO), is reduced to a stable radical anion in DMF. Lami and Laustriat[14] report reduction of PPD in DMF at about -2 V (reference electrode not specified), based on unpublished results of Plazanet. PPD in AN–TBABF$_4$ solution undergoes an apparent one-electron oxidation at $+2.20$ V vs. the silver wire reference; the PPD cation is very unstable, as evidenced by the lack of a reversal current, and there is filming of the electrode.

Spectroscopic Data. Fluorescence spectra of TH and PPD are shown in Figure 3. These spectra were normalized for presentation in the figure; at equal
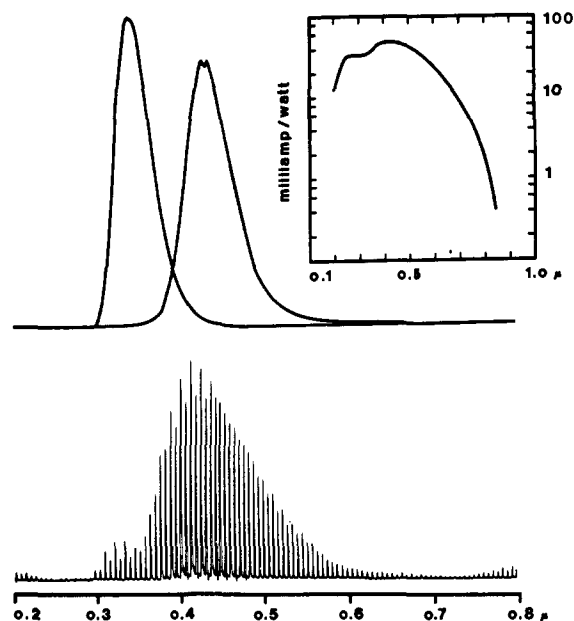
Figure 3. Top: scaled fluorescence spectrum of thianthrene ([TH] = 3.4 mM) and of 2,5-diphenyl-1,3-4-oxadiazole ([PPD]) = 1.2 mM) taken in a quartz cuvette using nondegassed acetonitrile as solvent with excitation at 310 nm. The true intensity of PPD fluorescence is about 50 times that of TH at these concentrations. Inset: nominal spectral response of the HTV 456 photomultiplier tube which was used to take all spectra shown in figures. Bottom: ecl emission spectrum of the TH–PPD mixed system recorded from 2000 to 8000 Å using a cyclic square wave at 0.2 Hz between ±3.30 V; [TH] = 7.3 mM, [PPD] = 7.0 mM.

concentrations and equal excitation intensities (uncorrected for inner filter effect), the fluorescence of PPD is essentially 50 times more intense than that of TH. The fluorescence of TH is characterized by a large Stokes shift, with the wavelength of maximum excitation at 250 nm and the emission maximum at 434 nm.[15] The fluorescence and phosphorescence of TH in cyclohexane have recently been investigated by Bonnier and Jardon,[6] who found similar results. They report the following singlet and triplet yields and lifetimes: Φ_F = 0.036, Φ_T = 0.94, $^1\tau$ = 3 $\times$ 10^{-8} sec, $^3\tau$ = 1.72 $\times$ 10^{-4} sec. Strong fluorescence of PPD has also been reported.[16] The fluorescence peaks at 347 nm for PPD and 434 nm for TH allow assignment of first-excited-state singlet energies (E_s) of about 3.58 eV for PPD and 2.84 eV for TH. In a system composed of an equimolar mixture of TH and PPD, the TH fluorescence peak cannot be observed due to overlap of the long wavelength tail of the PPD peak; the PPD fluorescence is essentially unchanged by addition of TH. Phosphorescence of TH in an ethanol glass at liquid nitrogen temperature shows a peak at 480 nm, corresponding to a first-excited triplet energy (E_T) of 2.58 eV. This result is in excellent agreement with the previous measurement of TH phosphorescence in an EPA glass.[15a]

Ecl Spectra. A comparison of the electrochemical and spectroscopic results leads to the prediction that the energy available from the reaction of TH cation radical (TH·$^+$) and PPD anion radical (PPD·$^-$) will be

(10) H. J. Shine, C. F. Dais, and R. J. Small, *J. Org. Chem.*, **29**, 21 (1964).

