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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The thermolysis of 1-phenylethylperoxyacetate and a series of substituted 1-phenylethylperoxybenzoates was investigated. Thermolysis in benzene gives acetophenone and the corresponding carboxylic acid. The study of the reaction kinetics and kinetic isotope effect indicate that the unimolecular thermolysis proceeds by homolysis of the oxygen-oxygen bond. Electronically excited states are formed in the thermolyses of these peroxyesters. These are detected by their characteristic direct chemiluminescence or by indirect (cont.)		

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chemiluminescence. In the presence of easily oxidized catalysts these peresters give excited states by the chemically initiated electron-exchange luminescence (CIEEL) path. The mechanism of these luminescent reactions was investigated.

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Chemiluminescence of Secondary Peroxyesters

by

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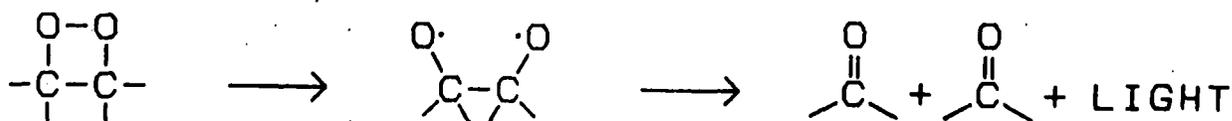
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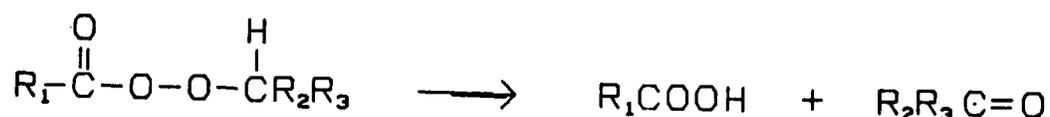
The chemical generation of electronically excited states from the thermolysis of appropriate organic peroxides is an area of active and increasing interest.<sup>2</sup> Most of the peroxides thus far found to generate excited states are cyclic compounds. This fact is the result of two important considerations. First, one of the key prerequisites for efficient excited state generation is that the energy available at the reaction transition state be at least as great as the energy of the lowest excited state of one of the reaction products. Often the strain released in converting a cyclic peroxide to acyclic products provides a significant portion of the energy required to form excited states. A classic example of this is found in the 1,2-dioxetanes where ca. 25 kcal/mole of strain energy is released on fragmentation of the four-membered ring.<sup>3</sup> Second, incorporating the peroxide linkage in an appropriate cycle provides a path whereby cleavage of two or more bonds can result in the formation of closed-shell products. Thus a typical chemiluminescent pathway might involve homolysis of the peroxide linkage to form a biradical followed by cleavage of a second bond to generate the ultimate products. Again, the 1,2-dioxetane ring system provides the most thoroughly studied examples of this behavior. The mechanism for chemiluminescence of these peroxides appears to proceed through the 1,4-dioxybiradical, eq. 1.<sup>4</sup>



One of the difficulties associated with the study of cyclic peroxides is that they are difficult to prepare. This stems in large part from the competition between cyclization and polymerization of their precursors. A second difficulty with strained cyclic systems is that the very strain that contributes to the reaction exothermicity also lowers the reaction activation enthalpy thereby making

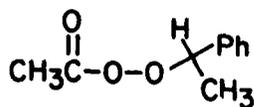
isolation and purification of these molecules difficult at best.

With these restrictions on the properties of cyclic peroxides in mind we were attracted to a report by Hiatt, Glover and Mosher<sup>5</sup> on the thermal chemistry of acyclic secondary peroxyesters. This report revealed that these compounds undergo unimolecular thermolysis to generate the appropriate carboxylic acid and carbonyl compound; eq. 2. We estimated, using Benson's group equivalent method,<sup>6</sup> that the prototypical reaction, shown in eq. 2 is exothermic by ca. 60 kcal/mole. When the exothermicity is combined with the reaction activation energy, reported

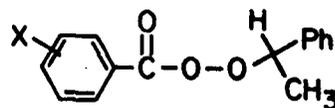


to be ca. 25 kcal/mole,<sup>5</sup> it is clear that there is sufficient energy available at the transition state of the secondary peroxyester reaction for the formation of the excited state of the carbonyl compound.<sup>7</sup> Unknown at the outset of this work was whether a mechanism exists to channel this energy to the formation of electronically excited states.

We report herein the results of our investigation of both the thermal and electron donor induced reactions of 1-phenylethyl peroxyacetate (1) and a series of substituted 1-phenylethyl peroxybenzoates (2a-2e). These results provide new insight into the direct generation of electronically excited states from unimolecular thermolyses, and into the details of the chemically initiated electron-exchange luminescence (CIEEL) mechanism.<sup>8</sup>



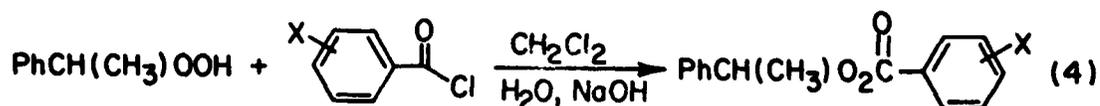
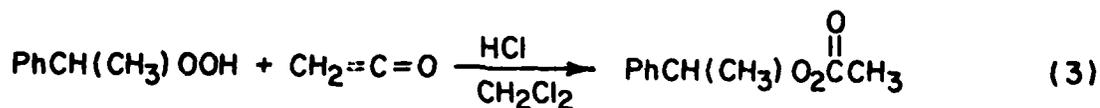
1



- 2a X=H
- 2b X=p-OMe
- 2c X=p-N(Me)<sub>2</sub>
- 2d X=p-NO<sub>2</sub>
- 2e X=m-NO<sub>2</sub>

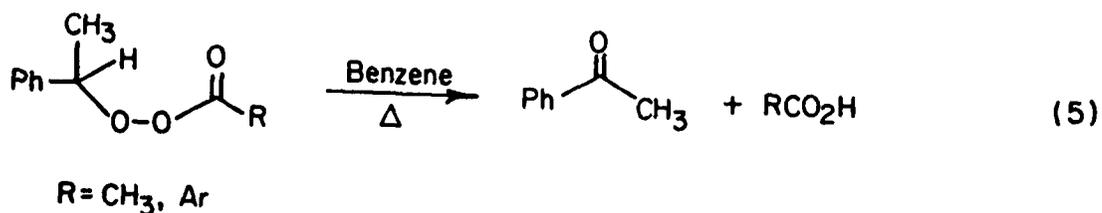
## Results and Discussion

Synthesis of Secondary Peroxyesters. All of the peroxyesters investigated can be conveniently prepared by reaction of 1-phenylethyl hydroperoxide with the appropriate activated acid precursor. We prepared the hydroperoxide by two different routes; oxidation of ethylbenzene,<sup>9</sup> and acid catalyzed substitution of hydrogen peroxide on 1-phenylethanol.<sup>10</sup> The details for preparation of the hydroperoxide by both procedures are given in the experimental section. The acid catalyzed substitution must be carried out with extreme caution. We experienced two violent explosions when we attempted to scale up this preparation. Reaction of the hydroperoxide with ketene in  $\text{CH}_2\text{Cl}_2$  and HCl followed by vacuum distillation gives analytically pure peroxyacetate **3**, eq. 3. The substituted peroxybenzoates are prepared by reaction of the hydroperoxide with the appropriately substituted acid chloride in a two phase basic mixture, eq. 4. Recrystallization, in some cases at low temperature, gives analytically pure peroxyesters. In addition to the normal spectroscopic characterization, all of the peroxyesters except **2c**<sup>11</sup> were reduced with triethylphosphite or triphenylphosphine to the corresponding ester and this product compared to authentic material. The details of the synthesis, purification, and characterization of



the peroxyesters are given in the experimental section.

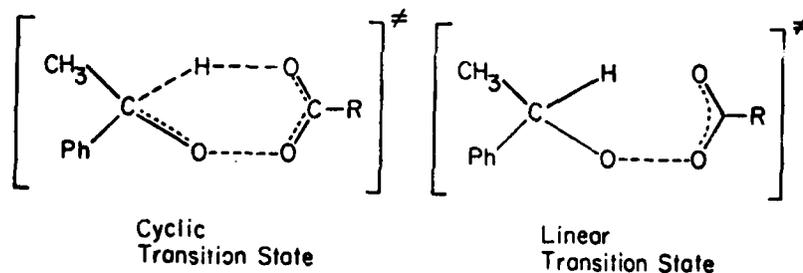
Thermolysis of peresters in benzene. In all cases examined the only products formed from the thermolysis of dilute solutions of the peroxyesters in benzene are the appropriate acid and acetophenone, both in essentially quantitative yield, eq. 5. This observation is particularly pertinent for the case



of peroxyacetate  $\downarrow$  where formation of the acetyloxy radical is expected to lead to rapid loss of CO<sub>2</sub><sup>12</sup> and thus to a concomitant decrease in the yield of acetic acid.

The rates of thermolysis of the peroxyesters in argon purged benzene can be followed conveniently by their direct, indirect, or activated chemiluminescence. The details of these procedures are described completely below. For the present discussion it is critical to point out only that the chemiluminescent intensity obtained in these kinetic studies is directly proportional to the concentration of the peroxyester and that the derived rate constants are identical to those obtained using more conventional spectroscopic techniques to monitor the peroxyester concentration. In all of the cases examined, carefully purified benzene and peroxyester solutions show clean first order consumption of the peroxide. Typical kinetic runs are shown in Figure 1, Eyring plots are shown in Figure 2, and the first order rate constants with their derived activation parameters are listed in Table 1. It should be noted that for peroxyacetate  $\downarrow$  at initial concentrations above 10<sup>-2</sup> M, the first order rate constants obtained, and the activation parameters derived therefrom, are dependent on the initial peroxyester concentration. However, at low initial peroxyester concentration (10<sup>-5</sup> - 10<sup>-3</sup> M) the rate constants are independent of the initial peroxide concentration. Apparently, at the higher concentrations a second reaction path, perhaps radical induced homolysis,<sup>13</sup> becomes significant. All of the kinetic and chemiluminescent experiments on peroxyester  $\downarrow$  are carried out in the low concentration region.

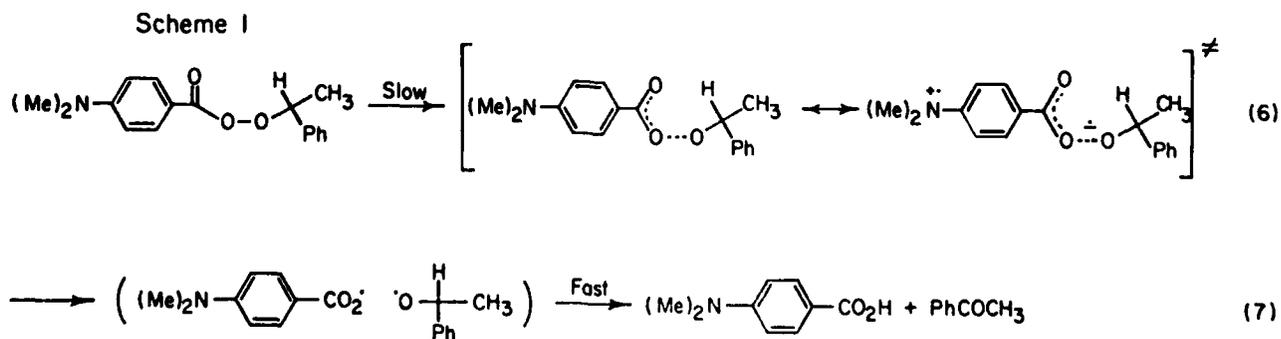
The activation parameters for the peroxyester thermolyses reveal some important details of the reaction mechanism. The activation enthalpy obtained for peroxyester  $\lambda$  is quite similar to that reported by Hiatt and coworkers<sup>5</sup> for related secondary peroxyesters in the vapor-phase, but is considerably higher than the values obtained by these workers for solution-phase reactions. Similarly, the activation entropies we obtain are more closely aligned with the vapor-phase values of Hiatt.<sup>5</sup> This observation is of significance since the rather small activation enthalpy and negative activation entropy reported earlier were used to support the notion of a cyclic transition state for these reactions. In contrast, the activation parameters we obtain for peroxyacetate  $\lambda$  resemble closely the values measured for tertiary peroxyesters where the cyclic transition state is not possible and simple oxygen-oxygen bond homolysis is the accepted mechanism.<sup>14</sup>



To analyze further the degree of carbon-hydrogen bond involvement in the rate determining step of the unimolecular thermolysis of  $\lambda$  we measured the kinetic isotope effect that results from replacement of the methine hydrogen of  $\lambda$ <sup>15</sup> with deuterium (peroxyester  $\lambda_d$ ). In benzene at 100°  $k_H/k_D$  is  $1.11 \pm 0.10$ . We consider this value to be too small to be indicative of significant cleavage of the carbon-hydrogen bond at the reaction transition state.<sup>16</sup> Thus, in contrast to the modified Russel mechanism<sup>17</sup> proposed by Hiatt and coworkers,<sup>5</sup> we favor the linear representation for the reaction transition state.

