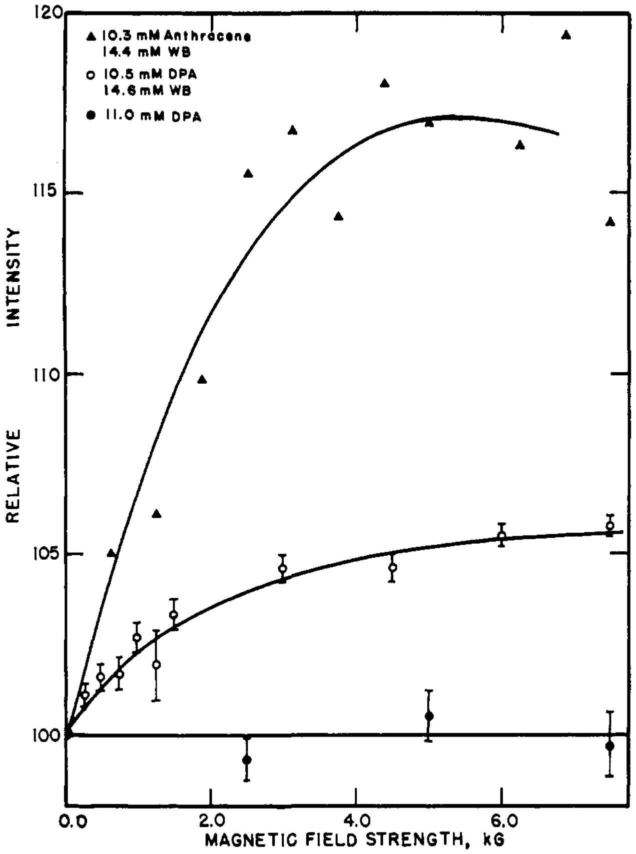

Figure 1. Effect of magnetic field on electrogenerated chemiluminescence. Solutions were all 0.2 *M* in tetra-*n*-butylammonium perchlorate. Error bars denote average deviations in the DPA experiments.

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 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.[2] In contrast, the reaction involving annihilation of DPA$\cdot^+$ and DPA$\cdot^-$ is believed to result directly in a DPA molecule in its first excited singlet.[8,9] 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.[10] 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.[11,12] Indeed, he has presented some evidence that reaction may occur *via* a resonance energy-transfer mechanism over larger distances than a molecular diameter.[11] 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[1] and Rhodes and Blake.[2] 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.[3] 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.

(1) B. Jaselskis and J. P. Warriner, *Anal. Chem.*, **38**, 563 (1966).

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(3) R. H. Krueger, Ph.D. Thesis, Loyola University, 1967.

A small aliquot of aqueous xenon trioxide–hydrofluoric acid solution containing not more than 20 mg of solid xenon trioxide was placed in a Teflon microbeaker and evaporated under vacuum leaving solid xenon trioxide powder. The beaker containing the xenon trioxide was placed behind an explosion shield and approximately 4 ml of pure *t*-butyl alcohol was poured into the microbeaker rapidly. After 1 min the solution was carefully stirred by alternately drawing in and discharging from a dropper. It was necessary to stir without touching the solid xenon trioxide to avoid exploding the sample. Most of the supernatant was transferred to a volumetric flask using the medicine dropper technique, and new portions of *t*-butyl alcohol were added until all xenon trioxide dissolved. Trace impurities of transition metal ions, peroxides, or the deformations of the Teflon beaker due to previous decomposition of xenon trioxide caused the sample to explode. Traces of HF had no apparent effect.

The amount of xenon trioxide in *t*-butyl alcohol was determined iodometrically. The stability of the pure xenon trioxide solutions was followed for over a period of 6 weeks showing no loss in oxidizing power, but in the presence of trace amounts of impurities the concentration of xenon trioxide diminished on standing. Since the xenon trioxide was prepared from the xenon hexafluoride hydrolysate, the fluoride ion impurity was determined using the Orion fluoride activity electrode. The amount of fluoride found in *t*-butyl alcohol–xenon trioxide solutions did not exceed 1% of the xenon trioxide concentration. This fact eliminates the possibility of the presence of a significant amount of the $HF\cdot XeO_3$ species. The alkali salt of $HF\cdot XeO_3$, as $CsFXeO_3$, was reported by Selig[4] and Spittler, *et al.*[5]