(11) A. Zweig and A. K. Hoffman, *ibid.*, **30**, 3397 (1965).

(12) N. P. Shimanskaya and V. D. Bezuglyi, *Zh. Obshch. Khim.*, **33**, 1683 (1963).

(13) W. N. Grieg and J. W. Rogers, *J. Electrochem. Soc.*, **117**, 1141 (1970).

(14) H. Lami and G. Laustriat, *J. Chem. Phys.*, **48**, 1832 (1968).

(15) (a) H. V. Drushel and A. L. Sommers, *Anal. Chem.*, **38**, 10 (1966); (b) M. Furst, H. Kallmann, and F. H. Brown, *J. Chem. Phys.*, **26**, 1321 (1957).

(16) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 150.
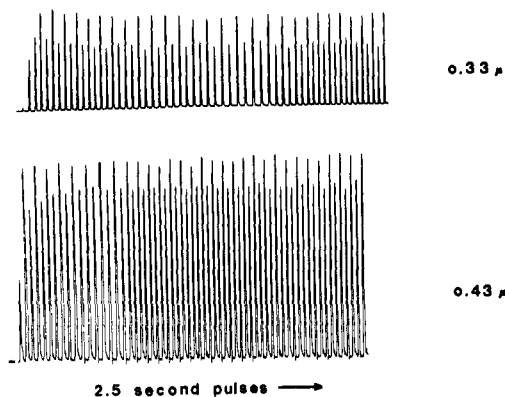
Figure 4. Ecl emission *vs.* time of the TH–PPD mixed system at 3300 and 4300 Å. The concentrations were 5×10^{-4} M for both TH and PPD; ± 3.30-V cyclic square waves at 0.2 Hz were applied between the two platinum electrodes. The taller peaks at 3300 Å occur upon stepping to $+3.30$ V, while at 4300 Å the taller peaks occur upon stepping to -3.30 V.

Figure 5. Frequency dependence of the TH–PPD mixed-system ecl described in Figure 4; concentrations were 5×10^{-4} M in TH and PPD, ± 3.30-V cyclic square waves were applied between the two platinum electrodes. Ordinates show duration of one applied pulse, abscissas follow spectral scan in μ units.

Figure 6. Time averaged ecl intensity measured at 4300 Å *vs.* applied frequency of electrogeneration in the TH–PPD mixed system. Concentrations were [TH] = [PPD] = 5×10^{-3} M. Results of three different solutions. (■) experiment where magnitude of applied voltage was maintained at ± 3.40 V.