The activation parameters obtained for the substituted peroxybenzoates show a slight dependence on the nature of the substituent which has statistical significance only for the dimethylamino substituted peroxybenzoate  $2c$ . In this case both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are considerably smaller than for the other structures examined. For this reason, and because this compound also exhibits unusual chemiluminescent properties (see below), we measured the kinetic deuterium isotope effect when the methine hydrogen of this compound is replaced by deuterium. In this case the value of  $k_H/k_D$  obtained is  $1.18 \pm 0.04$  which again fails to indicate significant involvement of the carbon-hydrogen bond at the transition state.

In sum, the thermal and isotopic data indicate that the mechanism for thermolysis of these peroxyesters has as the rate determining step the cleavage of the oxygen-oxygen bond without much, if any, carbon-hydrogen bond cleavage. The substituent on the peroxybenzoates may influence the relative position of the transition state along the reaction coordinate by donating more, or less, electron density to the antibonding  $\sigma$  oxygen-oxygen orbital as this bond cleaves.<sup>18</sup> Our findings, particularly the nearly quantitative yield of acetic acid from  $1$ , indicate that transfer of the hydrogen atom to generate the final products competes successfully with escape from the solvent cage and with decarboxylation. This mechanism is shown for  $2c$  in Scheme 1.

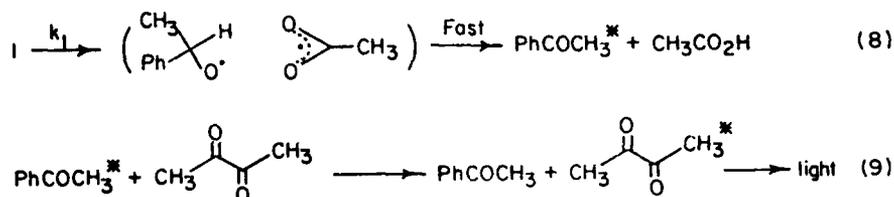


Direct and Indirect Chemiluminescence. Direct chemiluminescence is observed when one of the products of a unimolecular thermal reaction is formed in an electronically excited state and subsequently emits a photon of light. Thus the emission, fluorescence or phosphorescence, from excited acetone that results from thermolysis of tetramethyldioxetane ( $\text{3}$ ) is an example of direct chemiluminescence.<sup>19</sup> Indirect chemiluminescence occurs when energy transfer from the initially formed excited state to an added emitter precedes the generation of light. Thus thermolysis of  $\text{3}$  in the presence of 9,10-diphenylanthracene (DPA) produces indirect chemiluminescence emission from excited DPA formed by energy transfer from the first generated excited singlet acetone.<sup>20</sup>

We examined the thermal reactions of peroxyacetate  $\text{4}$  and substituted peroxybenzoates  $\text{2}$  for both direct and indirect chemiluminescence. Thermolysis of peroxyacetate  $\text{4}$  in benzene solution at 100° gives very weak direct chemiluminescence. The emission is so weak that we are unable to obtain its spectrum. However, we can place the emission maximum between 420 and 480 nm, which is consistent with phosphorescence from triplet acetophenone.<sup>21</sup> The indirect chemiluminescence experiment gives a more satisfying result. When biacetyl, which has a considerably higher phosphorescence quantum efficiency than acetophenone,<sup>22</sup> is used as the energy acceptor a reasonably strong chemiluminescent emission is observed. The spectrum of the emission, shown in Figure 3, is identical to that of biacetyl phosphorescence. Within our limit to detect it, there is no fluorescence component to the indirect chemiluminescence of  $\text{4}$  and biacetyl. This observation indicates either that the excited state formed in the thermal reaction is a triplet, or that intersystem crossing of the first formed state is more rapid than singlet-singlet energy transfer to biacetyl. In either case, we assign the structure of the first formed excited state to acetophenone. The yield of excited acetophenone is very low. We estimate, by comparison with tetramethyldioxetane indirect chemiluminescence

with biacetyl,<sup>23</sup> that excited acetophenone is formed under these conditions with a yield of about 0.02%, Scheme 2. Finally, we should point out that, as expected for indirect chemiluminescence, the addition of biacetyl has no effect on the rate of the reaction for low peroxyacetate concentrations.

Scheme 2



The direct and indirect chemiluminescence observed from the substituted peroxybenzoates is remarkably dependent upon the nature of the substituent. The parent peroxybenzoate 2a, and the *p*-OMe (2b), *p*-NO<sub>2</sub> (2d), and *m*-NO<sub>2</sub> (2e) substituted peroxybenzoates show very little direct chemiluminescence, a result similar to that obtained for the peroxyacetate. Also, the indirect chemiluminescence with 9,10-dibromoanthracene (DBA) as an energy acceptor is very weak with these peroxides. In contrast to these results, the dimethylamino substituted peroxybenzoate (2c) gives reasonably intense direct and indirect chemiluminescence.

Thermolysis of peroxide 2c in benzene solution gives an emission whose spectrum, Fig 1, is identical to the fluorescence spectrum of photoexcited *p*-dimethylaminobenzoic acid under similar conditions. We therefore attribute this observed direct chemiluminescence to the formation of the singlet excited acid. The yield of directly generated excited acid was determined, by comparison with the indirect chemiluminescence of dioxetane 3 and DBA, to be 0.24%.<sup>24</sup> Since none of the other peroxybenzoates generate detectable direct chemiluminescence it is not possible to compare this yield directly to these other peroxides. However, by considering the limit to detectability set by the

signal to noise ratio of our chemiluminometer, the dimethylamino substituted peroxide  $2c$  generates excited singlet products at least one thousand times more efficiently than do any of the other peroxybenzoates examined.<sup>25</sup>

Indirect chemiluminescence with DBA as the energy acceptor is unusual in that the DBA is able to accept energy from sufficiently energetic triplets and form its emissive excited singlet state (triplet to singlet energy transfer).<sup>26</sup> Thus it is possible to use the indirect chemiluminescence of DBA as an indicator of excited triplet state formation. Figure 5 shows a double reciprocal plot of indirect chemiluminescence intensity against DBA concentration for peroxybenzoates  $2a$  and  $2c$ . By comparison with a similar experiment using dioxetane  $3$  the yields of directly formed triplet dimethylaminobenzoic acid and benzoic acid obtained from thermolysis of the peroxyesters are 3.8 and 0.002% respectively. The yields of triplet acid generated from peroxybenzoates  $2b$ ,  $2d$ , and  $2e$  as indicated by the DBA indirect chemiluminescence intensity are similar to that obtained from the unsubstituted peroxide  $2a$ .

Evidently, the p-dimethylamino substituent greatly alters the ability of these secondary peroxybenzoates to generate electronically excited state products directly. There are two likely rationalizations for this effect. The first is that the powerfully electron-donating amino substituent somehow alters the reaction transition state to facilitate excited state formation. Or, second, that the lower energy of the excited singlet state of dimethylaminobenzoic acid (the singlet energy of benzoic acid and p-dimethylaminobenzoic acid are 98.3 and 83.5 kcal/mole, respectively) directs the reaction to excited products. As indicated above, the activation enthalpy obtained for  $2c$  is lower than that of the other peroxyesters examined. This indicates some special stabilization of the transition state. However, the kinetic isotope effect indicates that the linear oxygen-oxygen homolysis model remains an acceptable representation of the structure of the transition state. It should

be noted also that there is not a significant primary isotope effect on the direct or indirect (with DBA) chemiluminescence of  $\text{ZC}$ . The lowered excited state energy explanation, however, does not appear to hold for the formation of the triplet acids. We have determined the triplet energy of p-dimethylaminobenzoic acid to be 73.3 kcal/mole, which is only 3.8 kcal/mole below the triplet of benzoic acid. Yet the yield of triplet excited states differ by a factor of ca. 2000. We, at this time, cannot offer an unambiguous explanation for the increased excited state yield from peroxybenzoate  $\text{ZC}$ . However, we do note that a similar effect of amino substitution has been reported in the luminol series.<sup>27</sup> We are continuing to investigate the direct chemiluminescence of secondary peroxyesters in the hope of both increasing the efficiency of excited state formation and gaining insight into the detailed structural requirements and the mechanism of this system.

Chemically Initiated Electron-Exchange Luminescence. Activated chemiluminescence is observed when an electronically excited state is formed as a direct consequence of the bimolecular reaction of a catalytic activator and an energy rich compound. Usually the excited state formed is that of the activator. For example, we have shown that dimethyldioxetanone reacts with easily oxidized aromatic hydrocarbons (rubrene, for example) to give the excited state of the hydrocarbon.<sup>28</sup> Activated chemiluminescence differs conceptually and mechanistically from both direct and indirect chemiluminescence. The two most critical observable differences are that for activated chemiluminescence by the CIEEL path the effectiveness of an activator is determined in large part by its oxidation potential, and, second, that the addition of the activator may increase the rate of consumption of the peroxide.<sup>29</sup> We examined the possibility that activated chemiluminescence by the CIEEL path occurs for peroxyacetate  $\text{Z}$  and for peroxybenzoates  $\text{Z}$

When the thermolysis of peroxyacetate  $\overset{\sim}{\text{A}}$  in benzene solution is carried out in the presence of a small amount of an easily oxidized substance the course of the reaction is changed. For example, addition of N,N-dimethyldihydrodibenzo[ac]phenazine (DMAC) to peroxyester  $\overset{\sim}{\text{A}}$  in benzene results in an accelerated rate of reaction of  $\overset{\sim}{\text{A}}$ , Figure 6, and the generation of a modest yield of singlet excited DMAC. This is evidenced by the chemiluminescence emission spectrum, Figure 7, which is identical to the fluorescence spectrum of DMAC obtained under similar conditions. Spectroscopic measurements indicate that the DMAC is not consumed in its reaction with peroxyester  $\overset{\sim}{\text{A}}$  even when the peroxyester is present in 30 fold excess. The products of the reaction in the presence of DMAC remain acetophenone and acetic acid. These observations indicate that DMAC is a true catalyst for the reaction of peroxyacetate  $\overset{\sim}{\text{A}}$ . The catalytic rate constant,  $k_{\text{CAT}}$ , can be extracted from the kinetic results shown in Figure 6 according to:

$$k_{\text{obsd}} = k_1 + k_{\text{CAT}} [\text{DMAC}] \quad (10)$$

where  $k_{\text{obsd}}$  is the observed first order rate constant for reaction of  $\overset{\sim}{\text{A}}$  in the presence of ACT, and  $k_1$  is the rate constant for the unimolecular reaction of the peroxyacetate. The results of this experiment with DMAC, plotted according to eq. 10, gives  $k_{\text{CAT}} = 9.73 \times 10^{-2} \pm 1.87 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$

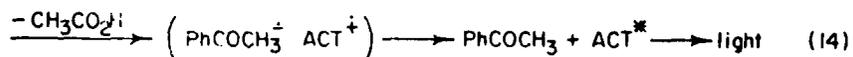
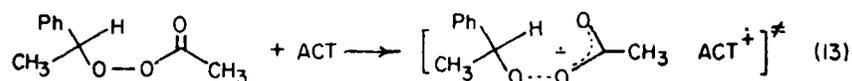
DMAC is not unique in its ability to catalyze the reaction of peroxyacetate  $\overset{\sim}{\text{A}}$  and provoke the formation of excited singlet states. The chemiluminescent intensity (corrected for changes in fluorescence efficiency, and photomultiplier and monochromator spectral response) is a sensitive function of the nature of the activator. Under conditions of low, but constant, activator concentration the magnitude of this corrected chemiluminescent intensity is related to the one electron oxidation potential of the activator, Figure 8. Under these experimental conditions  $k_1 \gg k_{\text{ACT}} [\text{ACT}]$  which insures that the

corrected chemiluminescence intensity is proportional to the magnitude of the catalytic rate constant, eq. 12, where  $\phi_{F1}$  is the fluorescence quantum efficiency of the activator,  $\phi^*$  is the efficiency of forming excited singlet states by the activated chemiluminescence path, and  $F$  is a constant factor that contains the photomultiplier tube spectral response, light gathering efficiency of the chemiluminometer and counting efficiency of the apparatus.

$$I_{\text{corr}} = F \left( \frac{k_{\text{cat}} [\text{ACT}]}{k_{\text{cat}} [\text{ACT}] + k_1} \right) \phi_{F1} \cdot \phi^* \quad (12)$$

The inverse linear relationship between the log of the corrected chemiluminescent intensity and the oxidation potential of the activator is prima-facie evidence for the operation of the CIEL mechanism, Scheme 3. In this

Scheme 3



mechanism the initiating step for light generation is the thermally activated transfer of an electron from the activator to the peroxide. The electron transfer is followed by the very rapid cleavage of the oxygen-oxygen bond of the reduced peroxide<sup>18</sup> and then by transfer of hydrogen to form acetic acid. This leaves acetophenone radical anion and activator radical cation within a solvent cage. Annihilation of these oppositely charged radical ions leads to the formation of the excited state we detect by its luminescence.

