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## Physical and Inorganic Chemistry

### Electrogenerated Chemiluminescence. VII. The Influence of an External Magnetic Field on Luminescence Intensity

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**Abstract:** The effect of an external magnetic field on the intensity of electrogenerated chemiluminescence (ecl) was determined for nine systems involving anthracene, 9,10-diphenylanthracene (DPA), rubrene, 1,3,6,8-tetraphenylpyrene (TPP), and fluoranthene as emitting species in *N,N*-dimethylformamide (DMF) solutions. Enhancements in emission intensity up to 27% with increasing field strength were noted for the energy-deficient oxidations of anthracene, DPA, rubrene, and TPP anion radicals by Wurster's Blue cation, for the energy-deficient oxidation of fluoranthene anion radical by the cation radical of 10-methylphenothiazine, and for the energy-deficient reduction of the rubrene cation radical by the anion radical derived from *p*-benzoquinone. No field effect was seen on luminescence arising from the apparently energy-sufficient mutual annihilation of the anion and cation radicals derived from DPA. The field enhanced luminescence from the reaction between the rubrene anion and cation radicals, but it exerted no effect on the intensity of emission from the TPP anion-cation radical annihilation. These results have been interpreted as reflecting a dual mechanism for chemiluminescent electron-transfer processes which divides on or about the line of energy sufficiency. In particular it is suggested that the field effect accompanying luminescence from energy-deficient systems arises from an inhibition by the field of the rate of quenching of emitter triplets by radical ions. Thus, the results are consistent with the triplet mechanism for luminescence from energy-deficient systems. This interpretation also indicates that energy-sufficient systems yield luminescence without required triplet intermediates. For the two marginal systems involving rubrene and TPP alone, it is suggested that the rubrene anion-cation annihilation gives rise to luminescence predominantly *via* the triplet mechanism, while the TPP anion-cation reaction may be essentially energy sufficient, and that most luminescence from this process arises by direct population of the emitting state.

Early in 1969, we first reported our observation that an external magnetic field exerts unusual effects on the intensity of electrogenerated chemiluminescence (ecl) from two widely studied systems.<sup>1</sup> Specifically, an enhancement of luminescence intensity was seen with increasing field strength for the light arising from the oxidations of the anthracene and 9,10-diphenylanthracene (DPA) anion radicals by the Wurster's Blue cation (the cation radical of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine, WB) in *N,N*-dimethylformamide (DMF). In an interesting contrast, the intensity of light accompanying the mutual annihilation of DPA anion and cation radicals was unaffected

by the field. The two reactions involving the Wurster's Blue cation as an oxidant are energy deficient in the sense that the energy contained in a single emitted photon is greater than the energy available from a single electron-transfer event. The third system is apparently energy sufficient. Thus, the contrast in the field effect on luminescence from these two kinds of systems was taken as evidence for long-suspected mechanistic differences between them.<sup>2-4</sup> Specifically, the results suggested that there exists at least one elementary reaction in the mechanism for luminescence from the energy-deficient systems whose rate is influenced by the

(1) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 209 (1969).

(2) K. S. V. Santhanam and A. J. Bard, *ibid.*, **87**, 139 (1965).

(3) A. Weller and K. Zachariasse, *J. Chem. Phys.*, **46**, 4984 (1967).

(4) G. J. Hoytink, *Discuss. Faraday Soc.*, No. **45**, 14 (1968).

field and is a primary factor governing emission intensity. Presumably these field-influenced reactions involve paramagnetic species. Conversely, the mechanism for luminescence from the energy-sufficient system apparently does not contain a field-influenced step or alternatively, the field-influenced steps are not primary factors controlling emission intensity.

In the years just prior to this early work, Johnson, *et al.*, had discovered magnetic field effects on the rate of triplet-triplet annihilation in crystalline anthracene.<sup>5-8</sup> Thus, we originally suggested that our observations might be manifestations of (and the first direct evidence for) triplet-triplet annihilation as an intermediate elementary reaction in the energy-deficient emission scheme. The process had been widely suggested in prior years as the energy-doubling step required to reconcile the energy difference between electron transfer and excitation of the emitting species to its first excited singlet state. Certainly, the solid-state results pointed to a field dependence for the rate of fluid-solution triplet-triplet annihilation, even though none had been seen at the time.

This supposition was later discredited by a study of the effect of a magnetic field on the anthracene annihilation rate in fluid solution *via* the field effect on the resulting delayed fluorescence. The annihilation rate in DMF, cyclohexane, and methylene chloride was inhibited at all field strengths up to 10,000 G.<sup>9</sup> These observations have recently been corroborated by Avakian, *et al.*, who concluded that the anthracene annihilation rate in ethanol also declines monotonically with increasing field strength.<sup>10</sup> Thus, one cannot explain the enhancement of ecl intensity for the anthracene-WB system in terms of an increase in the triplet-triplet annihilation rate. Moreover, Merrifield's theoretical studies have indicated that one cannot hope to invoke that explanation to deal with an enhancement in any system.<sup>11</sup>

In a third communication, we have more recently suggested that the key to understanding the magnetic effects may lie in the role that the radical ions play as quenching agents in the overall kinetic scheme for emission.<sup>12</sup> Hoytink suggested several years ago that radical ions generally should be effective quenchers of excited states.<sup>4</sup> Since any excited states generated in ecl must be formed in a region cooccupied by ion radicals, the rate of rapid quenching by those species would doubtlessly be a primary factor controlling the intensity of luminescence arising from any mechanism requiring triplet intermediates. Of course, excited singlet states would be quenched to a lesser degree because their lifetimes are typically quite short. Thus, accompanying this hypothesis there is the expectation that fundamental differences exist between the schemes for energy-

deficient and energy-sufficient luminescence regarding the importance of radical ion quenching effects.

