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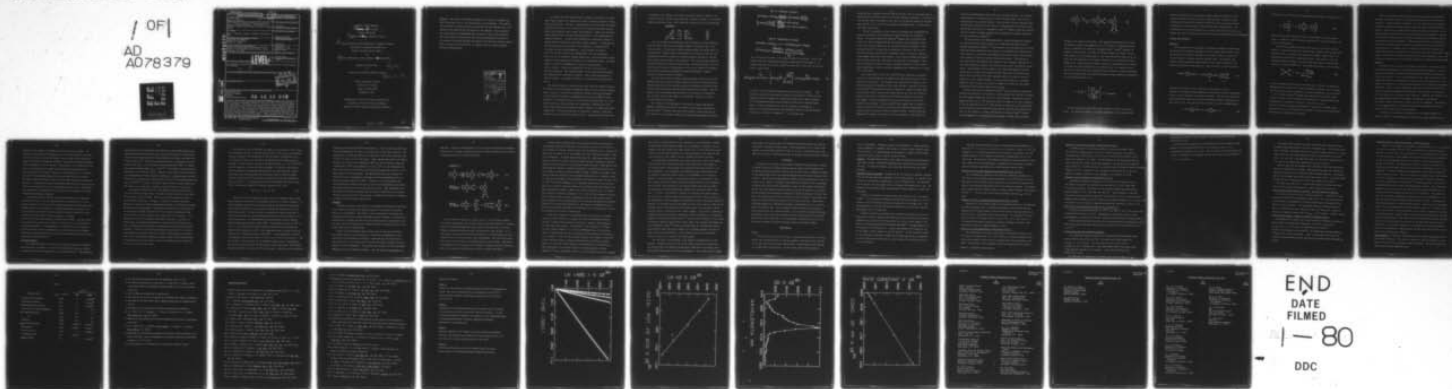
ILLINOIS UNIV AT URBANA-CHAMPAIGN DEPT OF CHEMISTRY  
ELECTRON TRANSFER INITIATED REACTIONS OF ORGANIC PEROXIDES. THE--ETC(U)  
DEC 79 G B SCHUSTER , J J ZUPANCIC , K A HORN N00014-76-C-0745

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6) Electron Transfer Initiated Reactions of Organic Peroxides.

The Reaction of Phthaloyl Peroxide with  
Olefins and Other Electron Donors.

by

10) Gary B./Schuster, Joseph J./Zupancic ~~and~~ Keith A./Horn

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Abstract: The reaction of phthaloyl peroxide with a variety of compounds capable of reacting as one or two electron donors was investigated. The products and the kinetics of these reactions indicate that the rate-limiting step is the transfer of one electron from the reactant to the peroxide. This conclusion was substantiated by investigating these reactions by laser flash photolysis. This study showed conclusively that odd electron intermediates are formed in the reaction of phthaloyl peroxide with ground and excited state electron donors. These reactions may be prototypical of a general class of electron transfer initiated transformations.

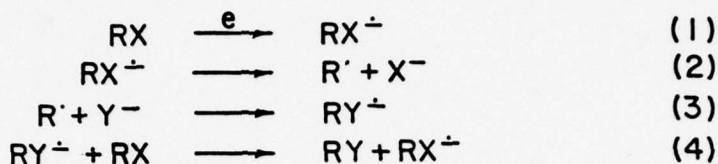
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To a large extent the reactions and the relative reactivities of closed-shell organic reagents are formulated in terms of classical concepts of Lewis acidity and basicity. Thus most transformations of such molecules are conceptualized as the result of the interaction of an electron pair donor (nucleophile) with an electron pair acceptor (electrophile). Indeed, this formalism serves remarkably well, and has contributed greatly to our understanding of chemical reactivity. In recent years evidence has accumulated in support of another mode of reaction for closed shell organic reagents. In this mode the initiating process of the reaction is the transfer of a single electron to produce odd electron intermediates. If the reagents are neutral, as they are in the systems we have investigated, then the intermediate state is a pair of oppositely charged radical ions. With electrically charged reagents neutral radicals may be formed at the intermediate stage. The first formed odd electron intermediates are typically quite reactive, and may undergo rapid bond fragmentation reactions to generate new odd electron species. The eventual products of the single-electron-transfer route typically are closed-shell molecules. Thus at some stage during the reaction sequence a coupling of radicals or a second electron transfer must occur.