The one exception to the correlation of corrected chemiluminescence intensity and oxidation potential shown in Figure 8 is for dimethyldihydrophenazine (DMP), and this is readily understood with the CIEEL mechanism shown in Scheme 3. In order to form an electronically excited state by an ion annihilation the energy released by the annihilation must be at least as great as the energy of the excited state. The energy released on annihilation ( $\Delta E_{+/-}$ ) can be estimated using available redox potentials,<sup>30</sup> and is summarized for the systems of interest in Table 2. The energy of the target excited state in this case the singlet, ( $\Delta E_S^*$ ) can be estimated from optical absorption and emission data and is also shown in Table 2 for the compounds of interest. It is clear from the data of Table 2 that for all of the activators used except DMP there is sufficient energy released to form the excited singlet. DMP still catalyzes the reaction of peroxyacetate  $\downarrow$ , see  $k_{cat}$  in Table 2, but it cannot be promoted to its excited singlet state on annihilation because insufficient energy is released. These observations offer convincing evidence for the intermediacy of radical ions in the activated chemiluminescence of peroxyacetate  $\downarrow$ .

The response of the peroxybenzoates to the CIEEL activators depends remarkably on the nature of the substituent. In principle, the substituent on the peroxybenzoate might influence one or several of the steps in the proposed CIEEL mechanism. In fact, an entire spectrum of reactivity, depending upon the substituent, is observed.

The unsubstituted peroxybenzoate  $\downarrow_a$  behaves in a fashion nearly identical to that observed for the peroxyacetate  $\downarrow$ . The reaction of  $\downarrow_a$  is catalyzed by DMAC to give singlet excited DMAC with  $k_{cat} = 2.6 \times 10^{-1} \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$ , Figure 9. Similarly, other activators catalyze the chemiluminescent reaction of  $\downarrow_a$ . The dependence of the corrected chemiluminescence intensity on activator oxidation potential is shown in Figure 10.

The p-methoxy substituted peroxybenzoate  $2b$  behaves quite like the parent, but the nitro substituted compounds  $2d$  and  $2e$  and the p-dimethylamino substituted peroxybenzoate  $2c$  behave quite differently. The behavior of these compounds, however, can be understood within the CIEEL mechanism. For example, the nitrosubstituted peroxybenzoates  $2d$ , and  $2e$  exhibit  $k_{cat}$  with DMAC approximately ten times greater than for the unsubstituted peroxide  $2a$ . Yet the yield of excited singlet DMAC generated by  $2d$  and  $2e$  is 700 times less than from  $2a$ , Figure 10. This seeming inconsistency can be easily understood. In the postulated CIEEL path, the reduction of the peroxide results in its fragmentation to acetophenone and an acid. One of these species must be a radical anion. For the peroxyacetate and all of the substituted peroxybenzoates examined with the exception of the nitro substituted examples the more easily reduced species of this pair is acetophenone. Thus, in these cases the annihilation takes place between acetophenone radical anion ( $E_{red} = -2.00-2.50$  V vs SCE)<sup>31</sup> and activator radical cation. The reduction potentials of the nitro substituted acids are below the reduction potential of acetophenone.<sup>32</sup> Thus when these reduced peroxides fragment the radical anion species is probably the acid. Annihilation between the nitro-substituted acid radical anions and the activator radical cations used in this work is not sufficiently energetic to form the excited singlet state of the activator. Thus, just as was observed for the peroxyacetate and DMP, an activator can retain its catalytic function, but because of the energetics of the reaction of the postulated intermediates, lose its chemiluminescent ability.

The final experiments to be discussed are the reactions of dimethylamino substituted peroxyester  $2c$  with these activators. For these cases a third type of behavior is observed. The corrected chemiluminescence intensity obtained is independent of the structure of the activator, Figure 10. This is just what is expected for simple indirect chemiluminescence where the activator is

excited by energy transfer from some first-formed singlet state. As indicated above, the initial excited state in this system is p-dimethylaminobenzoic acid. Evidently, the electron donating p-dimethylamino substituent renders the peroxybenzoate 2c sufficiently difficult to reduce<sup>32</sup> that the value of  $k_{cat}$  is so small that the bimolecular path never is able to compete successfully with unimolecular decomposition.

In sum, three types of behavior are observed with these peroxyesters and easily oxidized fluorescers. Each of these can be understood within the CIEEL mechanism based simply on expected reactivity of the postulated intermediates.

Conclusions. The primary question posed at the outset of this work was whether the energy released on thermal conversion of a secondary peroxyester to a ketone and a carboxylic acid could be directed to the formation of excited state products. The answer to that question is a resounding yes. We have discovered also that, depending on the specific structure of the secondary peroxyester, modest yields of direct, indirect, or activated chemiluminescence can be obtained. These initial findings point the way to further exploration of the chemistry of these compounds. We are continuing to examine the effect of structural variation on the chemical behavior of these systems.

## EXPERIMENTAL SECTION

### General

Gas chromatographic separations were done using a Varian-Aerograph Model 2700 chromatograph equipped with dual flame ionization detectors. NMR spectra were recorded on a Varian Associates EM-360 or an HR 220 instrument using tetramethylsilane, hexamethylbenzene or dioxane as the internal standard. UV adsorption spectra were measured on a Cary 14 spectrometer, or on a Perkin Elmer Model 552 UV-Vis spectrophotometer. All chemiluminescence data were obtained using standard photon counting techniques. Light emission was detected by an EMI 9813B or

9816B photomultiplier tube. Spectral resolution was accomplished using a Jarrel Ash 0.25 M monochromator. The band-pass under high resolution conditions is calculated from manufacturers data to be 5 nm. For the low resolution condition, the band-pass is calculated to be 26 nm. Chemiluminescence cell temperature was regulated within  $\pm 0.1^\circ\text{C}$  by either a constant temperature recirculating water bath or an electrically heated jacket. All elemental analyses were carried out by the Analyses Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois. Fluorescence spectra were obtained on a Farrand Optical Mark I Spectrofluorometer.

All oxidation potentials were run in acetonitrile under an argon atmosphere. The cyclic voltammograms were run on a polarographic analyzer and recorded on a Tectronix 915 X-Y recorder. The electrolyte used was tetrabutylammonium perchlorate (TBAP) at a concentration of 0.1 M. The cell consisted of a saturated calomel electrode as reference, a platinum working electrode and a platinum wire counter electrode. The platinum working electrode was polished prior to each set of runs. All voltammograms were reversible.

### Materials

Acetonitrile (Aldrich spectrophotometric grade) was dried over calcium hydride with stirring and then slowly distilled from calcium hydride through a 30 cm Vigreux column. The first and last 10% of the distillate were discarded. Benzene (Burdick and Jackson distilled in glass) was washed successively with concentrated sulfuric acid, water (twice), and a saturated water solution of sodium carbonate. It was then thoroughly dried over calcium chloride, run through a basic alumina column and then slowly distilled. The first and last 10% of the distillate were discarded. Carbon tetrachloride (Mallinckrodt spectrophotometric grade) was washed successively with a concentrated potassium hydroxide-methanol solution and then water (three times). It was then dried thoroughly over calcium

chloride and distilled from phosphorous pentoxide, discarding the first 10%. Methylene chloride was washed successively with concentrated sulfuric acid, water, a saturated aqueous sodium carbonate solution and water. It was then dried over calcium chloride and distilled from phosphorous pentoxide, discarding the first and last 10% of the distillate.

9,10-Diphenylanthracene (DPA) (Aldrich Gold Label) was used without further purification. 9,10-Dibromoanthracene (DBA) was recrystallized from acetonitrile. Rubrene (Aldrich) and 9,10-diphenylethynyl anthracene<sup>1</sup> (DPEA) were first chromatographed on neutral alumina, using benzene as eluant, and then recrystallized from benzene. Perylene (Aldrich) was chromatographed on basic alumina using methylene chloride as eluant and then recrystallized from benzene. The three phenazines, N,N-dimethyl-dihydrodibenzo [a.c.] phenazine (DMAC), N,N-dimethyl-dihydrophenazine (DMP) and N,N-dimethyldihydrodibenzo [b.i] phenazine (DMbi) as well as N,N-diphenyl-1-amino pyrene (DPAP) (see below) were synthesized and purified by Dr. S. P. Schmidt.<sup>28</sup> DMAC and DMP were recrystallized from hexane and acetonitrile respectively just prior to use. Biacetyl (Aldrich) was distilled prior to use.

#### N,N-diphenyl-1-aminopyrene

1-Aminopyrene (488 mg, 2.25 mmol, Aldrich) was stirred in 15 mL of dry THF and 10 mL of HMPT, under a nitrogen atmosphere. Bromobenzene (230  $\mu$ L, 2.25 mmol) was added to the solution. Lithium tetramethylpiperidide (prepared from the addition of n-butyllithium, 5.0 mmol, to 760  $\mu$ L of tetramethylpiperidine (4.5 mmol) in 5 ml of THF) was added dropwise over 20 min, affording a deep blue, then deep red solution, which was stirred at room temperature for 2 h, then at reflux for 5 h. After cooling, bromobenzene (230  $\mu$ L, 2.25 mmol) and then 7.4 mmol of lithium tetramethylpiperidide were added. The mixture was heated at reflux for 14 h. Bromobenzene (6.75 mmol) and then 10 mmol of lithium tetramethylpiperidide were added and the mixture heated at reflux an additional

8 h. After cooling, the mixture was poured onto 40 mL of ice, and extracted with ether. Evaporation gave 950 mg of a black oil, which was chromatographed on a 40x4 cm silica gel (Brinkmann 0.05-0.2) column, packed in a 25% methylene chloride/hexane slurry. Elution with 1:1 methylene chloride in hexane yielded N,N-diphenyl-1-aminopyrene as yellow crystals (35 mg, 5%) after recrystallization from benzene-hexane.

Anal. Calcd for  $C_{28}H_{19}N$ : C, 91.02; H, 5.18; N, 3.79. Found: C, 90.77; H, 4.99; N, 3.78.

#### 1-Phenylethylhydroperoxide

Method I: Caution! Syntheses of the hydroperoxide by this method resulted in two violent explosions during preparation carried out as described in the literature.<sup>10</sup> The following smaller scale procedure has proved innocuous, but caution is still strongly advised. One mL (8 mmol) of 1-phenyl ethanol (Aldrich) was stirred in a round bottom flask with 0.02 mL of concentrated  $H_2SO_4$  and cooled to 0°C. Behind an explosion shield, 2.7 mL (0.11 mole) of 90%  $H_2O_2$  was dropped in very slowly with stirring and the mixture stirred at 0°C for 2 h. The mixture was then warmed to 22-28°C and stirred another 4 h. Ether (10 mL) was added followed by 10 mL of water. The ether layer was washed twice with a 10% aqueous  $NaHCO_3$  solution and then water. The ether solution was dried with  $Na_2SO_4$ . After stripping off the ether in vacuo, the residue, a clear to slightly yellow liquid was distilled at 0.1 mm on a hanging cup distillation apparatus to give 66% yield of the hydroperoxide.  $^1H$  NMR ( $CCl_4$ ):  $\delta$  1.35 (d, 3H, methyl), 4.90 (q, 1H, methine), 8.0 (broad s, 1H, hydroperoxy), 6.85 (s, 5H, aromatic). Distillation of larger quantities of the hydroperoxide gave a boiling range of 48-52°C at 0.1 mm.