Hoytink's hypothesis has been bolstered by evidence, provided by two groups, that anthracene triplet excitons are quenched by radicals introduced into the crystalline material by irradiation.<sup>13,14</sup> Furthermore, the efforts of Ern and Merrifield have provided theoretical and experimental evidence that quenching of triplet excitons by the (doublet) radicals is inhibited by a magnetic field.<sup>14</sup>

By adding Wurster's Blue perchlorate to anthracene solutions in methylene chloride, we were able to extend the test of Hoytink's hypothesis to fluid media.<sup>12</sup> The considerably shortened delayed fluorescence lifetimes observed in the presence of Wurster's Blue showed that particular ion radical to be an effective triplet quencher; indeed, it probably quenches nearly at the diffusion-controlled rate. Moreover, magnetic studies revealed that in the presence of Wurster's Blue at  $10^{-7}$  M or greater, the anthracene-delayed fluorescence intensity increases with field strength. This result was interpreted as reflecting an inhibition by the field of the rate of anthracene triplet quenching by Wurster's Blue. Apparently, the effect of the consequent longer triplet lifetimes more than offsets the decline in annihilation rate at higher applied fields. The magnetic field effects on the three previously examined systems can then readily be explained in terms of the usual mechanisms simply by recognizing the importance of radical ions as triplet quenchers.

A significant benefit of magnetic field studies, if the proposed hypothesis is correct, is that they provide a means by which one can distinguish those systems that depend heavily upon the "triplet route" to luminescence from those that do not. We have, therefore, undertaken an extension of the earlier studies using improved instrumentation and techniques, so that the plausibility of the hypothesis might be examined within the context of results obtained from a larger number of well-behaved systems.

## Experimental Section

The anthracene used in this work was blue-violet fluorescence grade material supplied by Matheson Coleman and Bell and was used without further purification. Aldrich Chemical Co. manufactured the 9,10-diphenylanthracene (mp 250-251°), which was also used as received. Rubrene (mp >300°) and 1,3,6,8-tetra-phenylpyrene (TPP, mp 295-298°) were also obtained from Aldrich Chemical Co. Both compounds were fractionally resublimed twice before use. The fluoranthene was produced and purified by the Aldrich Chemical Co. (zone refined, 99.9+%, mp 100.30°) and was used as received. Eastman Organic Chemicals manufactured the dihydrochloride of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine which was used subsequently as a source of the free amine. After the salt had been neutralized with NaOH solution, the free base was extracted with benzene. The benzene was then evaporated, and the amine was purified by two sublimations *in vacuo*. Eastman Organic Chemicals also supplied the 10-methylphenothiazine (10-MP, mp 99-100°). It was recrystallized three times from benzene beforehand. Matheson Coleman and Bell produced the *p*-benzoquinone (BQ) utilized here; it was purified by two sublimations *in vacuo*. In all experiments, tetra-*n*-butylammonium perchlorate (TBAP) served as the supporting electrolyte. The polarographic grade salt was obtained from Southwestern Analytical Chemicals and was dried *in vacuo* at 100° for 48 hr before use. The TBAP concentrations were always 0.1 M. *N,N*-Dimethyl-

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(6) R. E. Merrifield, *Accounts Chem. Res.*, **1**, 131 (1968).

(7) P. Avakian and R. E. Merrifield, *Mol. Cryst.*, **5**, 37 (1968).

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(9) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6495 (1969).

(10) P. Avakian, R. P. Groff, R. E. Kellogg, R. E. Merrifield, and A. Suna in "Organic Scintillators and Liquid Scintillation Counting," Academic Press, New York, N. Y., 1971, pp 499 ff.

(11) R. E. Merrifield, *J. Chem. Phys.*, **48**, 4318 (1968).

(12) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 6497 (1969).

(13) S. Z. Weisz, P. Richardson, A. Cobas, and R. C. Jarnagin, *Mol. Cryst.*, **3**, 168 (1967).

(14) V. Ern and R. E. Merrifield, *Phys. Rev. Lett.*, **21**, 609 (1968).

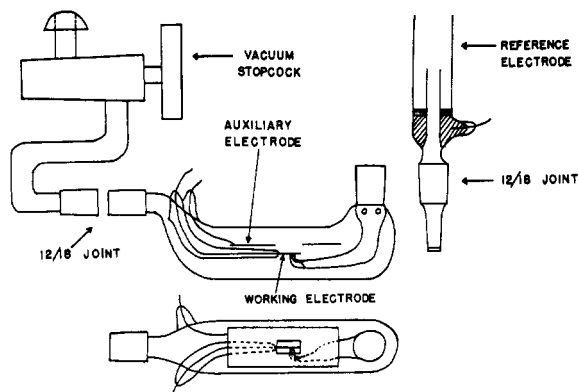


Figure 1. Cell used for generation of luminescence at controlled potential.

formamide supplied by Matheson Coleman and Bell (bp 152–154°) was used as the electrochemical solvent. It was purified by a published procedure and stored permanently under a helium (99.995%) atmosphere.<sup>15</sup>

The electrolysis cell employed for the ecl emission measurements is shown in Figure 1. The working electrode is a 1-cm length of Pt wire (0.46-mm diameter). A graded seal insulates the lead-in portion from the bulk of the solution and provides for an external connection. The auxiliary electrode is made of Pt foil (15 × 45 mm) which is attached to a Pt wire inserted through a graded seal in the Pyrex cell wall. One views the working electrode from above the cell, through the window in the auxiliary electrode. This arrangement effectively eliminates contributions to the photodetector signal resulting from light generated at the auxiliary electrode. An aqueous sce serves as the reference electrode. It is connected to the solution *via* an internal agar salt bridge which itself joins an additional salt bridge filled with the working solution. The capillary tip of the second bridge is located less than 0.5 mm from the working electrode. This arrangement helps to eliminate leakage of water from the sce into the solution bulk and to reduce the effects of uncompensated resistance.

Solutions were prepared in the auxiliary preparation vessel shown in Figure 2. After the measured reagents were placed in the test tube at the bottom of the apparatus, they were degassed. The solvent was then introduced from its pressurized storage flask, and the components were stirred magnetically under helium atmosphere until dissolution had occurred. Finally, the solutions were degassed by four freeze–pump–thaw cycles.

During the pumping phase of the final cycle, the cell was pumped out through the auxiliary preparation vessel to about  $10^{-5}$  Torr and filled with about 0.5 atm of helium. The stopcock separating the vessel from the cell was closed. After the sample had melted, helium was introduced into the vessel and the vessel was inverted. When the stopcock to the cell was opened, the solution filled the cell. Finally, the reference electrode was placed into the cell under a positive helium pressure.

