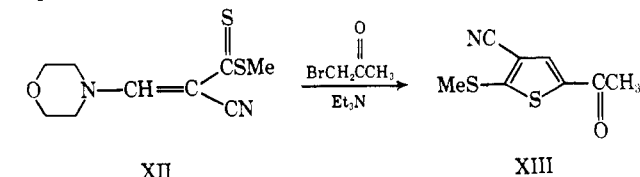


yield). The anilide III does not give a thiophene product with ethyl  $\alpha$ -bromoacetate.

The mechanism of this reaction we believe to proceed as follows: the dithioacrylate (VII) reacts with ethyl  $\alpha$ -bromoacetate to form salt IX, but in the presence of base is immediately converted to the sulfur ylide X and triethylammonium bromide. The ylide reacts intramolecularly to compound XI, which in the presence of base loses morpholine to produce the 2,5-disubstituted thiophene. All by-products are explainable by this mechanism as is the requirement of excess ethyl  $\alpha$ -bromoacetate and base.

The reaction was extended to the electronegatively substituted dithioacrylate ester XII. In this case, the expected 2-acetyl-4-cyano-5-thiomethylthiophene (XIII)



was isolated.

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#### Electrogenerated Chemiluminescence. IV. Magnetic Field Effects on the Electrogenerated Chemiluminescence of Some Anthracenes<sup>1</sup>

Sir:

Reports have recently appeared describing a substantial group of "energy-deficient" chemiluminescent electron-transfer reactions involving the ion radicals of various aromatic hydrocarbons.<sup>2,3</sup> The term "energy-

pounds of interest at a platinum electrode in DMF. The oxidation and reduction products are the ion radicals of the parent species, but the hydrocarbon cations are unstable in DMF.<sup>4-7</sup> The electrogenerated chemiluminescence of the anthracene<sup>6</sup> and DPA<sup>7</sup> systems in DMF has been discussed recently. In addition, Table I displays the energies of the hydrocarbon triplet and first excited singlet levels. Following the reasoning previously employed,<sup>2,3</sup> it is evident that the energy of the ion-radical annihilation between  $WB^{\cdot+}$  (the Wurster's Blue cation) and a hydrocarbon anion radical is indeed insufficient to produce the hydrocarbon in its first excited singlet. In contrast, this state is attainable in the reaction between  $DPA^{\cdot+}$  and  $DPA^{\cdot-}$ . Since the emission spectrum is always identical with the fluorescence spectrum of the hydrocarbon, one must classify the hydrocarbon-WB systems as energy-deficient.

The reactants for the magnetic field experiments were produced electrolytically from DMF solutions which were about 10 mM in the organic solutes. A small cell containing two platinum electrodes<sup>6</sup> was employed. The electrolysis source was a 10-cps square-wave generator whose output was adjusted to a value about midway between the voltage of maximum emission and the voltage for which emission was just detectable. This procedure assured that only the anion radical of the hydrocarbon and the cation radical of the most easily oxidized species in solution were formed at the electrodes. One then observes two light spikes per cycle. The emission intensity was recorded using an apparatus similar to that used in earlier experiments,<sup>3</sup> except the photomultiplier tube was removed 90 cm from the magnet to ensure that the detection system was unaffected by the field. The detection system was tested for magnetic field dependence by positioning its components exactly in their

Table I. Electrochemical and Spectroscopic Data

Compound (A)	$E_p$ (A <sup>+</sup> /A), V vs. sce	$E_p$ (A/A <sup>-</sup> ), V vs. sce	Lowest triplet, eV	First excited singlet, eV
WB	+0.24	(Not reduced)	...	...
Anthracene	+1.38	-1.96	1.8	3.2
DPA	+1.35	-1.89	1.6-1.8	3.0

deficient" denotes that the energy of the light produced is much greater than the enthalpy of the redox reaction for a single pair of reacting species producing ground-state products. We have examined the magnetic field dependence of the chemiluminescence intensity for two reactions in this category, *i.e.*, the reactions of the cation radical of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (WB) with the anion radicals of anthracene and 9,10-diphenylanthracene (DPA) in *N,N*-dimethylformamide (DMF). For comparison, we have also studied the field effects on one reaction which is not energy deficient, the mutual annihilation of the anion and cation radicals of DPA.

Table I summarizes the cyclic voltammetric peak potentials for oxidation and reduction of all the com-

operating configuration and allowing a leak of room light to enter the photomultiplier tube. This system was completely unaffected by the applied field, even at the highest photomultiplier sensitivity.