energy sufficient with respect to production of the first excited singlet of TH ($^1TH_1$), but energy deficient with respect to $^1PPD_1$. The ecl spectrum resulting from applying a ± 3.30-V cyclic square wave at a frequency, f, of 0.2 Hz to platinum electrodes immersed in a solution containing 7.3 mM TH and 7.0 mM PPD in 0.1 M TBAP–AN is shown in Figure 3. The ecl spectrum shows emission at wavelengths corresponding to both TH and PPD fluorescence, as well as some additional emission between about 490 and 650 nm (the apparent ecl peaks at 200 and 800 nm are artifacts that result from a small amount of scattering of emitted light in the spectrophotofluorometer). The intensity of ecl is quite constant with time at both 330 and 430 nm, as shown in Figure 4, justifying the continuous scanning procedure used to obtain the ecl spectrum. An alternation of peak heights is observed in both Figures 3 and 4. In the region around 330 nm the taller peaks correspond to stepping the voltage in a positive direction (TH·+ production), while in the region of 430 nm the taller peaks correspond to voltage steps in the negative direction (PPD·⁻ production). The effect of the frequency of the cyclic square wave on the ecl spectrum is shown in Figure 5. The peak at 340 nm, corresponding to the region of PPD fluorescence, decreases relative to the 430-nm TH fluorescence peak, as f is increased. When $f = 0.2$ Hz, this ratio (I_{340}/I_{430}) is $^1/_8$, while at $f = 10$ Hz this has decreased to $^1/_{20}$. The peak at 340 nm has virtually disappeared at an f of 500 Hz. The frequency dependence of the magnitude of the main ecl peak (430 nm) is shown in Figure 6. Although there have not been many studies of the variation of ecl emission with frequency, the usual observation is a decrease of ecl intensity with increasing frequency, with ecl emission ceasing at relatively low frequencies (10–100 Hz). The intensity here represents the output from the spectrophotofluorometer, so that the signal has been passed through the low pass filter of the instrument.[17] For this system, using a cell with platinum electrodes spaced 1-mm apart, and applying a cyclic square wave with the amplitude adjusted to yield the maximum luminescence at a given frequency, ecl emission was observed up to a frequency of 60 kHz. The increase in voltage

(17) S. A. Cruser and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 267 (1969).
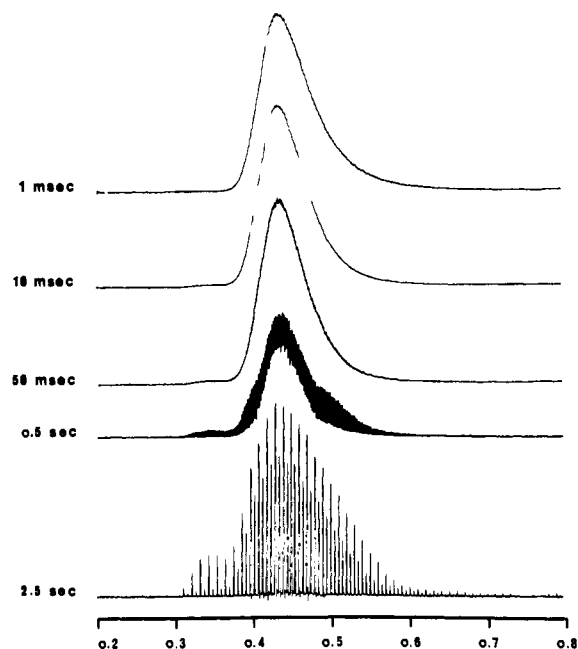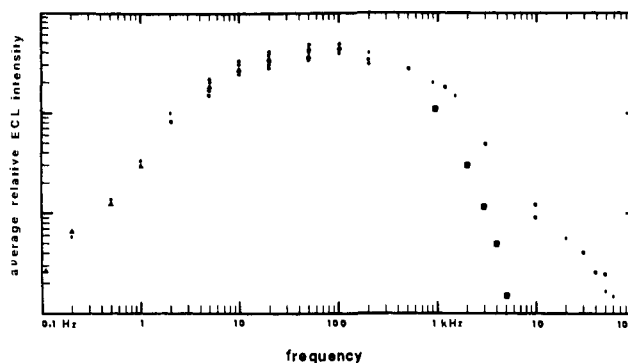
amplitude, from 3.3 V at low frequencies to 6.9 V at 60 kHz, is required to increase the rate of charging of the electrical double layer so that appreciable faradaic currents could flow during the short pulses. It is interesting to note that at the highest frequencies, luminescence ascribable to faradaic processes can be observed in times ($\sim$10 μsec) shorter than that necessary for complete charging of the electrical double layer in these experiments.