The general sequence of events outlined above (electron transfer followed by reaction to give eventually closed-shell product) has been found to predominate in a group of chain reactions generally labeled as the  $S_{RN}1$  mechanism.<sup>3</sup> In this process initiation is accomplished by one electron reduction of the substrate (by a solvated electron, an electronically excited state, or a cathode) to generate a reactive radical ion intermediate. Substrates for this reaction are typically easily reduced aromatic halides, or  $\alpha$ -substituted nitroalkanes (RX).<sup>4</sup> The reduced substrate is postulated to undergo a rapid bond cleavage to form a radical and an anion ( $R^{\cdot} + X^{-}$ ). The radical reacts next with

a nucleophile ( $Y^-$ ) forming a new radical anion ( $RY^{\cdot-}$ ) which is capable of continuing the chain. The basic  $S_{RN}1$  mechanism, outlined in Scheme 1, has withstood numerous experimental tests, and is generally considered to be well established.

### Scheme 1

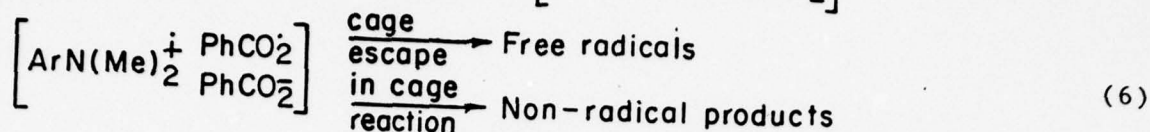
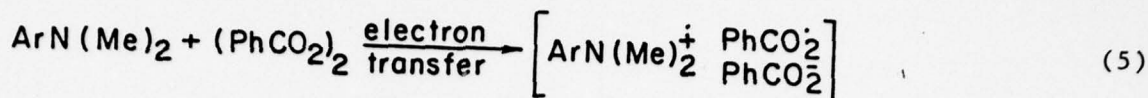


Not less studied, but certainly less well understood, are the transformations of organic peroxides with reagents capable of reacting as one or two electron donors. The reaction of benzoyl peroxide (BPO) with amines serves as a typical case. Horner's early investigation of the reaction of BPO with dimethylaniline led him to postulate a reaction sequence initiated by one electron transfer from the amine to the peroxide.<sup>5</sup> This proposal neatly explained the rapid formation of radical derived products, and was shown later to be consistent with the effect of substituents on the reaction kinetics for symmetrically substituted benzoyl peroxides<sup>6</sup> and substituted amines.<sup>7</sup> Horner's postulate is shown as Path A in Scheme 2.

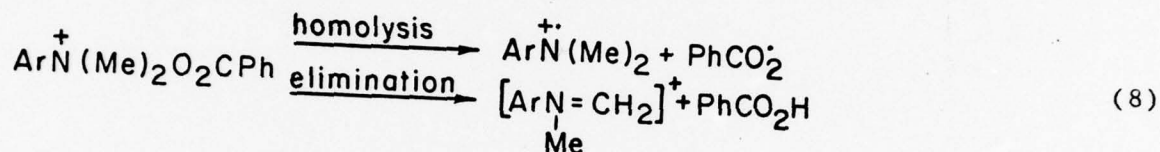
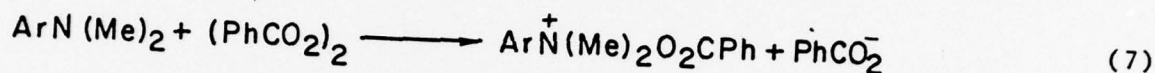
Not long after Horner's proposed sequence appeared, Walling and Indictor<sup>8</sup> suggested that the reaction of tertiary amines with benzoyl peroxide proceeds through the formation of an unstable quaternary hydroxylamine derivative which reacts further to give both radical and non-radical derived product. The formation of this intermediate was postulated to be the result of nucleophilic (two electron) attack by the amine on the peroxide. Walling's postulate is shown as Path B in Scheme 2.