Method II:<sup>9</sup> Ethyl benzene (150 mL, Aldrich) and 0.15 g (1.6 mmoles) AIBN was bubbled with oxygen for 24 h at 110°C. The hydroperoxide is precipitated from solution with 50% aqueous NaOH, ether is added and the peroxide freed by

acidification with a 6 M HCl solution. This process is repeated, the ether stripped off and the hydroperoxide distilled as above. The NMR ( $\text{CCl}_4$ ) spectrum of this material was identical to that of the peroxide prepared by Method I.

#### 1-Phenylethyl Peroxyacetate (1)

Ketene was generated by cracking acetone according to the literature procedure.<sup>33</sup> The ketene was passed through successive dry ice-acetone traps to remove less volatile contaminants and then into the reaction solution. 1-phenylethyl hydroperoxide (0.5 mL, 4.7 mmol) was added to 15 mL of  $\text{CH}_2\text{Cl}_2$  containing 1.6 g of  $\text{Na}_2\text{SO}_4$  and saturated with gaseous HCl. Ketene was bubbled through the solution for 4 h. Completion of the reaction was determined by NMR spectroscopy. The reaction mixture was washed successively with water, saturated aqueous  $\text{K}_2\text{CO}_3$ , and twice with a  $1 \times 10^{-3}$  M aqueous solution of  $\text{Na}_4\text{EDTA}$ , and dried with  $\text{Na}_2\text{SO}_4$ . The  $\text{CH}_2\text{Cl}_2$  was removed in vacuo leaving a light yellow liquid. This liquid was placed under a vacuum of 0.05-0.1 mm for 2 h at 20-28°C to remove acetophenone. Distillation on a hanging cup apparatus at 0.05-0.07 mm and a surrounding oil bath temperature of 85-95°C gave a clear, colorless liquid (31%) identified as peroxyacetate 1.  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.50 (d, 3H, methyl,  $J=7\text{Hz}$ ), 1.90 (s, 3H, methyl), 5.17 (q, 1H, methine,  $J=7\text{Hz}$ ),  $\delta$  7.3 (s, 5H, aromatic). IR ( $\text{CCl}_4$ ): 3000, 1785, 1500, 1285  $\text{cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{10}\text{H}_{12}\text{O}_3$ ; C, 66.64; H, 6.73; Found: C, 66.98; H, 6.66.

Deuterated peroxyacetate (1d) was prepared from deuterated hydroperoxide.<sup>34</sup>  $^1\text{H}$  NMR ( $\text{CCl}_4$ ):  $\delta$  1.48 (broadened singlet, 3H, methyl), 1.85 (s, 3H, methyl) and 7.20 (s, 5H, aromatic)

#### Reduction of 1 to 1-Phenylethyl Acetate

Triethylphosphite (0.25 mL, 2 mmoles) in 4 mL of  $\text{CCl}_4$  was added under nitrogen to 2 mmoles of 1 in 4 mL of  $\text{CCl}_4$  with stirring.<sup>35</sup> The reaction was run for 5 h and followed by NMR spectroscopy which showed the consumption of the phosphite protons and appearance of the phosphate product. Also, absorptions

due to  $\lambda$  were replaced by the following spectrum:  $^1\text{H NMR (CCl}_4\text{)}$ :  $\delta$  1.5 (d, 3H, methyl,  $J=6\text{Hz}$ ), 2.00 (s, 3H, methyl), 5.75 (q, 1H, methine,  $J=6\text{Hz}$ ), 7.25 (s, 5H, aromatic). This product was shown to be identical to 1-phenylethyl acetate.<sup>36</sup>

#### 1-Phenylethyl peroxybenzoate (2a)

A solution of 1-phenylethylhydroperoxide (0.1 mL, 0.75 mmole) and benzoyl chloride (0.09 mL, 0.75 mmole) in 5 mL  $\text{CCl}_4$  was cooled to  $0^\circ\text{C}$ . A solution of 10% NaOH, saturated with NaCl, (5 mL) was added and the mixture stirred vigorously for 5 min. The  $\text{CCl}_4$  layer was washed successively with 10%  $\text{H}_2\text{SO}_4$  and water, dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated to give a clear colorless liquid. Low temperature ( $-20^\circ$ ) recrystallization from pentane gave 0.01 mL  $2a$ .  $^1\text{H NMR (CCl}_4\text{)}$ :  $\delta$  1.60 (d, 3H, methyl,  $J=6\text{Hz}$ ), 5.30 (q, 1H, methine,  $J=6\text{Hz}$ ), 7.30 (m, 7H, aromatic), 7.82 (d, 2H, aromatic). IR ( $\text{CCl}_4$ ):  $1757\text{ cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{O}_3$ : C, 74.35; H, 5.84. Found: C, 74.25; H, 5.96.

#### 1-Phenyl-4-methoxyperoxybenzoate (2b)

A solution of 1-phenylethylhydroperoxide (0.1 mL, 0.75 mmole) and anisoyl chloride (0.1 mL, 0.75 mmole) were warmed to  $40^\circ\text{C}$  in 5 mL  $\text{CCl}_4$ . A solution of 10% NaOH, saturated with NaCl, (5 mL) was added and the mixture stirred vigorously for 10 min. Workup of the reaction mixture was as described for  $2a$ . Low temperature ( $-20^\circ$ ) recrystallization gave 0.01 mL of  $2b$ .  $^1\text{H NMR (CCl}_4\text{)}$ :  $\delta$  1.60 (d, 3H, methyl,  $J=6\text{Hz}$ ), 3.7 (s, 3H, methyl), 5.30 (q, 1H, methine,  $J=6\text{Hz}$ ), 6.81 (d, 2H, aromatic), 7.3 (m, 5H, aromatic), 7.60 (d, 2H, aromatic) IR ( $\text{CCl}_4$ ):  $1751\text{ cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{16}\text{H}_{16}\text{O}_4$ : C, 70.56; H, 5.93. Found: C, 70.27; H, 6.00.

#### 1-Phenylethyl-4-dimethylaminoperoxybenzoate (2c)

A solution of 1-phenylethylhydroperoxide (0.3 mL, 2.25 mmole) and 4-dimethylaminobenzoyl chloride (0.42 g, 2.29 mmole) was prepared in 15 mL  $\text{CCl}_4$

at 25°C A solution of 18% NaOH, saturated with NaCl (15 mL) was added and stirred vigorously for 12 min. The  $\text{CCl}_4$  solution was washed successively with 10%  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , 10%  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{O}$ , then dried ( $\text{Na}_2\text{SO}_4$ ). Crystallization from a minimum of  $\text{CCl}_4$ , followed by recrystallization from ether-pentane gives 0.03 g of 2c as white crystals.  $^1\text{H NMR}$  ( $\text{CCl}_4$ ):  $\delta$  1.60 (d, 3H, methyl,  $J=6\text{Hz}$ ), 3.05 (s, 6H, methyl), 5.45 (q, 1H, methine,  $J=6\text{Hz}$ ), 6.62 (d, 2H, aromatic), 7.55 (m, 5H, aromatic), 7.82 (d, 2H, aromatic) IR ( $\text{CCl}_4$ ):  $1744\text{ cm}^{-1}$

Anal. Calcd for  $\text{C}_{17}\text{H}_{19}\text{NO}_3$ : C, 71.55; H, 6.72; N, 4.91. Found: C, 71.18; H, 6.53; N, 4.61.

1-Phenylethyl-3-nitroperoxybenzoate (2e)

A solution of 1-phenylethylhydroperoxide (0.2 mL, 1.5 mmoles) and 3-nitrobenzoyl chloride (0.28 g, 1.5 mmoles) were cooled in 10 mL  $\text{CH}_2\text{Cl}_2$ , to 0°C. A solution of 10% NaOH saturated with NaCl was added (10 mL) and the mixture stirred vigorously for 1.5 min. Workup of the  $\text{CCl}_4$  layer was as described for 2a and the  $\text{CH}_2\text{Cl}_2$  removed in vacuo leaving a white oily residue that was washed twice with pentane. Repeated crystallization from ether-pentane resulted in 0.02 g of 2e as white crystals.  $^1\text{H NMR}$  ( $\text{CCl}_4$ ):  $\delta$  1.60 (d, 3H, methyl,  $J=6\text{Hz}$ ),  $\delta$  5.52 (q, 1H, methine,  $J=6\text{Hz}$ ), 7.55 (m, 5H, aromatic), 8.55 (m, 3H, aromatic), 8.80 (m, 1H, aromatic). IR ( $\text{CCl}_4$ ):  $1770\text{ cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_5$ : C, 62.71; H, 4.57; N, 4.88. Found: C, 62.35; H, 4.30; N, 5.09.

1-Phenylethyl-4-nitroperoxybenzoate 2d

A solution of 1-phenylethylhydroperoxide (0.1 mL, 0.75 mmole) and 4-nitrobenzoyl chloride (0.14 g, 0.75 mmole) were cooled in 5 mL  $\text{CCl}_4$  to 0°C. A

solution of 10% NaOH (10 mL) was added and stirred vigorously for 3 min. The  $\text{CCl}_4$  layer was washed, dried and concentrated as described for 2a leaving a heavy oil. The oil was washed with pentane and repeatedly crystallized from ether-pentane to give 0.015 g of 2d as a white solid.  $^1\text{H NMR}$  ( $\text{CCl}_4$ ):  $\delta$  1.60 (d, 3H, methyl,  $J=6\text{Hz}$ ), 5.33 (q, 1H, methine,  $J=6\text{Hz}$ ), 7.30 (m, 5H, aromatic), 7.80 (d, 2H, aromatic), 8.10 (d, 2H, aromatic). IR ( $\text{CCl}_4$ ):  $1767\text{ cm}^{-1}$ .

Anal. Calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_5$ : C, 62.71; H, 4.57; N, 4.88 Found: C, 62.74; H, 4.44; N, 4.59.

#### Thermolyses Product Analyses:

1-Phenylethylperoxyacetate (1). Product analyses was done by gas chromatography (6'x1/4" Poropak Q,  $245^\circ$ ) for acetic acid, and (6'x1/4" SE-30 (3%) on chromasorb Q,  $100^\circ$ ) for acetophenone. Samples of 1 were thermolyzed in benzene at  $100^\circ$  until reaction was complete under the following conditions: with DPA, concentration of (1)  $3 \times 10^{-4}\text{ M}$ ; of DPA  $6 \times 10^{-4}\text{ M}$ ; with DMAC as activator, the concentration of DMAC was  $1.61 \times 10^{-3}\text{ M}$  and 1 was  $5 \times 10^{-4}\text{ M}$ . As a standard, a stock solution of acetic acid ( $3 \times 10^{-4}\text{ M}$ ) and acetophenone ( $3 \times 10^{-4}\text{ M}$ ) in benzene with DMAC ( $1.2 \times 10^{-3}\text{ M}$ ) or DPA ( $6 \times 10^{-4}\text{ M}$ ) was prepared. Comparison between the samples and the stock solution showed that acetophenone and acetic acid were formed quantitatively from 1.

Peroxybenzoates (2a-e). The acetophenone yield was determined by gas chromatography under the same conditions and column type as described for 1. The substituted benzoic acid yields were determined by  $^1\text{H NMR}$  (acetone  $d_6$ , 220 MHz) using hexamethylbenzene as an internal standard.

Rate of Reaction of 1 determined by NMR spectroscopy. The rate of thermolysis of 1 was determined by  $^1\text{H NMR}$  spectroscopy as follows. p-Dioxane (Mallinckrodt) was used as an internal standard at a concentration of  $5 \times 10^{-3}\text{ M}$  and 1

was  $5 \times 10^{-2}$  M in  $\text{CCl}_4$ . Duplicate runs were made by sealing evacuated NMR tubes containing the samples and following the change in methyl resonances of 1 (disappearance) and acetophenone (appearance) with time. A chemiluminescence decay run was made concurrently under the same conditions with an equivalent sample. These runs both at  $72^\circ\text{C}$ , gave the same rate for consumption of 1.