Electrode potentials were controlled by a Wenking Model 61RH fast-rise potentiostat. The desired potential program was generated by a Wavetek Model 114 function generator operating in the square-wave mode at 10 Hz, but an auxiliary programmer served to trigger the function generator and the oscilloscope. A Fairchild Model 7050 digital voltmeter was used to monitor the working electrode potential.

Cyclic voltammetric data were gathered with a Princeton Applied Research Model 170 electrochemistry system using a three-electrode cell of conventional design. A Pt disk microelectrode was employed in all measurements. Solutions used for this work were also deaerated by the freeze–pump–thaw method.

The magnetic field studies were carried out in the phosphorimeter described by Faulkner and Bard.<sup>16</sup> This instrument was designed and constructed especially to operate with the sample immersed in a magnetic field, and the detection system has been demonstrated to have a response which is independent of the magnetic field at strengths below 8000 G. Furthermore, the high light-gathering

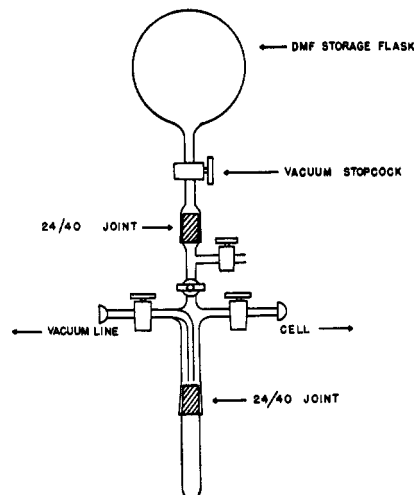


Figure 2. Auxiliary solution preparation vessel.

power of the optical train which monitors sample emission serves these experiments quite usefully. When the ecl intensity measurements were carried out, the chopper was locked so that the optical path from the sample to the phototube was always clear. For studies of systems featuring emission by anthracene, DPA, TPP, and fluoranthene, a Corning No. 5030 glass filter (C.S. 5-57), which passes radiation with wavelengths between 350 and 520 nm,<sup>17</sup> was inserted in this optical train. However, rubrene emission was filtered by Corning No. 3484 glass (C.S. 3-68), which transmits only light of wavelength greater than 525 nm.

The detector was a Dumont Model 6467 end-window photomultiplier. Its photocurrent was measured across a 100-ohm resistor using a Tektronix Type 564 storage oscilloscope.

The magnet which furnished the field in which the sample was immersed was manufactured by the Harvey–Wells Corp. A power supply similar to the Harvey–Wells Model HS-1050 servo power supply provided a regulated but variable current to the magnet. Field strengths up to 7500 G were applied to the samples.

Finally, an Aminco–Bowman spectrophotofluorometer was used to obtain ecl spectra from the various systems.

## Results

In each experiment discussed here, the two reactant radical ions were generated alternately from their aromatic precursors during several cycles of a 10-Hz square-wave potential control program. The working electrode potentials that served as the alternate limits of the program were chosen as values in the diffusion-limited regions of the current–potential curves for reduction of the most easily reduced and for oxidation of the most easily oxidized one. Thus, in each case the reactant ions were exclusively the anion and cation radicals formed with greatest facility. The electron-transfer reaction occurred in the diffusion layer adjacent to the working electrode, and emission was observed as a series of spikes, one of which followed each change in potential.

In each study described here, the intensity of luminescence has been taken as the height of a selected pulse in this train. The pulse chosen for repeated measurement was selected solely for its intensity reproducibility at zero field strength. In several systems, especially those featuring unstable cations, one observes a large pulse and a small one during each cycle in the potential program.<sup>18</sup> In each case where this occurs, the larger pulses were found to be more reproducible and were always employed for the measurements displayed here.

(15) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968); **91**, 2411 (1969).

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

(17) C. W. Sill, *Anal. Chem.*, **33**, 1584 (1961).

(18) S. A. Cruser and A. J. Bard, *J. Amer. Chem. Soc.*, **91**, 267 (1969).

Ordinarily, the pulse chosen for measurement was within the first dozen cycles. Nevertheless, one should realize that the essentials of the results were unchanged regardless of which pulse was employed; pulse selection served only to improve precision. In any system there were always several pulses that could have served this purpose equally well.

Even aside from consistently measuring the same pulse in the train, the procedure used to obtain the results required rigorous regularity to yield satisfactory precision. The solution was typically electrolyzed for about 20 cycles (2 sec) during each measurement. The peak height was then recorded directly from the oscilloscope screen. Experience proved that the interval between measurements ought to be no less than 2 min so that convection and diffusion processes could homogenize the solute concentrations at the electrode-solution interface. Again, in precision's interest, this interval was held constant. Intensity measurements at zero field were habitually alternated with those at higher field, and the order of higher field strengths was usually random with time. The intensity recorded at a given field strength was divided by the average of the two adjacent zero-field intensity values to yield the relative intensities plotted in the accompanying figures. The same results were obtained for each system whether the measurements were recorded in order of increasing, decreasing, or random field strengths. This fact precludes the possibility that the effects observed are merely temporal artifacts.

All the systems studied feature chemiluminescence spectra that are characteristic of emission from the first excited singlet state of the solute hydrocarbon. Complications in the magnetic field behavior resulting from multiple emitters are, therefore, not present.

Electrochemical characteristics of the eight compounds used in this work are outlined in Table I. The

Table I. Cyclic-Voltammetric Data<sup>a</sup>

Compound (R)	Reduction		Oxidation	
	$E_p$ (R/R <sup>·-</sup> ), V vs. sce	Scan rate, V/sec	$E_p$ (R/R <sup>·+</sup> ), <sup>b</sup> V vs. sce	Scan rate, V/sec
Anthracene	-2.00	0.258	+1.36*	0.224
DPA	-1.89	0.228	+1.35*	0.228
TPP	-1.83	0.200	+1.25*	0.200
Fluoranthene	-1.76	0.100	(Not oxidized)	
Rubrene	-1.48	0.249	+0.97*	0.249
BQ	-0.52	0.248	(Not oxidized)	
10-MP	(Not reduced)		+0.82	0.100
WB	(Not reduced)		+0.24	0.220

<sup>a</sup> For  $10^{-4}$ - $10^{-3}$  M solutions in DMF containing 0.1 M TBAP.