The debate over the mechanism of the reaction of amines with BPO was seemingly convincingly resolved by the classic isotope tracer experiments of Denny and Denny.<sup>9</sup> Dibenzyl amine and benzoyl peroxide, labeled specifically with oxygen-18 in the carbonyl oxygens, gave O-benzoylhydroxylamine containing

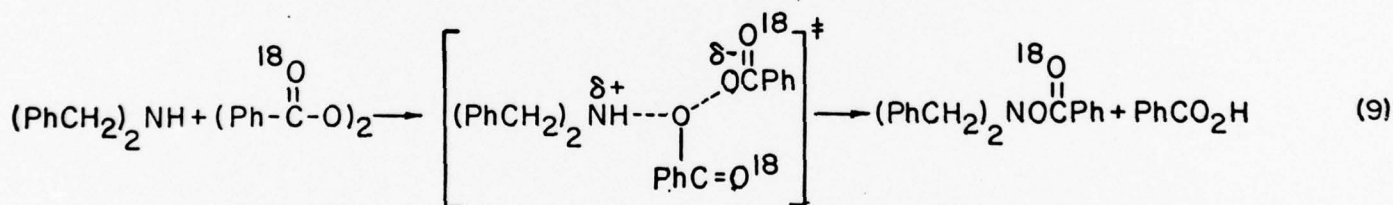
## Path A (Electron Transfer)



## Path B (Nucleophilic Attack)



all of the excess oxygen-18 in the carbonyl oxygen of the product. Thus it was reasoned that this reaction must proceed by nucleophilic displacement; eq 9. Indeed, faced with this result, Horner<sup>10</sup> conceded that at least part of the reaction of amine and BPO



proceeds by the nucleophilic displacement path postulated by Walling. This conclusion, which has been adopted by numerous investigators,<sup>11</sup> rests upon the assumption that the formation of a benzoyloxy radical (eq 5) before formation of the hydroxylamine product would scramble the labeled and unlabeled oxygen atoms. A recent interpretation of the epr spectrum of the benzoyloxy radical in a crystalline matrix at low temperature indicates that the unpaired electron is an orbital of  $\sigma$ -symmetry.<sup>12</sup> It is possible that

during the short lifetime of Horner's radical ion pair that the two oxygen atoms of the postulated benzoyloxy radical do not become chemically equivalent. If this is the case, then the lack of scrambling of the label is an acceptable result for the electron transfer as well as for the nucleophilic displacement path. We will discuss this point further below.

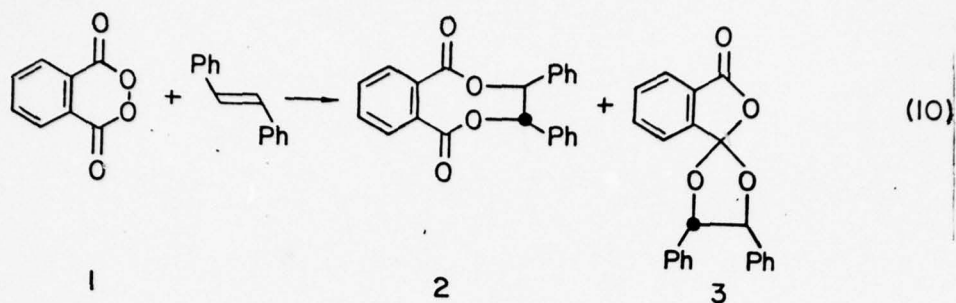
Further investigation of the reaction of peroxides with nucleophiles has resulted alternatively in postulation of electron transfer or nucleophilic attack. For example, Kashino and coworkers<sup>13</sup> suggest that the relative reactivity of a series of amines with BPO is consistent with nucleophilic attack if the rate of proton transfer in the activated complex is considered. Also, Pryor and Bickley<sup>14</sup> conclude that the mechanism of reaction of BPO with sulfides and disulfides involves the nucleophilic attack of the sulfur compound on the oxygen-oxygen bond of the peroxide. More recently, Hoffman and Cadena<sup>15</sup> have concluded, based upon comparison of the magnitude of the Hammett  $\rho$  value, that the oxidation of amines by sulfonyl peroxides proceeds by initial nucleophilic displacement to give a covalent intermediate which eliminates in a second step to give imine.