General Chemiluminescence Conditions: To obtain reproducible results it is important that the glassware used be carefully cleaned. We suspect that trace metal ions adsorbed on the glass may catalyze the decomposition of these peroxyesters. All glassware was cleaned according to the following procedure. The item was heated (steam bath) for 2 hr in a  $1 \times 10^{-3}$  M aqueous solution of tetrasodium ethylenediaminetetraacetic acid ( $\text{Na}_4\text{EDTA}$ ) rinsed thoroughly with distilled water, acetone, and then purified benzene. The item was dried at room temperature under a stream of argon.

The chemiluminescent thermolysis were carried out in 10 mm quartz cuvettes equipped with teflon stopcocks. The solutions were purged with argon for 3-4 min immediately before heating. Typical experimental procedures are given.

a) Direct chemiluminescence of 2c. A solution of 2c ( $1 \times 10^{-4}$  M), 2 mL in benzene was purged for 3 min with argon and then placed in a cell-holder preheated to  $100^\circ$ . The chemiluminescence intensity was recorded at the emission maximum, following a 5 min equilibration period, for 128 equal time intervals covering 4 half-lives. The first-order rate constant was obtained by a linear least-squares analysis. Total chemiluminescent intensities were obtained by integration of the area under the decay curve extrapolated to infinite time.

b) Indirect chemiluminescence of peroxyacetate 1. A solution of 1 ( $2.3 \times 10^{-5}$  M) and biacetyl (Aldrich, distilled immediately before use,  $4.5 \times 10^{-2}$  M) in 2 mL of benzene was prepared and purged with argon. The solution was heated at  $100^\circ$  and the emission intensities at 128 wavelengths equally spaced between 350 nm and 550 nm were recorded. The average of four of these spectra gave the emission spectrum shown in Figure 1.

c) Activated chemiluminescence of peroxybenzoate 2a. Solutions of 2a ( $3 \times 10^{-4}$  M) and DMAC ( $1 \times 10^{-4}$  M) were prepared in 2 mL of benzene, purged with argon and the rate of reaction of 2a determined by the decay of the DMAC emission intensity as described above. The derived first-order rate constants at increasing DMAC concentration are shown in Figure 6.

Determination of the fluorescence quantum yields ( $\phi_f$ ). The fluorescence yields of the various activators of Table 2 at high temperature were determined by comparison of the fluorescence intensity at 95-100° with that obtained at 25-28° on the same sample in argon purged benzene solution. With the exception of DPAP the room temperature fluorescence yields were obtained from the literature<sup>37</sup> (rubrene, perylene, DPA and DPEA) or determined by comparison with an appropriate standard (DMP, DMAC and DMBI). Experimental details of the latter determinations have been recently published.<sup>38</sup> The fluorescence yield of DPAP was determined relative to perylene ( $\phi_f = 1.0$  in benzene at 25°C) to be 1.0 at 25° and was unchanged at 95°. The fluorescence yield of 4-dimethylaminobenzoic acid at 25°C was determined using DPA as a standard ( $\phi_f = 0.85$  at 25°), to be 0.025. At 94.0°C this fluorescence yield decreases to 0.0064. Table 3 contains the fluorescence yields at 25-28° and 94-100°, and oxidation potential of all of the activators used in this work.

Estimation of yield of singlet and triplet excited states from the thermolysis of 1 at 100°C. The direct chemiluminescence from 1 was too weak to permit determination of the yield of excited states. In the presence of perylene, a double reciprocal plot of perylene concentration against the integrated intensity was done for dioxetane 3 and for 1, both at  $1 \times 10^{-3}$  M in benzene. Comparison of the total intensities at infinite perylene concentration gives a singlet yield from 1 and perylene by activated chemiluminescence of 0.02%. This assumes a singlet yield from IMD of 0.2%.<sup>38</sup> A similar comparison, using biacetyl indirect chemiluminescence, to obtain the yield of triplet, was not

possible due to the very low indirect chemiluminescence intensities observed for I and biacetyl. However, an upper limit of 0.02 was established by comparison of the total intensities of I (1) and I ( $2.3 \times 10^{-5}$  M) in the presence of biacetyl ( $4.5 \times 10^{-2}$  M) in benzene assuming a triplet yield of 30% for TMD.

Determination of the yield of singlet and triplet p-dimethylaminobenzoic acid from the thermolysis of 2c at 94°C. The yield of singlet acid from 2c was determined by comparing the total intensity of 2c ( $1 \times 10^{-4}$  M) with the extrapolated intensity obtained from a double reciprocal plot of DBA concentration against intensity with TMD ( $1 \times 10^{-5}$  M). The intensities are corrected for photomultiplier tube response. DBA fluorescence yield at 95°C (0.017) TMD yield of triplet acetone (30%), efficiency of energy transfer from acetone to DBA (0.2), and the fluorescence yield of p-dimethylaminobenzoic acid at 94°C (see above).

The yield of triplet acid from 2c was determined by comparing the extrapolated intensity values of double reciprocal plots of DBA concentration versus total intensity for 2c and TMD. The appropriate corrections, as described above, were made. The assumption is made that the energy transfer efficiencies of acetone and p-dimethylaminobenzoic acid to DBA are the same.

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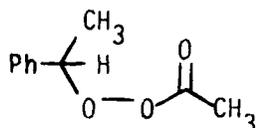
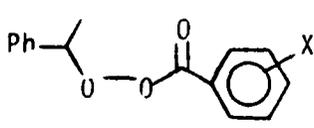
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- 24) The efficiency of triplet to singlet energy transfer from acetone and from p-dimethylaminobenzoic acid triplet to DBA is assumed to be the same.
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- 29) Of course it may prove to be experimentally impossible to detect the rate increase if  $k_{cat} [ACT] \ll k_f$ . Yet it is still possible that the activated chemiluminescence accounts for all of the observed light.
- 30)  $\Delta E_{+/-} = E_{ox} - E_{red} + E_{coul}$  where  $E_{ox}$  is the one electron oxidation potential,  $E_{red}$  the one electron reduction potential and  $E_{coul}$  is the coulombic work term. It should be noted that the values of  $E_{ox}$  and  $E_{red}$  are often solvent dependent. The electrochemical values used to estimate  $\Delta E_{+/-}$  were obtained in  $CH_3CN$  with tetra-n-butylammonium perchlorate supporting electrolyte. There is undoubtedly some change in these values in the benzene solvent used in the chemiluminescence experiments. However, the relative magnitudes, and the general trends observed are probably reliable.
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Table 1 - Rate Constants and Activation Parameters  
for Thermolysis of Peroxyesters 1 and 2.

Peroxyester <sup>a</sup>	Conc. (M)	Temp (°C)	$k_1^b$ (S <sup>-1</sup> ) at	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (e.u.)
	$3 \times 10^{-4}$	100.0	$1.14 \times 10^{-4} \pm 7.2 \times 10^{-7}$	$33.1 \pm 0.7$ $7.2 \times 10^7$	$16.8 \pm 1.9$
					
X=H	$3 \times 10^{-4}$	99.7	$4.03 \times 10^{-4} \pm 3.0 \times 10^{-6}$	$29.5 \pm 3.3$	$4.6 \pm 8.9$
P-OCH <sub>3</sub>	$3 \times 10^{-4}$	99.7	$3.50 \times 10^{-4} \pm 2.44 \times 10^{-6}$	$32.0 \pm 3.1$	$11.4 \pm 8.3$
P-N(CH <sub>3</sub> ) <sub>2</sub>	$1 \times 10^{-4}$	100.0	$2.16 \times 10^{-3} \pm 9.6 \times 10^{-6}$ <sup>c</sup>	$26.6 \pm 0.5$	$0.5 \pm 1.4$
MONO <sub>2</sub>	$3 \times 10^{-4}$	100.0	$5.97 \times 10^{-4} \pm 5.1 \times 10^{-6}$	$32.5 \pm 1.1$	$14.1 \pm 6.1$
P-NO <sub>2</sub>	$3 \times 10^{-4}$	100.0	$4.10 \times 10^{-4} \pm 4.4 \times 10^{-6}$	$34.9 \pm 3.6$	$19.8 \pm 10$

a. Benzene solutions were purged with argon before measurements.

b. Perylene ( $6 \times 10^{-4}$  M) indirect chemiluminescence was monitored to determine the rates.

c. Direct chemiluminescence of p-dimethylaminobenzoic acid was monitored to determine rates.

Table 2  
Comparison of the Singlet Energies  
and  
Energies Available Upon Ion Annihilation of the Various Activators

Activator	$E_s^a$ (kcal/mole)	Available Energy ( $E^+$ ) <sup>b</sup> (kcal/mole)	$k_{cat}$ ( $M^{-1} s^{-1}$ ) <sup>c</sup>
DMAC	58	59	$9.73 \times 10^{-2}$
DMP	72	59	$1.59 \times 10^{-1e}$
DMBI	68	67	$7.07 \times 10^{-3}$
Rubrene	54	75	$1.40 \times 10^{-4d}$
DPAP	68	76	$2.35 \times 10^{-4}$
Perylene	65	79	$1.19 \times 10^{-4}$
DPEA	62	82	$3.58 \times 10^{-5}$
DPA	72	84	$2.22 \times 10^{-5}$

- a. Assigned from the 0-0 band of the fluorescence spectrum.
- b. Calculated by taking the difference between the oxidation potential of the activator and the reduction potential of acetophenone.
- c. Calculated by comparing the total intensity to that of DMAC and assuming that the light intensity is proportional to the fraction of the reaction that proceeds through the CIEEL path.
- d. Unavoidable self absorption by rubrene leads to the observed low calculated value for  $k_{cat}$ .
- e. Measured by determining the apparent first order rate constant for reaction of  $\lambda$  at varying DMP concentration.

Table 3. Oxidation Potentials and Fluorescence Quantum Yields of the Activators of Figure 3

Activator	Fluorescence Yield <sup>a</sup>		Oxidation Potential (V)
	24-28°C	94-100°C	
DMAC	0.04	0.04	0.14
DMP	0.40	0.18	0.14
DMBI	0.88	0.88	0.46
Rubrene	1.00	0.56	0.82
DPAP	1.00	1.00	0.90
Perylene	0.84	0.84	1.00
DPEA	0.96	0.96	1.16
DPA	0.85	0.85	1.22
DBA	0.10	0.017	1.45

a. Determined in argon purged benzene solution. The previously unknown fluorescence quantum yields were determined relative to DPA (DMP, DMBI), Perylene (DPAP) or DPEA (DMAC).

Captions for Figures

Figure 1. First-order decay of indirect or direct chemiluminescence intensity from peroxyesters at 100° in benzene solution. Starting concentrations range from  $1 \times 10^{-4}$  M to  $3 \times 10^{-4}$  M. From the top-down the lines represent: circles,  $\lambda_b$ , squares,  $\lambda_a$ , circles,  $\lambda_c$ , triangles,  $\lambda$ , diamonds,  $\lambda_e$ , triangles,  $\lambda_d$ .

Figure 2. Eyring activation plots from the first-order chemiluminescence decay of peroxyesters in benzene solution. From the top-down the lines represent: squares,  $\lambda_c$ , circles,  $\lambda_e$ , triangles,  $\lambda_d$ , triangles,  $\lambda_a$ , diamonds,  $\lambda_b$ , circles,  $\lambda$ .

Figure 3. Emission spectrum of indirect chemiluminescence from peroxyacetate  $\lambda$  ( $2.2 \times 10^{-3}$  M) and biacetyl ( $2.0 \times 10^{-3}$  M) in benzene solution at 100°.

Figure 4. Emission spectrum of direct chemiluminescence from p-dimethylamino substituted peroxybenzoate ( $\lambda_c$ ),  $1.8 \times 10^{-2}$  M in benzene solution at 92.2°.

Figure 5. Double reciprocal plot of total indirect chemiluminescence intensity against DBA concentration for (A) peroxybenzoate  $\lambda_a$  and (B) p-dimethylamino substituted peroxybenzoate  $\lambda_c$  in benzene solution at 100°.