<sup>b</sup> An asterisk denotes chemical irreversibility indicated; see text.

cyclic-voltammetric peak potentials for the first reduction and oxidation waves in DMF solution are listed in the second and fourth columns, respectively. The scan rates at which the peak potentials were obtained are given in the third and fifth columns, and peak potentials are marked with an asterisk if cyclic voltammetry indicates chemical irreversibility at the recorded scan rate. Although these data were obtained using solute concentrations ranging from  $10^{-4}$  to  $10^{-3}$  M (usually depending on compound solubility), the peak potentials are independent of concentration within this range. Thus,

their utility for the enthalpy calculations (*vide infra*) is not compromised by variations in concentration. When one takes these potentials together with the procedure outlined above for setting the potential-control program, one observes that the hydrocarbon radical ions were always the reactants in the ecl process unless WB, 10-MP, or BQ was also present. The cation radicals of WB or 10-MP were the oxidants generated in the presence of those compounds, and the BQ anion radical acted as the reductant whenever BQ was available.

The nine systems investigated using these substances as solutes are listed in Table II. The third column lists

Table II. Reaction Enthalpies and Spectroscopic Data

Reactants		$-\Delta H^\circ$ , eV	Hydrocarbon energy levels	
Reductant (R <sup>·-</sup> )	Oxidant (R' <sup>·+</sup> )		$E_s$ , eV <sup>a</sup>	$E_T$ , eV
Anthracene (-)	WB (+)	2.08	3.20	1.8 <sup>b</sup>
DPA (-)	DPA (+)	3.08	3.00	1.8 <sup>b</sup>
DPA (-)	WB (+)	1.97	3.00	1.8
Rubrene (-)	Rubrene (+)	2.29	2.30	(1.1-1.2) <sup>c</sup>
Rubrene (-)	WB (+)	1.56	2.30	(1.1-1.2)
BQ (-)	Rubrene (+)	1.33	2.30	(1.1-1.2)
TPP (-)	TPP (+)	2.92	2.95	(2.0) <sup>d</sup>
TPP (-)	WB (+)	1.91	2.95	(2.0)
Fluoranthene (-)	10-MP (+)	2.42	3.0	2.3 <sup>e</sup>

<sup>a</sup> From fluorescence spectra in DMF. <sup>b</sup> J. S. Brinen and J. G. Karen, *Chem. Phys. Lett.*, **2**, 671 (1968). <sup>c</sup> Estimated from the value for tetracene. See R. E. Visco and E. A. Chandross, *Electrochim. Acta*, **13**, 1187 (1968). <sup>d</sup> Estimated from the pyrene triplet energy as given by D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949). <sup>e</sup> E. Clar and M. Zander, *Chem. Ber.*, **89**, 749 (1956).

the enthalpy of the charge-transfer reaction that yields the neutral reactant precursor molecules in their ground states. This figure has been estimated according to a procedure on the relationship of half-reaction emf to free energy.<sup>3,4</sup> It is rigorously true that the standard enthalpy of the ecl redox process is given at constant temperature by

$$-\Delta H^\circ = E^\circ(\text{R}'/\text{R}'^{\cdot+}) - E^\circ(\text{R}/\text{R}^{\cdot-}) - T\Delta S^\circ \text{ (eV)} \quad (1)$$

wherein the  $E^\circ$  values are the standard reduction potentials for the two half reactions comprising the redox process. The remaining symbols have their usual meanings. Unfortunately, the standard potentials are not easily obtained experimentally; hence an approximate form of eq 1 must be employed.

The standard potentials for the half reactions required here can be reliably estimated from the cyclic-voltammetric peak potentials listed in Table I. Nicholson and Shain have shown that for a fast, chemically reversible, one-electron electrode process involving oxidized and reduced forms having equal diffusion coefficients, the magnitude of  $E_p$  will exceed that of the standard potential by only 28.5 mV.<sup>19</sup> Thus, if both half reactions meet these kinetic criteria, the difference between their peak potentials will be 0.06 V larger than the difference between their standard potentials. Peover has pointed out that heterogeneous charge transfer rates for aromatic ion precursor couples are among

(19) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

the fastest known.<sup>20</sup> Furthermore, it probably is valid to assume that the ions and their precursors have equal diffusion coefficients, especially since the voltage error introduced by unequal coefficients is only about 3% of the logarithm of the ratio of the coefficient.<sup>19</sup> Thus, whatever error is introduced into the approximation

$$E^\circ(\text{R}'/\text{R}'\cdot+) - E^\circ(\text{R}/\text{R}\cdot-) = E_p(\text{R}'/\text{R}'\cdot+) - E_p(\text{R}/\text{R}\cdot-) - 0.06 \text{ (V)} \quad (2)$$

probably arises from radical ion instability. In such a case, the magnitude of  $E_p$  will be less than the magnitude of  $E_p$  seen for the perfectly reversible case by an amount which depends upon the ratio of the ion decay rate to the voltammetric scan rate.<sup>19</sup> Thus, using an  $E_p$  value for a half reaction involving appreciable cation decay creates a tendency for eq 2 to underestimate both the difference in standard potentials and, subsequently,  $-\Delta H^\circ$ . Such a situation has arisen here in the four cases in which cation radicals of DPA, TPP, and rubrene have been used as oxidants for the ecl reaction. Since reversal peaks can be seen in the anodic cyclic voltammograms for these compounds, the  $E_p$  values measured for the oxidations probably differ from the reversible values by no more than 0.05 V. In the case of rubrene, the cation radical is very nearly stable on the time scale employed for these measurements; hence the effect of cation decay probably contributes a negligible uncertainty in the estimate of  $-\Delta H^\circ$ .

Concern for these small corrections in  $-\Delta H^\circ$  is rendered at least partially academic by the reliability with which the  $T\Delta S^\circ$  term in eq 1 is known. In principle it can be evaluated from the temperature dependence of the half reaction potentials, but the term is very small, and measurement precision is not good. Relying on such measurements carried out with a series of aromatic hydrocarbons, Hoytink has asserted that the term is no larger than 0.2 eV.<sup>4</sup> More recently, Visco and Chandross have reported similar measurements for the rubrene redox couples in benzonitrile, and they found that the  $T\Delta S^\circ$  term for the rubrene anion-cation reaction in that solvent was *ca.* (but possibly less than) 0.1 eV.<sup>21</sup> Another recent estimate based on low-temperature electrochemical measurements of aromatic hydrocarbons in aprotic solvents yields a value close to 0.2 eV.<sup>22</sup> Thus, it seems wisest to use here a value of 0.1 eV while simultaneously recognizing an uncertainty of 0.1 eV in the term. Of course, this margin of uncertainty will then propagate to the enthalpy as calculated from eq 3. This relationship is the approximate form

$$-\Delta H^\circ = E_p(\text{R}'/\text{R}'\cdot+) - E_p(\text{R}/\text{R}\cdot-) - 0.16 \text{ (eV)} \quad (3)$$

of eq 1 that has been used to obtain the enthalpy data listed in Table II.