On the other hand, Vul'fson and coworkers<sup>16</sup> have found that the relative reactivity of phthalocyanines and porphines with BPO follows the ease of oxidation of the macrocycle. They interpret this observation to indicate a rate limiting one electron transfer step for these reactions. Similarly, Filliatre and coworkers<sup>17</sup> observed that the rate of reaction of a series of simple heterocyclic amines did not correlate with amine basicity, but that the activation energy of the reaction is related to the ionization potential of the amine. They suggest a reaction mechanism that has as a key feature a one electron transfer to the peroxide. Yassin and Rizk<sup>18</sup> have reported that the effect of solvent polarity on the products of the reaction of BPO and hydroquinone is consistent with an electron transfer initiated reaction. Recently, Pryor and Hendrickson<sup>19</sup> reported the results of their investigation of the reaction of

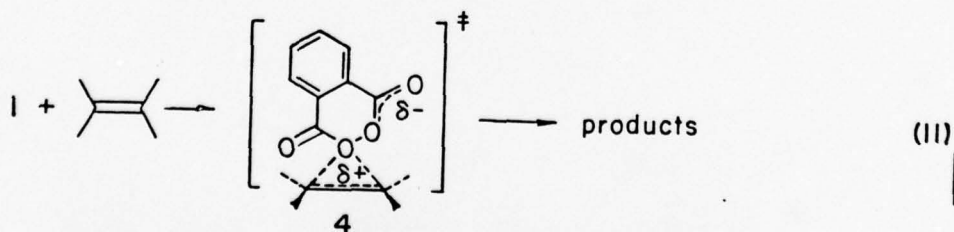
tert-butyl peroxybenzoates with dialkyl and aryl alkyl sulfides. They conclude, based primarily on the observation of radical derived products, that the rate determining step is electron transfer. This conclusion is quite startling since the same group contends that the reaction of these sulfides with the more easily reduced BPO is the result of nucleophilic attack.<sup>20</sup> Finally, Kochi has concluded that the reaction of organic peroxides with organometallic reagents proceeds by an electron-transfer mechanism.<sup>21</sup>

Our recent work on the chemiluminescence of organic peroxides has revealed an excitation process we have referred to as chemically initiated electron-exchange luminescence (CIEEL).<sup>22</sup> In the course of our investigation of the CIEEL mechanism we have demonstrated that radical ion intermediates are formed by electron transfer to a wide variety of peroxides from electron donors such as heterocyclic amines, and even from simple aromatic hydrocarbons. The existence of these odd electron intermediates was revealed by the systematic investigation of the reaction kinetics, products, and finally by their direct spectroscopic observation. These studies, and the results of the other investigations outlined above, led us to suspect that electron transfer might play a heretofore unsuspected role in the reaction of many compounds capable of serving as electron donors with easily reduced reagents. We chose to investigate, as a possible example of such a process, the reaction of phthaloyl peroxide ( $\lambda$ ) with simply substituted olefins and with other electron donors.

Phthaloyl peroxide was prepared by Greene,<sup>23</sup> and this synthesis initiated a detailed investigation of the reactions of this peroxide with a variety of olefins for which trans-stilbene will serve as a typical example. Thermolysis of  $\lambda$  and trans-stilbene in  $\text{CCl}_4$  at  $80^\circ$  was found to give two adducts, the cyclic phthalate  $\zeta$ , and the phthalide  $\eta$ ; eq 10.<sup>24</sup> This reaction was observed to be stereospecific and the reaction kinetics exhibited overall second order behavior; cleanly first order in each component. Further investigation by Greene and Rees<sup>25</sup> revealed that the magnitude of the bimolecular rate constant of these reactions depend



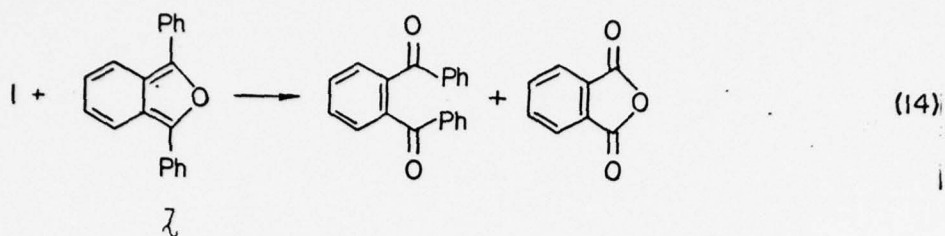
strongly on the nature of the olefin. Thus trans-dianisylethylene reacts about 50 times more rapidly than trans-stilbene, but curiously, 1,1-diphenylethylene reacts at essentially the same rate as trans-stilbene. Greene<sup>26</sup> examined by oxygen-18 tracer methods the extent of exchange between the carbonyl and peroxide oxygens of  $\text{1}$  and the phthalate  $\text{2}$ . This study showed that about 11% of the label that was originally in the carbonyl oxygens of  $\text{1}$  is incorporated in ether oxygens of  $\text{2}$ . These results led Greene to postulate a mechanism for the reaction of olefins with  $\text{1}$  that proceeds by a two electron path. The transition state structure for this reaction was represented as the complex of olefin and peroxide ( $\text{4}$ ). It was suggested that this complex rearranged through additional intermediates to the observed products; eq 11.