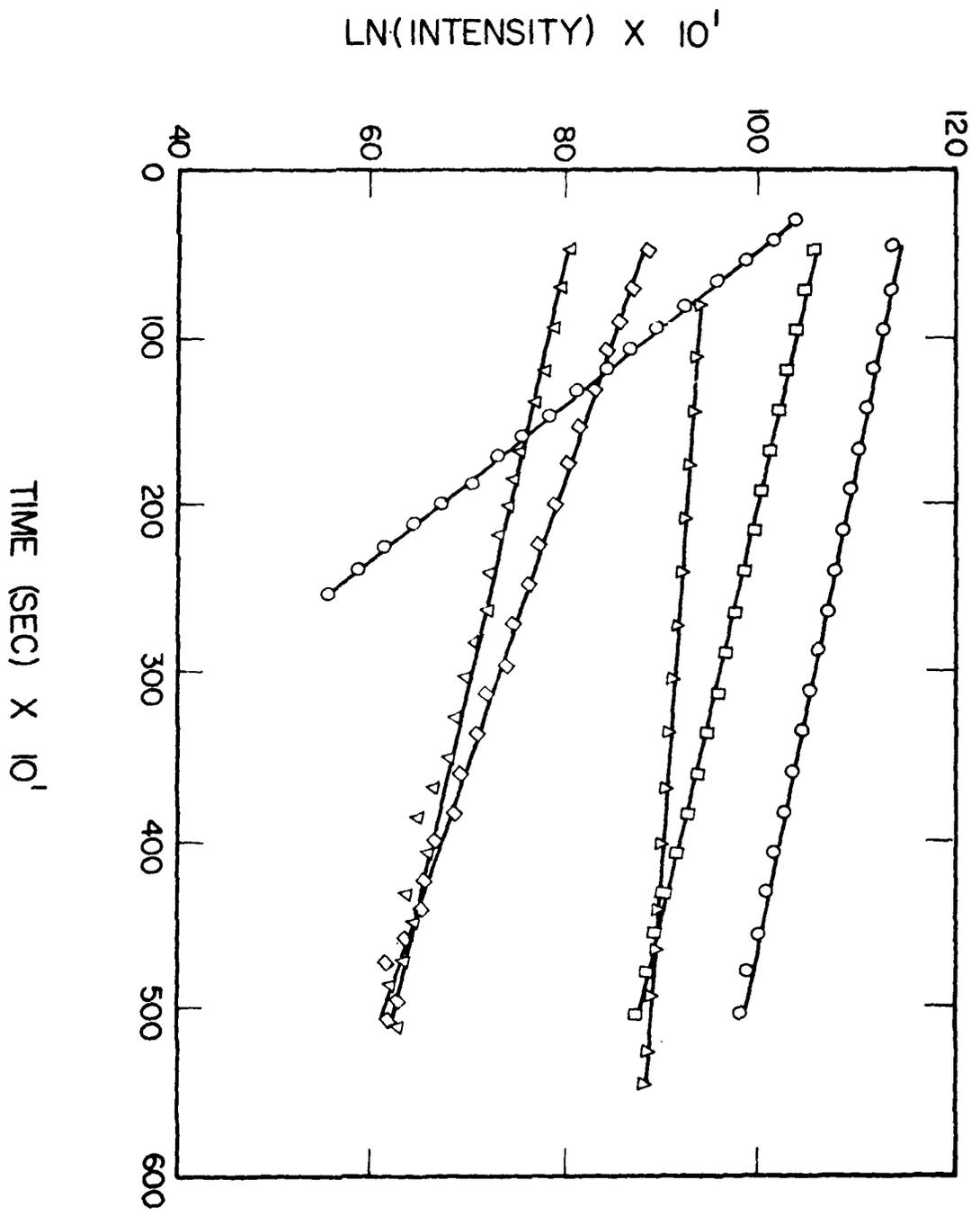
Figure 6. Effect of DMAC concentration on the observed rate of reaction for peroxyacetate  $\lambda$ ,  $3 \times 10^{-4}$  M in benzene at 100°.

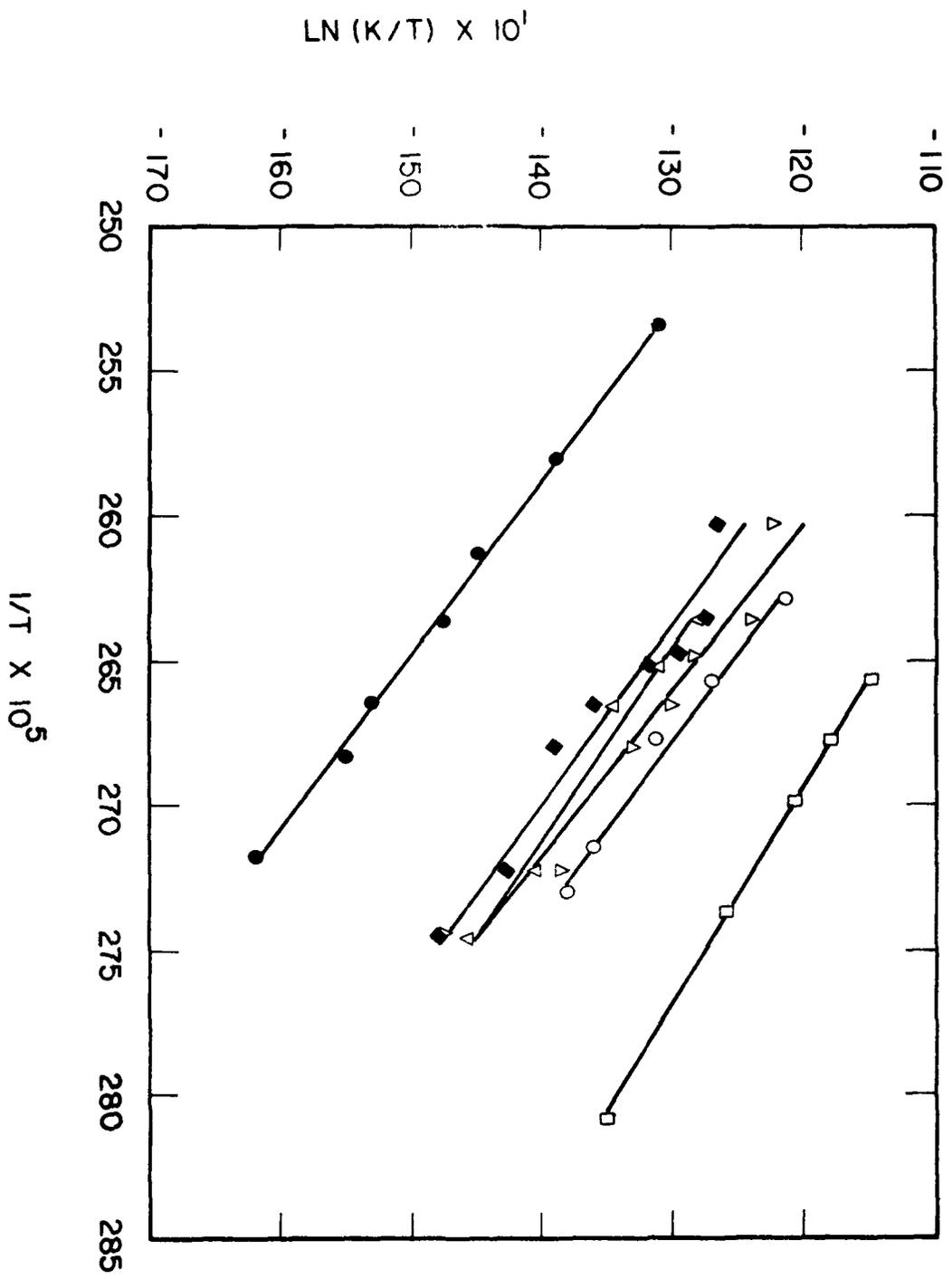
Figure 7. Emission spectrum of activated chemiluminescence from peroxyacetate  $\lambda$  ( $3 \times 10^{-4}$  M) and DMAC ( $6 \times 10^{-4}$  M) in benzene solution at 100°.

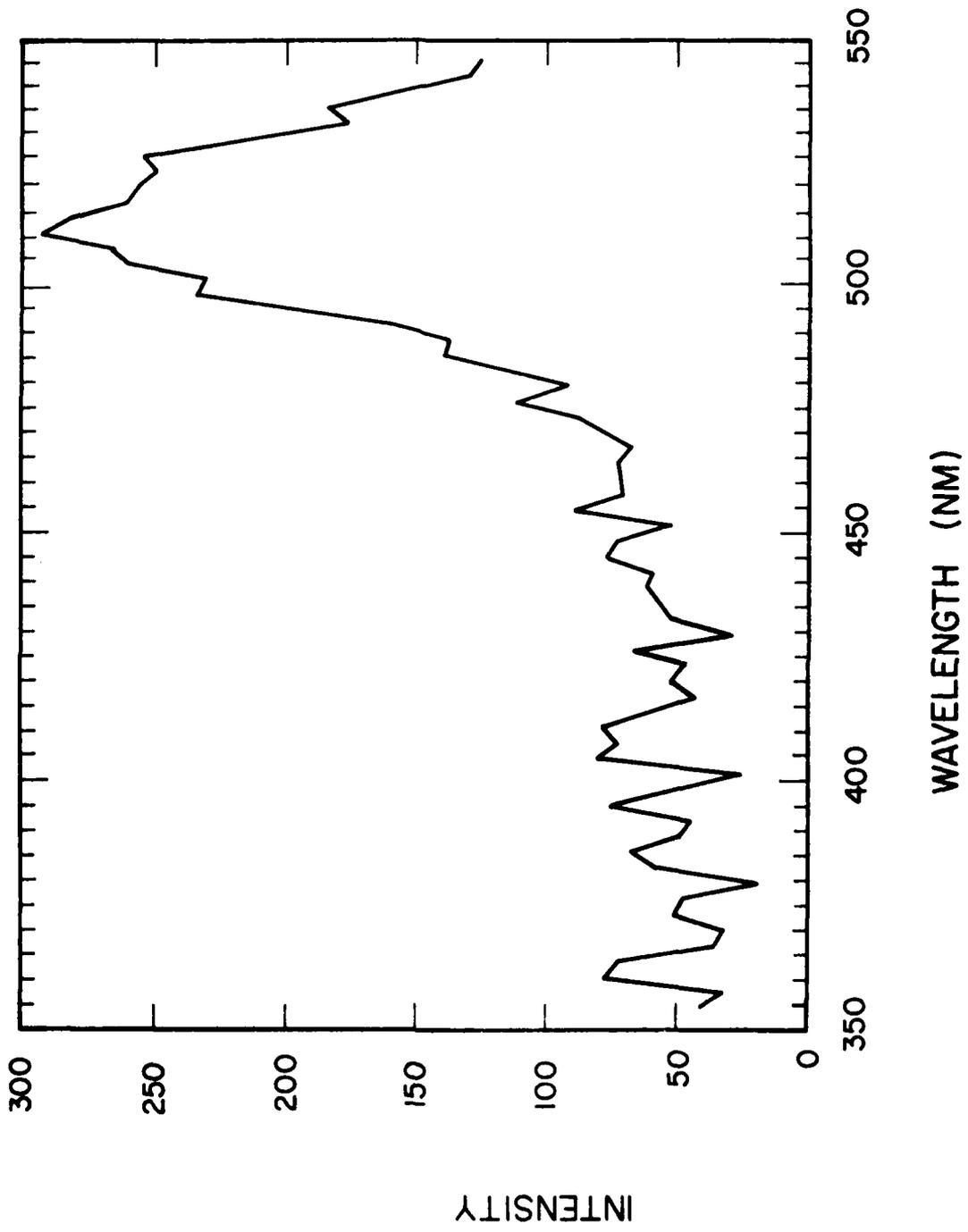
Figure 8. Correlation of total chemiluminescence intensity with activator oxidation potential ( $E_{ox}$ ) for peroxyacetate  $\downarrow$ . Measured in argon purged benzene with activator at  $1 \times 10^{-4}$  M and perester at  $1 \times 10^{-3}$  M at 99.5°C.