When one compares these estimates to the energies of the first hydrocarbon excited singlet states, one observes that only one reaction, *viz.*, the DPA anion-cation charge-transfer reaction, is fairly clearly energetic enough to populate the emitting singlet directly. Especially when one recalls that the enthalpy estimate

(20) M. E. Peover, *Electroanal. Chem.*, **2**, 1 (1967).

(21) R. E. Visco and E. A. Chandross, *Electrochim. Acta*, **13**, 1187 (1968).

(22) R. P. VanDuyne and C. N. Reilley, private communication.

for this process may be slightly low, it seems likely that even within the limits of uncertainty the reaction deserves to be labeled energy sufficient. The six reactions involving radicals derived from different precursors are doubtlessly unable to populate the hydrocarbon first excited singlet, hence they must be classified as energy deficient. The remaining two processes, the anion-cation annihilations of TPP and rubrene, are so marginal that one cannot rightly venture a label, even considering the likelihood that the enthalpy for the TPP reaction has probably been underestimated.

In the fifth column, Table II also shows the lowest hydrocarbon triplet state for each reacting system. That state is plainly accessible to all of the redox processes studied. The singlet and triplet states of WB (at 3.5<sup>23a</sup> and 2.7 eV,<sup>23b</sup> respectively) and of BQ (at 2.8<sup>24a</sup> and 2.3 eV,<sup>24b</sup>) are inaccessible to any reaction studied here from which these molecules result. The same is true of the first excited singlet state of 10-MP (at 3.4 eV in DMF), but the lowest 10-MP triplet may well be an accessible state for the fluoranthene (-)-10-MP (+) reaction. The energy of the lowest triplet state of phenothiazine is 2.4 eV,<sup>25</sup> and if one assumes the same figure applies to 10-MP, it is plain that the charge-transfer process in question yields very nearly the energy needed for that excitation. Nevertheless, emission is apparently observed only from fluoranthene. Freed and Faulkner have discussed the probable fate of any 10-MP triplets which might be generated by the process, and they have suggested that 10-MP triplets probably would be entirely quenched by fluoranthene, which has a lower lying triplet.<sup>26, 27</sup>

The effect of an externally applied magnetic field on the ecl intensity from the three systems involving anthracenes using a two-electrode cell configuration has been reported previously. Essentially, identical field effects are observed for the DPA alone system and DPA-WB system when the three-electrode cell and controlled-potential programming is employed. These systems show a significant enhancement by the field is observed for the two systems in which Wurster's Blue is the oxidant; no effect is seen for the system containing only DPA. Unfortunately, no data could be taken for the anthracene cation-anion annihilation because side reactions of the anthracene cation radical result in multicomponent chemiluminescence spectrum.<sup>15, 28</sup>

Figure 3 shows the results obtained with rubrene containing systems, Figure 4 presents data for systems containing TPP, and Figure 5 exhibits results gathered with the fluoranthene-10-MP solutions. Enhancements in ecl intensity are seen in each case with increasing field strength, except for the mutual annihilation of TPP anion and cation radicals. The data for the latter suggest that either no field effect on ecl intensity is observed or there is an extremely slight decrease of luminescence with increasing field strength.

(23) (a) Singlet energy from fluorescence measurements in DMF; (b) D. W. Skelly and W. H. Hamill, *J. Chem. Phys.*, **43**, 3497 (1965).

(24) (a) Singlet energy obtained from absorption measurements with DMF solutions; (b) J. M. Hollas, *Spectrochim. Acta*, **20**, 1563 (1964).

(25) J. M. Lhoste and J. B. Mercelle, *J. Chim. Phys. Physicochim. Biol.*, **65**, 1889 (1968).

(26) D. J. Freed and L. R. Faulkner, *J. Amer. Chem. Soc.*, **93**, 2097 (1971).

(27) D. J. Freed and L. R. Faulkner, *ibid.*, **93**, 3565 (1971).

(28) T. C. Werner, J. Chang, and D. M. Hercules, *ibid.*, **92**, 763 (1970).

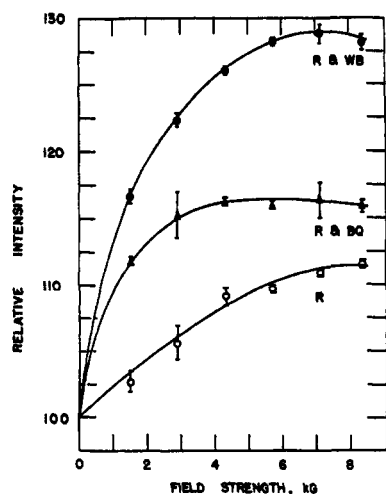


Figure 3. Magnetic field effects on luminescence from systems containing rubrene as an emitter. Error bars denote average deviations. Reactants: (●) rubrene anion and Wurster's Blue, (▲) rubrene cation and BQ anion, (○) rubrene anion and cation radicals. The solutions were 0.1 M TBAP in DMF containing 1.0 mM rubrene and 2.4 mM *p*-benzoquinone or 1.5 mM WB.

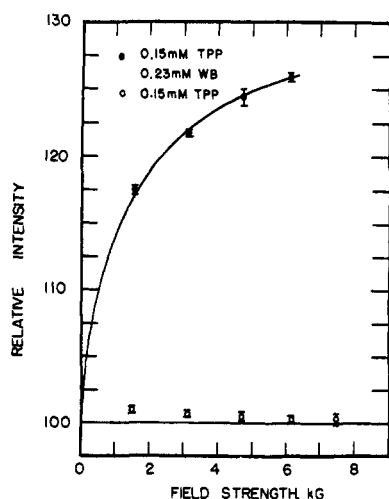


Figure 4. Magnetic field effects on luminescence from systems containing TPP as an emitter. Error bars denote average deviations. Reactants: (●) TPP anion and Wurster's Blue, (○) TPP anion and cation radicals.