The ecl intensity is also affected by the concentrations of TH and PPD. The ecl intensity decreases slightly when the TH and PPD concentration is changed from 8 to 0.5 mM. When the concentrations of the reactants are above 10 mM, however, the ecl emission is small, highly erratic, irreproducible, and sometimes even absent. To estimate the relative intensity of the ecl of the PPD–TH system, an approximate comparison with DPA ecl was undertaken. The DPA system has recently been shown to have an ecl efficiency (photons
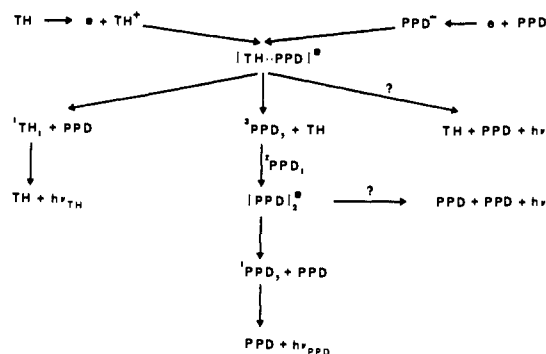
Figure 7. Proposed mechanism for ecl in the TH–PPD system.

emitted per radical ion annihilation) of about 0.1%.[18] In the same ecl cell, under similar conditions, the PPD–TH system shows an intensity at 430 nm, about an order of magnitude smaller than that of the DPA system.

Magnetic Field Effect. Previous experiments on the effect of magnetic field on ecl intensity[1,19] have led to the postulate that energy-sufficient reactions should show no field effect, while energy-deficient reactions should show a magnetic field effect, because of the involvement of triplet–triplet annihilation in the reaction. Results of a study of the effect of magnetic field on the ecl intensity of the peak at 435 nm for fields up to 7.5 kG are shown in Table I. Clearly, the ecl intensity here is independent of the field strength. We were unable to study a possible magnetic field effect of ecl at 340 nm, because the random deviations of the intensity of this relatively small wave were too large to obtain a reliable trend.

Table I. Effect of Magnetic Field on Ecl of
Thianthrene-2,5-Diphenyl-1,3,4-oxadiazole Solution[a]

Magnetic field, kG	Normalized ecl intensity	Av dev[b]
0.00	1.000	0.0042
1.51	0.9968	0.0039
3.12	0.9995	0.0016
4.70	0.9934	0.0009
6.15	0.9959	0.0027
7.50	0.9923	0.0007

[a] The solution contained 1.0 mM TH and 0.95 mM PPD in 0.1 M TBAP–acetonitrile. A three-electrode cell was employed, with the potential of the working electrode varied between +1.30 and −2.19 V vs. sce at $f = 10$ Hz. [b] Three measurements made at each field strength.

Ecl of TH Alone. A solution of TH alone in acetonitrile–TBAP in the absence of PPD shows very weak ecl emission when the electrode is stepped between +1.30 V (TH·+ production) and −1.4 to −2.4 V, with maximum emission occurring for steps to about −1.9 V. The emission is characterized by a broad band between 460 and 600 nm, with a peak at about 500 nm. TH is not reduced in the region scanned, and only a very small cathodic current is observed in cyclic voltammetric scans, so that the ecl emission is of a "preannihilation" type, and may involve small amounts

of products formed from TH·+. After 24 hr of continuous pulsing between +1.35 and −1.90 V at a frequency of 0.1 Hz, a new anodic peak at +1.20 V was found. This "preannihilation" emission was never larger than one-tenth of the PPD–TH emission and did not appear to be important in the mixed-system ecl, although some of the longer wavelength emission observed in the PPD–TH system may be from this source.

Ecl of PPD Alone. Very weak ecl is observed with acetonitrile–TBABF₄ solution containing only PPD upon stepping from the PPD⁻ peak potential to the foot of the PPD⁺ wave. Stepping only to the foot of the PPD oxidation wave was employed because the acetonitrile background decomposition potential moved in from +2.8 to about +2.3 V (vs. silver reference) when PPD was oxidized at +2.2 V, and products from the background reactions apparently quench the PPD ecl when the potential steps are extended to the PPD oxidation peak. The observed $^1PPD_1$ emission is very weak, and at an applied frequency of 2 Hz its intensity is approximately 1% of the corresponding peak in a TH–PPD mixture.