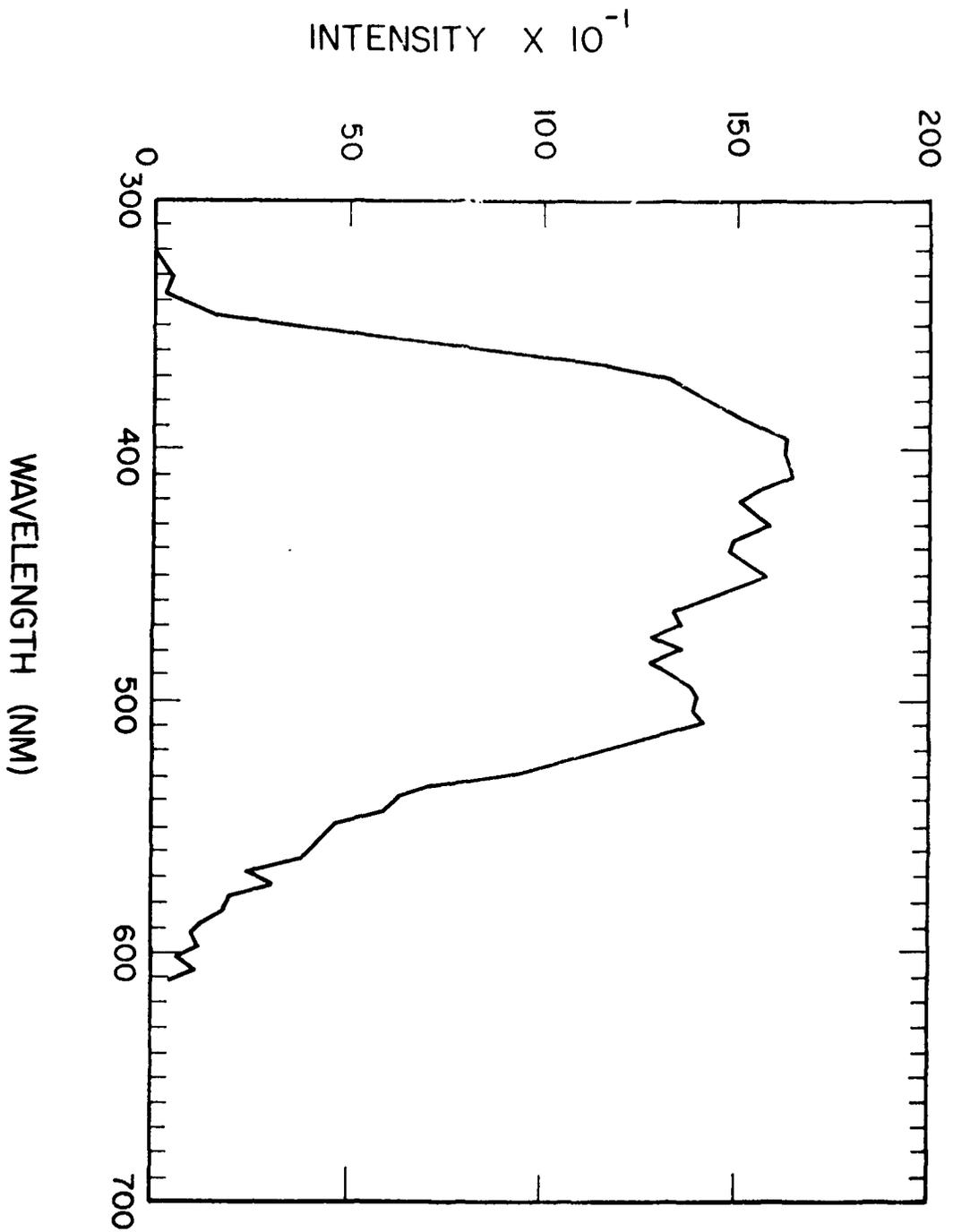
Figure 9. Effect of DMAC concentration on the observed rate of reaction of the substituted peroxybenzoates. The lines correspond to: squares,  $k_d$  at 100°, triangles,  $k_c$  at 92.2°, inverse triangles,  $k_b$  at 100°, circles,  $k_a$  at 100°. The data for  $k_d$  do not extrapolate to the proper  $k_1$ . This may be a result of a chain reaction of the nitro substituted acid radical anion at low DMAC concentration.

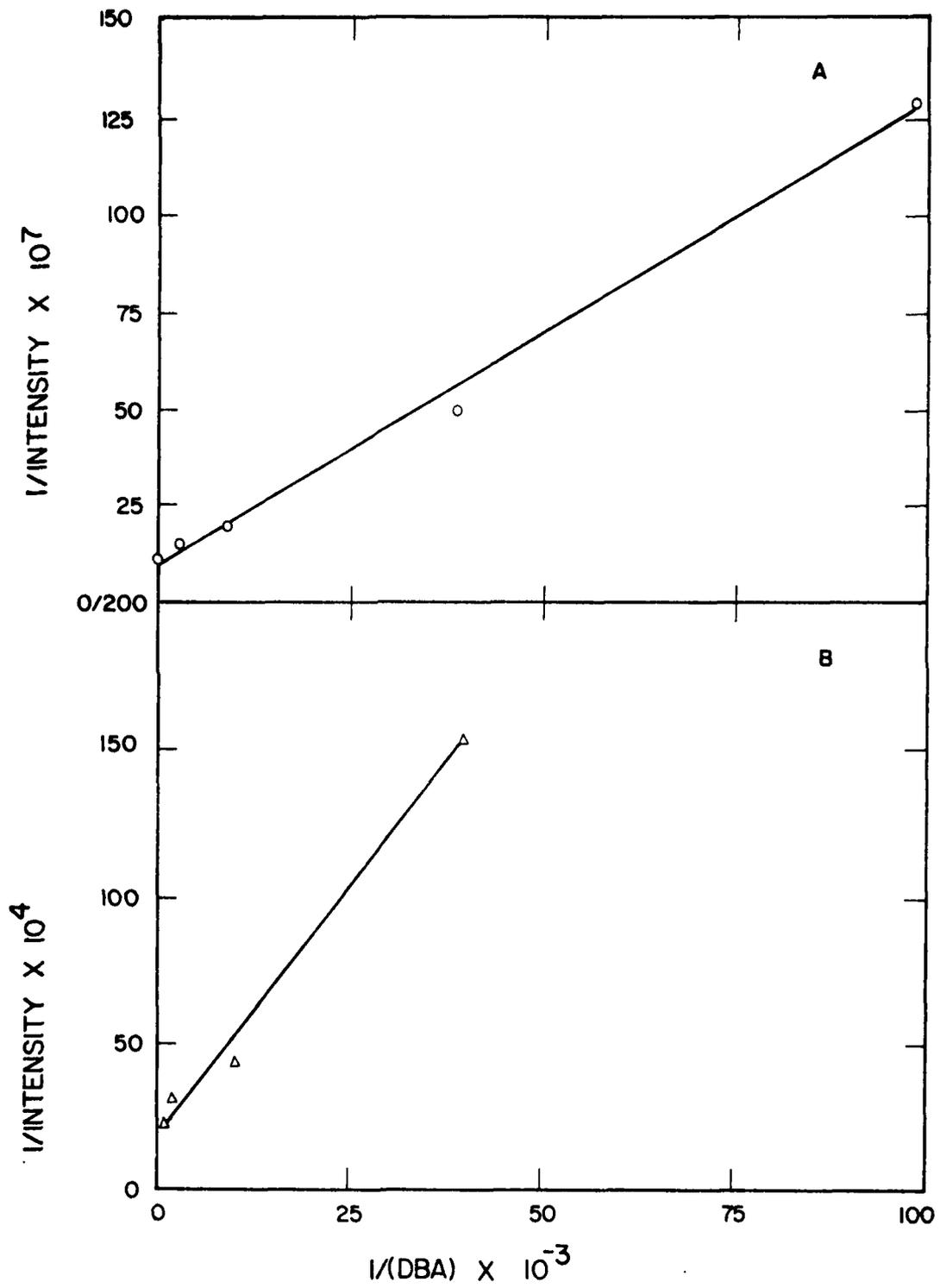
Figure 10. Correlation of activated chemiluminescence intensity with oxidation potential of the catalytic activators. In order of increasing oxidation potential the activators are: DMAC, DMBI, Rubrene, Perylene, DPEA, DPA. The activator concentration is  $1 \times 10^{-4}$  M in all cases the lines correspond to: squares,  $k_b$ , inverse triangles,  $k_a$ , triangles,  $k_c$ , circles,  $k_e$ .