## Discussion

The data summarized in Figures 3, 4, and 5 suggest that in general a study of the influence of a magnetic field on ecl intensity will yield one of two results: either the field will exert no effect, or it will enhance the intensity. These experiments indicate that in the mechanism for luminescence from the seven systems for which an enhancement was observed there is at least one elementary process whose rate is both field influenced and a fundamental factor governing the luminescence intensity. The field probably exerts its influence by altering the reactivities of paramagnetic precursors to emission. In addition, there are probably no fundamentally important, field-influenced steps in the kinetic scheme for emission from the two systems for which no effect was observed.

Leaving the two energetically marginal systems aside for the moment, it is interesting to consider the reaction

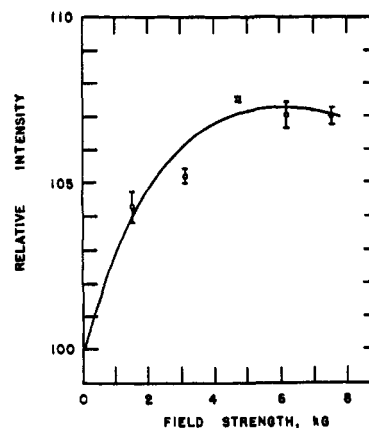
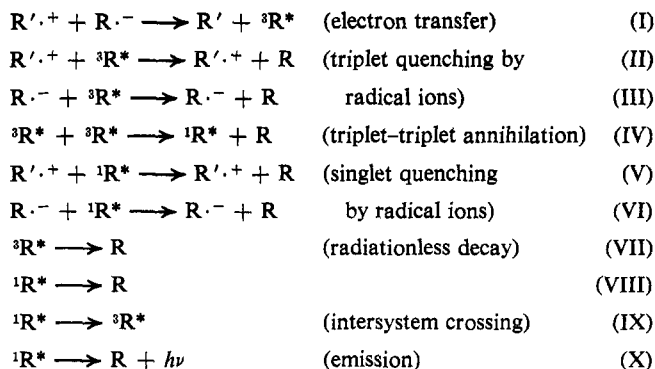


Figure 5. Magnetic field effects on luminescence from the fluoranthene-10-MP system. Error bars denote average deviations. The solution contained 3.0 mM fluoranthene, 2.4 mM 10-methylphenothiazine and 0.1 M TBAP in DMF.

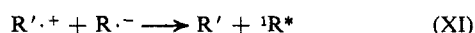
enthalpies together with the observed field effects. Luminescence from the single clearly energy-sufficient system, *viz.* the DPA anion-cation reaction, is unaffected by the field. In considerable contrast, however, the field induces a pronounced increase in ecl intensity for each of the six markedly energy-deficient systems. Furthermore, the field effects observed with the reduction of rubrene cation radical by BQ anion and with the oxidation of the fluoranthene anion radical by the 10-MP cation (and also that recorded for the rubrene anion-cation reaction) tend to vitiate the possibility that the enhancements communicated earlier, which were seen only for oxidations by Wurster's Blue, merely reflected some interaction peculiar to Wurster's Blue. Thus, the results obtained with these seven systems serve to enlarge one's confidence in the correlation between the field effect and reaction energetics, as it was recognized in the earlier work with systems containing only anthracenes as emitters.<sup>1</sup> This confidence is bolstered still further by the recent report of Keszthelyi, Tachikawa, and Bard that a magnetic field does not influence emission from the energy-sufficient reaction between the cation radical of thianthrene and the 2,5-diphenyl-1,3,4-oxadiazole anion radical in acetonitrile.<sup>29</sup>

By the arguments outlined in the introduction of this paper, these observations remain consistent with the dual mechanisms that have long served as useful working hypotheses. The differences in the mechanisms arise because the emitting first excited singlet state cannot be populated by an energy deficient electron transfer, whereas that state is accessible to a sufficiently energetic redox process. One usually envisions the product states of charge transfer as being partitioned in some manner between those available. Since the only possible emitter product states for the energy deficient processes studied here are the ground states and the lowest triplet states, one must apparently rely on the lowest triplet states to produce the emitting first excited singlets. Of course, triplet-triplet annihilation has long been favored to bridge the energy gap, as one sees in the usual scheme for luminescence from energy-deficient redox processes shown in reactions I-X (the

(29) C. P. Keszthelyi, H. Tachikawa, and A. J. Bard, *J. Amer. Chem. Soc.*, in press.



“triplet route”). In these reactions  $R$ ,  ${}^1R^*$ , and  ${}^3R^*$  represent respectively the ground state, the first excited singlet state, and the lowest triplet state of the anion precursor. Quenching of excited triplet and singlet states by the parent molecules, solvent, and supporting electrolyte ions is also possible, but the reactions are not included here, since they probably are not involved in the field effects under consideration. Energy-sufficient systems, in contrast, have available a singlet route featuring direct population of the emitting state during charge transfer, as in (XI). These systems clearly have



no need for the triplet route in order to rationalize emission, but that pathway may nevertheless contribute to emission if reactions I and IX are effective. The reactions that have been written here have carried the assumption that only the excited states of  $R$  are accessible and that those of  $R'$  are not. The opposite may well be true, as for the reduction of rubrene cation by BQ anion, but a mechanism symmetrical to the one above can easily be written for that case. One additional complication may arise when the lowest triplet of  $R'$  is accessible in addition to that of  $R$ , as may be true for the fluoranthene-10-MP system (*vide supra*), but it is probably not troublesome here.

Within this general mechanism there are four different kinds of bimolecular processes that involve paramagnetic reactants. They are the redox reactions, triplet-triplet annihilation, triplet quenching by the radical ions or other paramagnetic substances, and the analogous singlet quenching processes. Presumably, the observed field effects could arise as a consequence of an alteration by the field of the rates of any combination of these reactions. The unimolecular reactions VII and IX are apparently independent of field strength,<sup>9,10</sup> hence they cannot provide an explanation for the observations reported here. Of the four types of processes that remain as possible candidates, some can be discounted on the basis of the extensive theoretical work by Merrifield and by experimental observation.