Ecl of PPD–10-Methylphenothiazine Mixture. Freed and Faulkner[3] used 10-methylphenothiazine (10-MP) as the oxidant parent in a study of the energy-deficient ecl of the fluoranthene–10-MP system. To investigate further the mechanism of the PPD emission in the TH–PPD system, attempts were made to observe ecl in acetonitrile solutions containing 2.5 mM PPD and 2.5 mM 10-MP with either TBAP or tetrabutylammonium fluoborate as supporting electrolyte. No emission characteristic of PPD fluorescence was found upon cycling between PPD⁻ and 10-MP⁺ (+1.0 V vs. Ag) formation. Very weak emission in the regions of 430 and 550 nm is observed, but this same weak ecl has also been seen in systems containing 10-MP alone and is apparently a preannihilation-type ecl resulting from oxidation products of 10-MP.[20] Similarly, in mixtures containing equimolar amounts of TH, PPD, and 10-MP, only the very weak ecl emission characteristic of 10-MP was observed, regardless of whether, in addition to PPD⁻, only 10-MP⁺ or both 10-MP⁺ and TH⁺ were electrogenerated. Because 10-MP²⁺ is formed at potentials where TH is oxidized to TH⁺, the role of the dication may also be of importance in this experiment.

Discussion

The general mechanism shown in Figure 7 can be proposed to account for the experimental observations. The annihilation reaction apparently leads to both excited singlet TH and triplet PPD (perhaps through an intermediate exciplex). Excited PPD singlet then arises from a triplet–triplet annihilation reaction. The extent of quenching of $^1PPD_1$ by TH is small, as seen from fluorescence measurements in mixtures of TH and PPD. This is true because TH fluorescence is characterized by a large Stokes shift so that the molar absorptivity, ϵ, for TH[6,21] in the region of PPD fluorescence is small and energy transfer from $^1PPD_1$ to TH is inefficient.

(18) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 9568 (1971).
(19) L. R. Faulkner, H. Tachikawa, and A. J. Bard, *ibid.*, **94**, 691 (1972).

(20) N. E. Tokel and A. J. Bard, unpublished results.
(21) L. Lang, Ed., "Absorption Spectra in the Ultraviolet and Visible Region," Vol. II, Academic Press, New York, N. Y., 1961, pp 387–388.

An alternate explanation of the formation of ^{1}PPD$_1$ can also be given. The failure to obtain PPD ecl in the PPD–10 MP experiment can be attributed to quenching of ^{3}PPD by 10-MP. Since the triplet level for 10-MP is 2.4 eV[3] and that for TH is 2.6 eV, this would locate the energy level of ^{3}PPD at about 2.5 ± 0.1 eV. Similar quenching of an electrogenerated fluoranthene triplet intermediate by *trans*-stilbene has been observed by Freed and Faulkner.[3] If the ^{3}PPD level is lower than that of TH, then the following sequence can be invoked to explain the emission of ^{1}PPD$_1$.

$$^1TH_1 \longrightarrow {}^3TH$$

$$^3TH + PPD \longrightarrow {}^3PPD + TH$$

$$2^3PPD \longrightarrow {}^1PPD_1 + PPD$$
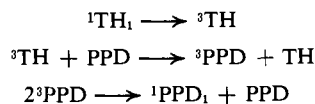
The rapid intersystem crossing of TH to the triplet state[6] is consistent with this mechanism. The disappearance of the PPD emission with increasing square-wave frequency can also be associated with the formation of the emitting species, ^{1}PPD$_1$, by secondary reactions which do not have sufficient time to occur within the short pulse lengths, although quenching of ^{3}PPD by the relatively higher radical ion concentrations existing during the short pulses is also possible. Possible candidates for the emission that occurs at wavelengths longer than that for TH singlet emission include excimers of TH and PPD or a PPD–TH exciplex. There appears to be no precedence for any of those species from previous spectroscopic work. Indeed, Lami and Laustriat[14] were unable to observe excimer emission in fluorescence of concentrated PPD, although related compounds (*e.g.*, PPO) did show excimer formation. Similarly, no previous reports of delayed fluorescence of PPD have been found.