The acid character of xenon trioxide and that of glacial acetic acid in *t*-butyl alcohol was determined by titrating aliquots with the standard potassium or rubidium *t*-butoxide in *t*-butyl alcohol using a pH meter and glass–calomel electrodes. The titration curves for both xenon trioxide and glacial acetic acid are shown in Figure 1. In both titrations the end point occurred at a 1:1 molar ratio of the substance titrated to the butoxide added. During the titration of xenon trioxide, an insoluble precipitate was formed which slowly decomposed on standing. The decomposition of this precipitate was followed not only by the "hi-low" titration method, but also by time-of-flight mass spectrometry. The wet analysis of the salt on standing indicated a gradual loss of the titer. Mass spectrometric measurements initially showed a substantial loss of *t*-butyl alcohol and small amounts of xenon and oxygen; then on gentle heating, the sample yielded more *t*-butyl alcohol and some acetone, xenon, oxygen, and carbon dioxide. The precipitate did not explode and showed no shock sensitivity, which is quite contrary to the alkali xenates.

The precipitate was isolated by centrifugation and was washed with ethyl ether. After drying for approximately 3 min the samples were analyzed immediately for the oxidation equivalent and for potassium or rubidium. The average values of the oxidation equivalents for potassium and rubidium salts were 61.3 ± 2 and 69 ± 2, respectively, corresponding to the calculated formula weights of 367 ± 12 for potassium salt and 413 ± 12 for the rubidium salt. These values compare well with the empirical formulas of $t\text{-BuO–XeO}_2\text{–OK}\cdot t\text{-BuOH}$ (363) and $t\text{-BuO–XeO}_2\text{–ORb}\cdot t\text{-BuOH}$ (410). However, it should be pointed out that these analyses cannot exclude the possibilities that the resulting salts may be $KHXeO_4\cdot 2\ t\text{-BuOH}$, $(t\text{-BuO})_2\text{XeO(OH)OK}$, or $(\text{t-BuO})_2\text{XeO}_2\cdot \text{K}^+\text{OH}^-$.

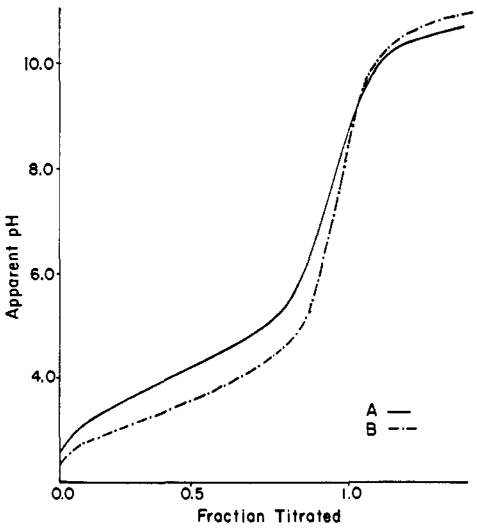

Figure 1. Apparent pH *vs.* fraction titrated. Curve A represents xenon trioxide and curve B glacial acetic acid.

Attempts to isolate a proposed xenon trioxide–t-butyl alcohol ester failed. In fact, the loss of xenon trioxide during the concentration of dilute xenon trioxide solutions was observed when the xenon trioxide concentration reached approximately 0.4 *M*. It appears that the hypothetical ester-like species decompose in the vapor phase.

The nmr spectrum of approximately 0.3 *M* xenon trioxide in the *t*-butyl alcohol–D_2O system showed no bands for the methyl protons. However, it indicated a marked catalytic effect on the hydroxyl proton exchange.

The kinetic data, titrimetric studies, and analysis of the corresponding unstable salts suggest that the behavior of xenon trioxide in *t*-butyl alcohol may be best explained by the following reactions.

$$XeO_3 + t\text{-BuOH} = t\text{-BuOXeO}_3\text{H (solvated)}$$

$$t\text{-BuOXeO}_3\text{H} + t\text{-BuOK} = t\text{-BuOXeO}_3\text{K}\cdot t\text{-BuOH}$$

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Non-Coulomb Variation of Ionic Association in Polar Solvents

Sir:

The association constant K_A of rigid charged spheres of diameter a in a continuum of dielectric constant D is given by the equation[1]

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