In particular, Merrifield has asserted that spin selection rules apply to any process that features a change in the total spin angular momentum as the reactant pair is transformed to a product pair.<sup>11</sup> Such a process, for example, is triplet-triplet annihilation. For each triplet participating in the reaction, there are three spin states; hence for a reactant pair there are nine possible pair states. Each of these nine pair states will be formed with equal probability at room temperature as a consequence of the random nature of diffusion. The reactant pair states can be described generally as comprising singlet, triplet, and quintuplet

compounds, whereas the product pair state for the reaction pathway of interest is purely singlet. Thus, there is for triplet-triplet annihilation a change in the total pair state spin angular momentum upon conversion to a product pair.

As his fundamental tenet, Merrifield has argued that only pair states with a singlet component can successfully convert to products and that the conversion probability depends upon the amplitude of the singlet component. In general, this assumption implies that the encounter reaction probability, *i.e.*, the average of the pair state reaction probabilities, will be a good deal less than unity, provided the time required for interconversion between reactant pair states is long compared to the encounter period (pair lifetime). Merrifield has further observed that, for crystalline anthracene as an example, only three of the nine reactant pair states possible for two triplet pairs at zero field contain singlet components. However, using fundamental principles of angular momentum theory, he has pointed out that at nonzero field strengths the nine pair states will be described as a set of combinations of the zero-field states. Thus, the amplitude of the singlet component for each pair state becomes a function of field strength, and its reactivity is thereby governed by the field. This effect is transmitted as a field influenced encounter reaction probability, and it is observed as a field effect on the macroscopic annihilation rate. In general, the theory predicts larger rate constants for situations in which a larger fraction of pair states have singlet components.

Using this treatment, Merrifield has been able to account for the complex behavior of the anthracene triplet exciton annihilation rate with field strength. The theory implies that at low fields, where the Zeeman splitting is less than or comparable to the zero-field splitting, the number of pair states containing a singlet component increases from the zero-field number of three. As a result, the annihilation rate ought to increase in this region. At higher fields, the Zeeman splitting becomes much larger than the zero-field splitting, and the spin states become quantized along the field axis. In this high-field limit, Merrifield has observed that there are only two reactant pair states with singlet components; hence the theory predicts that the annihilation rate will tend toward a high-field limit which is lower than the zero-field value. Each of these expectations is borne out by the solid state results of Johnson, *et al.*<sup>5,8</sup>

Although the theory developed by Merrifield was derived for solid-state processes, it is applicable to solution-phase reactions without extensive modification. Thus, our previously reported results regarding field effects on the anthracene triplet-triplet annihilation rate in fluid solutions are easily interpreted by this treatment, and indeed have been treated by Avakian, *et al.*<sup>10</sup> In fluid solutions, one does not observe an increase in the annihilation rate at low field. Instead, there is only a decline in the rate with increasing field strength toward a limiting value at high fields. The increase at low fields is apparently absent because there is no zero-field splitting in fluid solution. One therefore observes only the effects of progressive spin state quantization along the field axis. One interesting aspect of these results is that the magnitude of the field



effect in the solution phase is only about half that seen in the solid state. This may be an indication that the time required for interconversion of reactant pair states is comparable to the encounter period, which is possibly lengthened in solution by the cage effect. In any event, theory and experiment both strongly imply that one will not observe an enhancement in the fluid solution annihilation rate with field strength for any system. One therefore cannot use such a hypothesis to rationalize the observed field behavior of ecl. In fact, if the results are to be explained within the mechanism above, one of the other reactions involving paramagnetic species must be influenced by the field to a degree large enough to more than offset the demonstrated decline in the annihilation rate.

Of the reaction categories that remain as possibilities, only the quenching processes may be validly treated with Merrifield's theory. However, the theory continues to yield useful predictions, for it enables one to eliminate the singlet quenching processes immediately. Because the reactant and product pairs are both composed of a singlet and a doublet species, the pair states are purely doublet in both instances, and no change in angular momentum results upon conversion of products into reactants. In such a case, the theory yields the expectation that no field effect will be seen on the rate of this process, but there is no direct experimental evidence to support or refute this prediction. Even so, the magnitudes of the rates of these processes as compared to typical singlet lifetimes makes them of doubtful utility for explaining the observed field effects on ecl. Half-quenching concentrations for radical ion quenching of singlets are probably on the order of 5 mM.<sup>30</sup> The radical-ion concentration in the reaction zone for ecl is at a minimum and cannot possibly approach this figure; thus, the quenching of singlets by radical ions cannot be a primary factor governing the ecl intensity. Field effects on the rate of the process, therefore, cannot account for the field effect on ecl intensity even if, contrary to theory, they actually occur.

In contrast, the quenching of triplets by the radical ions certainly would be expected to be one of the more important factors controlling emission intensity resulting from the triplet route as described above. Half-quenching concentrations are on the order of  $10^{-7}$  M, a value which appears likely to be far lower than the average radical ion concentration in the ecl reaction zone. Moreover, Merrifield has indicated, using arguments similar to those employed to deal with triplet-triplet annihilation, that the quenching rate should be greatest at zero field and that it should decline as the field strength is increased.<sup>14</sup> The theory anticipates an approach to a limiting quenching rate at high field strengths. Ern and Merrifield have confirmed these predictions for solid-state processes,<sup>14</sup> and we have found them to be equally valid for the quenching of anthracene triplets by Wurster's Blue cation in fluid media.<sup>12</sup>

These experimental and theoretical observations provide a basis for interpreting the magnetic field effects observed with ecl within the framework of the dual mechanism given above. As we have noted in the early paragraphs of this paper, the increased anthracene triplet lifetimes resulting from the inhibition of Wur-

ster's Blue triplet quenching more than compensate for the decreased annihilation rate; hence one notes an increase in delayed fluorescence intensity with field strength whenever Wurster's Blue is present at a concentration greater than about  $10^{-7}$  M. Dealing strictly with the anthracene-WB system, if the triplet route is the mechanism responsible for ecl emission, the extent of enhancement of the ecl intensity by the field is about the amount expected from the experimental field effects on the critical elementary processes contained in that mechanism. This agreement lends considerable support to the proposed mechanism. Since there is no reason to believe any of the field effects to be peculiar to anthracene, these arguments can probably be extended to the remaining energy deficient systems. Recent experiments involving the interception of fluoranthene triplets generated by the oxidation of the fluoranthene anion by the 10-MP cation have provided extremely strong evidence that the triplet route is an operative pathway to luminescence in energy-deficient systems.<sup>26</sup> Thus, the consistency of the present experimental results with that mechanism provides support for both the proposed mechanism and for the ventured explanation for the field effects.