Palladium(II)-Catalyzed Exchange and Isomerization Reactions. II. Allylic Ester Exchange Catalyzed by Palladium(II) Chloride in Acetic Acid[1]
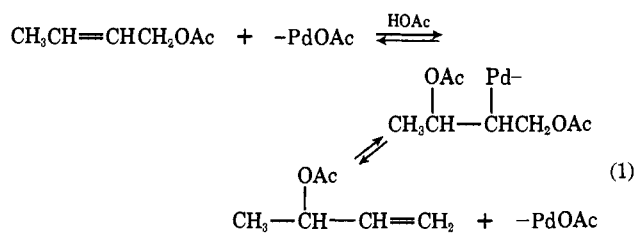
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Abstract: The exchange of allyl propionate with acetate in acetic acid to give allyl acetate has been found to obey the following rate expression: $-d[\text{allyl propionate}]/dt = [\text{Li}_2\text{Pd}_2\text{Cl}_6][\text{allyl propionate}]/[\text{LiCl}](k' + k'[\text{LiOAc}])$. Unsymmetrical allylic propionates such as crotyl and 3-buten-2-ol propionates exchange and undergo allylic isomerization simultaneously. This result is consistent with a mechanism involving addition of the elements of Pd(II) and acetate across the double bond (acetoxypalladation) followed by elimination of the elements of Pd(II) and propionate. The complete reaction sequence involves formation of a π complex between the olefin and Li$_2$Pd$_2$Cl$_6$ with release of LiCl to give a Pd(II) dimer π complex followed by attack of acetate to give the acetoxypalladation adduct in the rate-determining step, Li$_2$Pd$_2$Cl$_6$ + allyl ester $\rightleftarrows$ Li$_2$Pd$_2$Cl$_5$(allyl ester) + LiCl. Kinetic and ultraviolet spectral results indicate that a monomeric π complex is formed in larger quantities than the reactive dimeric π complex but is unreactive (Li$_2$Pd$_2$Cl$_6$ + 2 allyl ester $\rightleftarrows$ 2LiPdCl$_3$(allyl ester)). Trifluoroacetate esters exchange faster than propionate esters. Substitution on the double bond strongly inhibits exchange, indicating that steric effects are very important in the acetoxypalladation step.

The first paper[1] of this series described kinetic and mechanistic studies of vinyl ester exchange. It has been reported[3] that Pd(II) salts will also catalyze the exchange of allylic esters. This paper will be concerned with the kinetics and mechanism of the exchange of allylic propionate and trifluoroacetate esters with acetate in acetic acid.

A reaction which may be related to allylic exchange is allylic isomerization. Thus Pd(II) is reported[4,5] to catalyze the isomerization of allylic acetates, for instance, crotyl acetate to 3-buten-2-ol acetate. One mechanism that has been suggested[3,4] for this reaction involves an acetoxypalladation–deacetoxypalladation sequence. When crotyl acetate is the starting ester, the scheme is as follows

$$CH_3CH = CHCH_2OAc + -PdOAc \xrightarrow{HOAc}$$

$$\begin{array}{cc} OAc & Pd- \\ | & | \\ CH_3CH & -CHCH_2OAc \end{array}$$

$$\begin{array}{c} OAc \\ | \\ CH_3-CH-CH=CH_2 + -PdOAc \end{array} \qquad (1)$$

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