The results of these experiments are summarized in Figure 1. For solutions containing WB, the emission intensity increases with the applied field. This behavior contrasts markedly with that of the solution containing only DPA, where the field had no effect upon the emission intensity. The points for Figure 1 were taken in a random order. A zero-field intensity reading was obtained after each set of three data points measured at higher field strengths. The zero-

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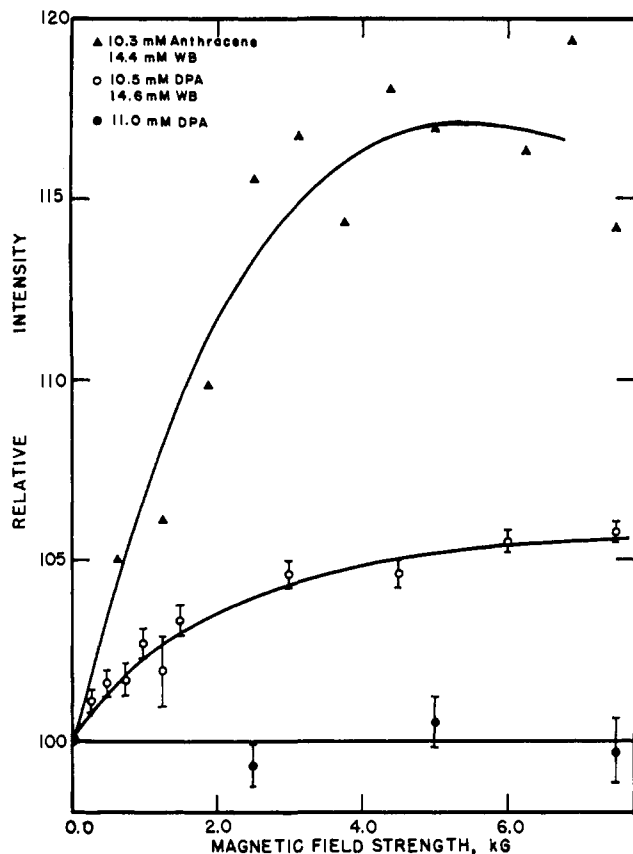


Figure 1. Effect of magnetic field on electrogenerated chemiluminescence. Solutions were all 0.2 *M* in tetra-*n*-butylammonium perchlorate. Error bars denote average deviations in the DPA experiments.

field value was reproducible throughout a given experiment. The field effect for a given system was reproducible whether the points were obtained in order of increasing, decreasing, or random field strengths; hence progressive heating of the solution, accumulation of impurities, etc., cannot account for the observed results.

Two conclusions may be drawn immediately from these observations. First, paramagnetic species are involved in at least one rate-controlling step for light emission in the energy-deficient case, and the rate of that step is field dependent. Secondly, either no paramagnetic species are involved in the rate-controlling steps for the light-producing process in the case of DPA alone, or, more likely, paramagnetic species are involved, but their behavior is unaffected by the field. Furthermore, unless one will admit field effects on the diffusion coefficients of reactants, the rate of a diffusion-controlled reaction cannot be altered by the field in the manner observed, and the rate-controlling steps for the energy-deficient reactions studied here quite probably are not entirely diffusion controlled. However, the case for which  $\text{DPA}^{\cdot+}$  is the oxidant may or may not have diffusion-controlled, rate-determining steps. These results cannot be attributed to field-induced level population changes, since at room temperature the level splittings are very small compared to  $kT$  at the field strengths employed here.

To rationalize the energy-deficient reactions, one usually postulates that the hydrocarbon triplet is formed in the radical-annihilation step. Then triplet-triplet

annihilation follows, creating a hydrocarbon molecule in its radiative first excited singlet state.<sup>2</sup> In contrast, the reaction involving annihilation of  $\text{DPA}^{\cdot+}$  and  $\text{DPA}^{\cdot-}$  is believed to result directly in a DPA molecule in its first excited singlet.<sup>8,9</sup> Since the radicals and triplets are paramagnetic, the electron-transfer steps and the triplet-triplet annihilation step could be influenced by the field.

It is pertinent to note that Johnson, *et al.*, have recently observed magnetic field effects of comparable magnitude on the rate of mutual annihilation of triplet excitons in anthracene.<sup>10</sup> The significance of their observations to the analogous solution phase process has not been investigated, but their work does provide a provoking precedent for magnetic field effects on kinetic processes. In any case Parker and his coworkers have provided substantial evidence to support the view that triplet-triplet annihilation is not generally a diffusion-controlled process for aromatic hydrocarbons.<sup>11,12</sup> Indeed, he has presented some evidence that reaction may occur *via* a resonance energy-transfer mechanism over larger distances than a molecular diameter.<sup>11</sup> Certainly, the triplet-triplet annihilation mechanism is an attractive explanation for the observed field behavior of these energy-deficient reactions.

We feel that these experiments have provided a novel tool with which to probe the mechanism of the ECL process. We are continuing our efforts toward satisfying some of the questions raised by these experiments.

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## Behavior of Xenon Trioxide in *t*-Butyl Alcohol

Sir:

Aqueous xenon trioxide reactions with tertiary alcohols are very slow as observed by Jaselskis and Warriner<sup>1</sup> and Rhodes and Blake.<sup>2</sup> In fact, in the absence of trace amounts of catalysts such as transition metal ions or other easily oxidizable impurities, *t*-butyl alcohol is not attacked by xenon trioxide. Kinetic studies of alcohol reactions with xenon trioxide suggest that the reaction intermediate may be an ester-like species which decomposes to yield organic products and xenon gas as observed by Krueger.<sup>3</sup> The greatest stability of the intermediate is observed with tertiary alcohols. Experiments to clarify the nature of xenon trioxide ester-like intermediates have been carried out in a tertiary alcohol system and are described as follows.

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