Of course, the electron-transfer processes remain as possible contributors to the observed field effects because their rates could conceivably be altered by the field. Since the overall rate of electron transfer is likely to be a diffusion-controlled process, the field probably would not exert any effect on that rate. However, the distribution of products among the available states could be dependent upon the magnetic field strength.<sup>31</sup> Unfortunately, the applicability of the Merrifield theory is compromised in this instance because there is an actual particle transfer. The relative rates of transition for reactant pairs into the various product pair states, therefore, must involve much more than angular momentum selection rules. Undoubtedly there are activation effects as well.<sup>4</sup> In any event, the fact that field effects are not observed with some systems tends to discount the probability that the field effects on ecl arise from this source.

The contention that the field effects arise from a field-influenced triplet-quenching rate is able to accommodate the lack of a field effect in the case of the energy sufficient DPA anion-cation annihilation. However, if the hypothesis is correct, then the triplet route must contribute negligibly to ecl emission from the system. Such a situation could arise either from a generation of first excited singlet states during charge transfer at an incidence rate much larger than the rate of triplet formation or from nearly total quenching of triplets by the radical ions. In the latter case, field effects on the quenching reactions would presumably occur, but a negligible effect on intensity would be observed because the triplet route would contribute little to emission.

When one turns at last to the two systems set aside earlier, one recognizes from the enthalpy data in Table II that one cannot discern whether the reactions are energy sufficient or not. The uncertainty in the evaluation of the reaction enthalpy is simply too great. Thus, one cannot use the systems as additional tests of the interpretation outlined above, but instead they present intriguing opportunities for inferences regarding the mech-

(30) L. R. Faulkner, unpublished results.

(31) B. Brocklehurst, *Nature (London)*, **221**, 921 (1969).

anisms for luminescence from these systems. If the interpretation given above is valid, and one sees magnetic field effects only when the triplet route is predominantly responsible for luminescence, then the zero (or very slight) effect observed with the TPP anion-cation reaction implies that the singlet route is much the predominant pathway to luminescence and the reaction is essentially energy sufficient. Such a suggestion is indeed quite plausible, and the energetics may only appear marginal because  $-\Delta H^\circ$  has been significantly underestimated (*vide supra*). In contrast, our hypothesis suggests that luminescence from the rubrene anion-cation annihilation arises predominantly from the triplet pathway. Interestingly, Maloy and Bard made the same suggestion as a consequence of their observation of a low emission efficiency from this system compared to that from the DPA anion-cation reaction.<sup>32</sup> Chang, Hercules, and Roe likewise concluded from their analysis of intensity-decay curves that the triplet pathway was an important route to emission from the rubrene anion-cation reaction,<sup>33</sup> and recent work by Bezman

(32) J. T. Maloy and A. J. Bard, *J. Amer. Chem. Soc.*, **93**, 5968 (1971).

and Faulkner using an extended Feldberg analysis has implied that it is the only route.<sup>34</sup> An intriguing issue raised in this work concerns the sharpness of the energy criterion. One wonders whether the line between energy sufficiency and energy deficiency is as distinct and important as these last two cases may suggest. In the marginal energy region it may in fact be that more specific system factors, such as relative geometries of the ions, the excited singlets, and the triplets, become extremely important for dictating the predominant luminescent pathway.

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## Temperature-Dependent $^{13}\text{C}$ Relaxation Studies of Small Molecules

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**Abstract:**  $^{13}\text{C}$  spin-lattice relaxation times ( $T_1$ ) are reported for 60% enriched samples of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CHBr}_3$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3^{13}\text{COOH}$ , and  $\text{CS}_2$ , each measured over a wide range of temperatures at 15.1 MHz. Data are also given on the magnetic field dependence of  $T_1(^{13}\text{C})$  in  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{I}$ , and  $\text{CH}_3^{13}\text{COOH}$ . The  $T_1$  results, together with nuclear Overhauser enhancements measured for the foregoing hydrogen-containing molecules, as well as for  $\text{CH}_3^{13}\text{COCH}_3$ ,  $^{13}\text{CH}_3\text{COOCD}_3$ , and  $(\text{CH}_3)_4\text{Si}$ , are interpreted in terms of the probable relaxation mechanisms.

The rapidly increasing use of  $^{13}\text{C}$  nmr has generated considerable interest in the mechanisms by which  $^{13}\text{C}$  nuclei relax. A knowledge of relaxation rates and the basic mechanisms that determine those rates is essential for the efficient application of Fourier transform<sup>2a</sup> and nuclear Overhauser enhancement (NOE) techniques.<sup>2b</sup>

Until the last year few data had been reported for  $^{13}\text{C}$  relaxation times, and little interpretation had been attempted. McConnell and Holm<sup>3</sup> speculated on a possible relaxation mechanism for  $^{13}\text{C}$  in  $\text{CS}_2$ ; Ettinger<sup>4</sup> and Hunter and Reeves<sup>5</sup> each reported values for  $T_1(^{13}\text{C})$  in a few compounds; and Kuhlmann and Grant<sup>6</sup>

interpreted NOE data for formic acid in terms of a dipolar relaxation mechanism for the  $^{13}\text{C}$ . Olivson, Lippmaa, and Past<sup>7</sup> reported  $T_1$ 's for  $^{13}\text{C}$  in a number of compounds, but later results cast considerable doubt on several of their values.

Recent studies have considerably extended our knowledge of  $^{13}\text{C}$  relaxation rates and mechanisms for some compounds. Jones<sup>8</sup> reported  $T_1$ 's for a number of compounds at room temperature. Spiess, *et al.*,<sup>9</sup> made a detailed temperature and field dependence study of  $T_1$  in  $\text{CS}_2$ , and Gillen, Schwartz, and Noggle<sup>10</sup> investigated  $\text{CH}_3\text{I}$  in detail. Grant and coworkers<sup>2,11,12</sup> used

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