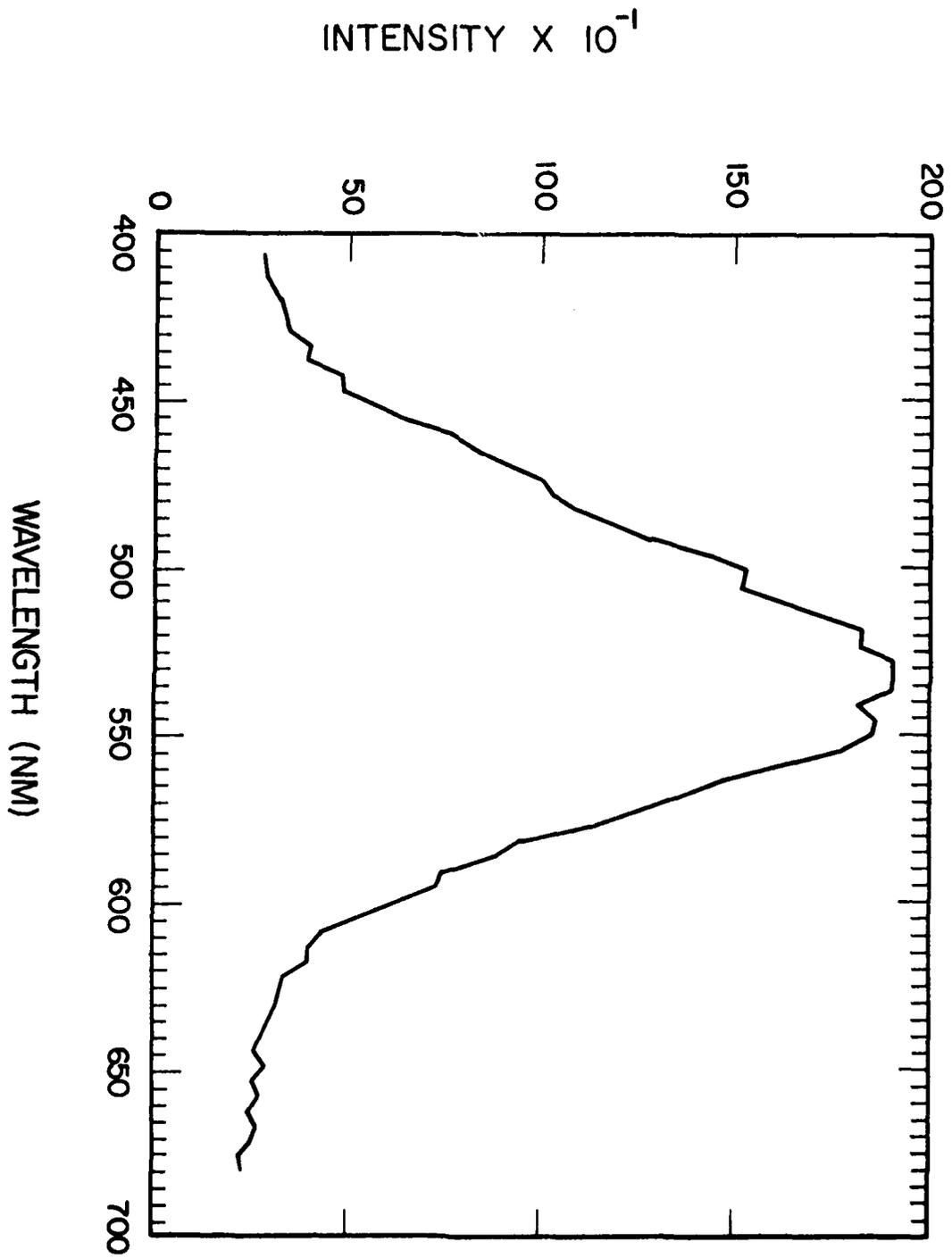


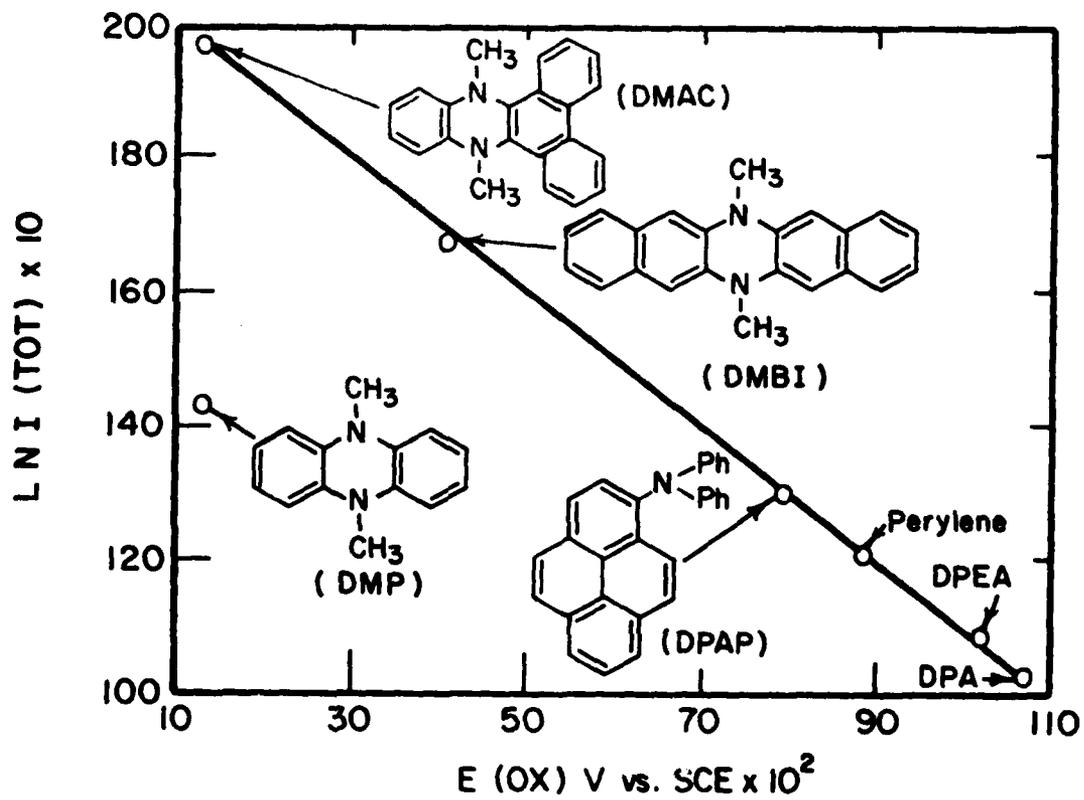


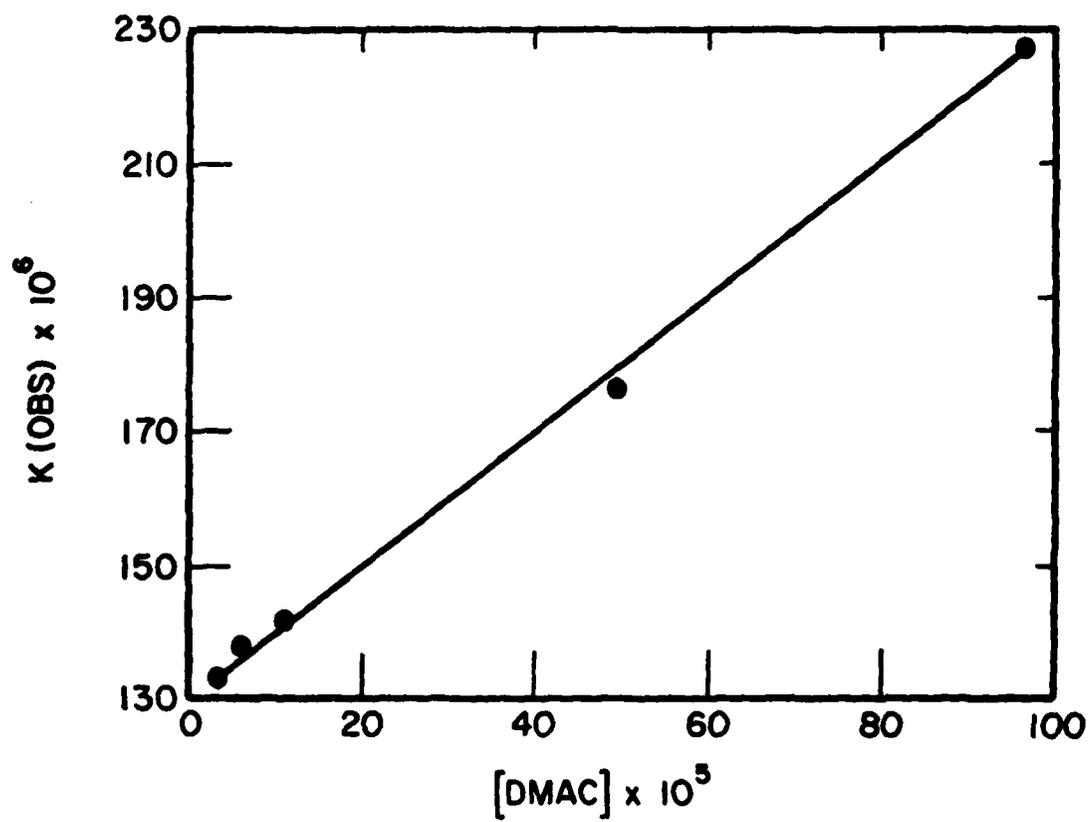


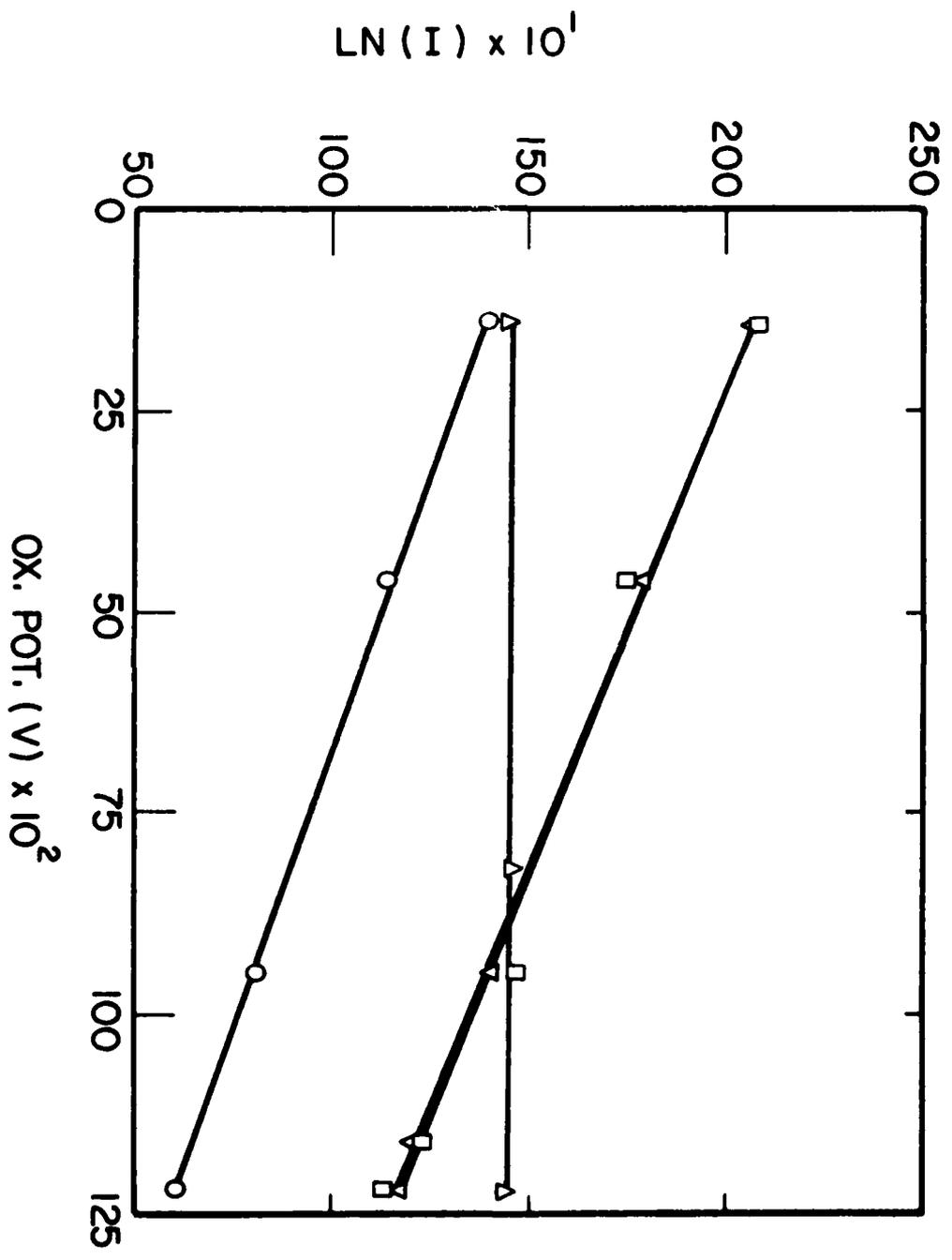


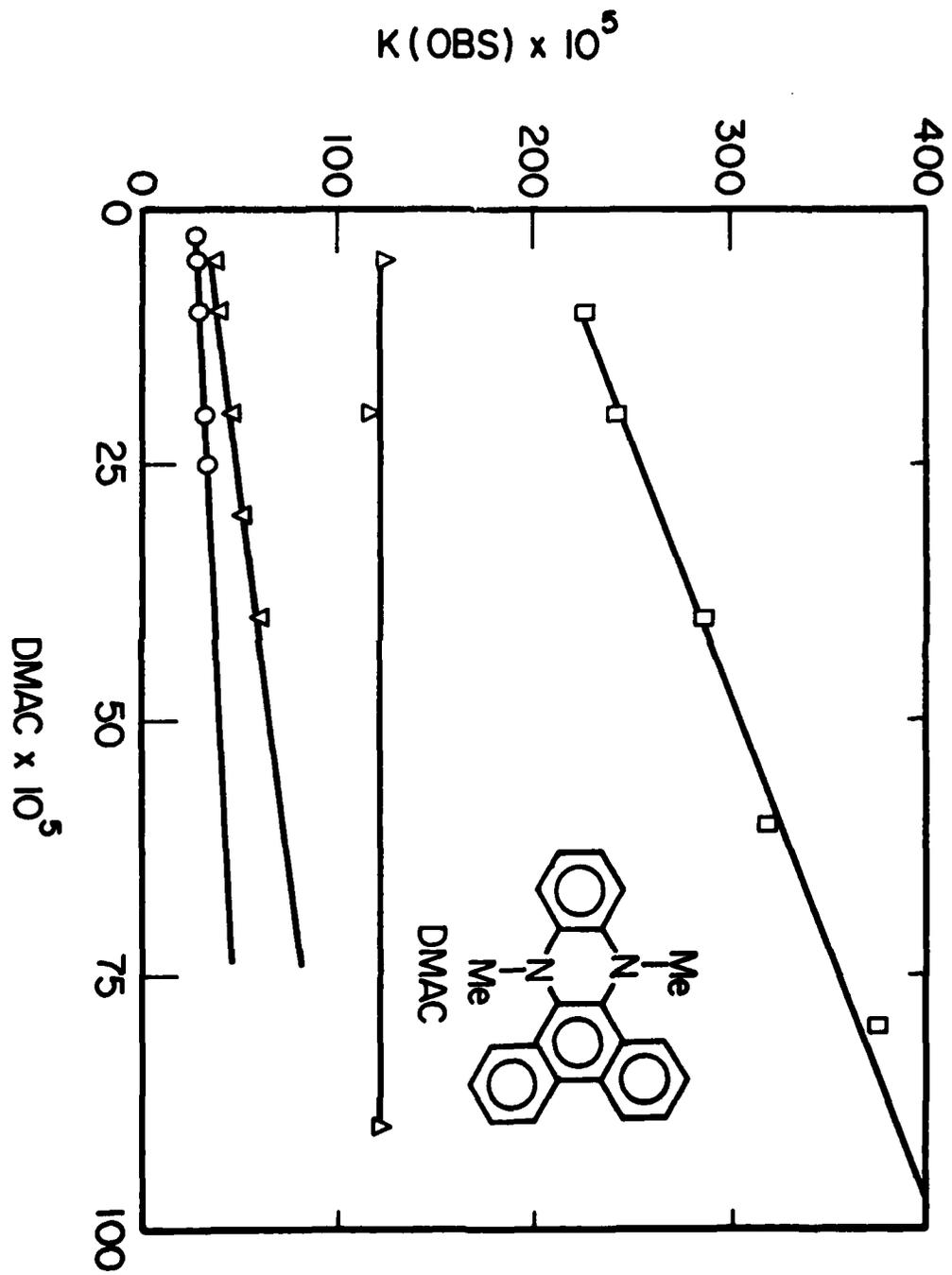












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