We have examined the reaction of  $\text{1}$  with a series of one and two electron donors. The kinetics, products, and solvent dependence of these reactions are

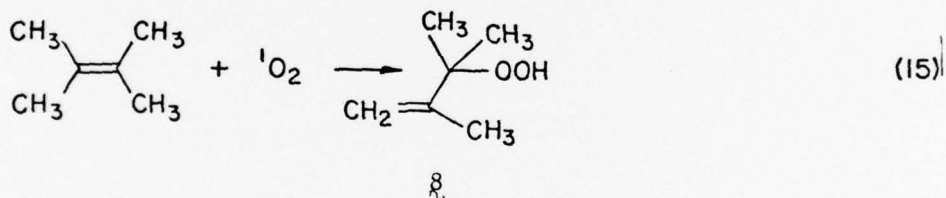


zofuran ( $\lambda$ ) are identified as o-dibenzoylbenzene and phthalic anhydride; eq 14.



These products result presumably from the rearrangement of an intermediate adduct. Attempts to detect this adduct kinetically, or spectroscopically, however, were unsuccessful.

The reaction of phthaloyl peroxide with furan  $\lambda$  is of special interest because it, among other reactions, has been used to support the conclusion that the thermolysis of  $\lambda$  leads to the generation of singlet oxygen ( $^1O_2$ ).<sup>27</sup> We examined this possibility in considerable detail. The reaction of  $^1O_2$  with tetramethylethylene is known to be quite rapid and to give the allylic hydroperoxide  $\delta$  in high yield;<sup>28</sup> eq 15. We examined the products of the reaction of



$\lambda$  with tetramethylethylene, and  $\delta$  is not among them. Moreover, we showed that hydroperoxide  $\delta$  is stable to the reaction conditions employed. Thus it appears that the previous report of formation of  $^1O_2$  from thermolysis of  $\lambda$  is incorrect.

As noted above, Greene<sup>25</sup> examined the products and the kinetics of the reaction of  $\lambda$  and a series of olefins in  $CCl_4$  solution. We have extended that investigation to benzonitrile solutions. In general, the reaction rate is much accelerated in benzonitrile, and there is a slight loss of stereospecificity, but the nature of the reaction products are not particularly sensitive to the identity of the solvent.

Reaction of phthaloyl peroxide with the polynuclear aromatic hydrocarbons tetracene and pyrene in benzo- or acetonitrile proceeds with a rapid rate and results in a complex mixture of products. For both hydrocarbons the phthaloyl peroxide is completely consumed before an equivalent amount of hydrocarbon has reacted. Analysis of the crude reaction mixture indicates incorporation of solvent molecules. However, in the case of tetracene it proved possible to isolate, in low yield, a product that has an infra red spectrum and an elemental analysis consistent with a cyclic phthalate. Complex reaction products are reported to result also from the reaction of aromatic hydrocarbons with benzoyl peroxide.<sup>29</sup> We should point out, however, that our analysis of the reaction kinetics (see below) indicates that the complexity of the reaction of  $\lambda$  with these aromatic hydrocarbons is the result of multiple reaction paths for some intermediate, and is not a result of multiple paths for the primary interaction of hydrocarbon and peroxide.

#### Kinetics:

The kinetics of the reaction of phthaloyl peroxide with the various ground and excited state reagents we investigated is particularly revealing. For all of the cases we examined the basic reaction between the peroxide and reactant was clearly second order. Due to the extraordinarily wide range of reactivity we investigated, a variety of techniques were used to measure the reaction rate. For example, the reaction of  $\lambda$  with N,N'-diphenylbenzidine was followed by stopped-flow techniques. Figure 1 shows a compilation of kinetic runs in THF solution over a range of benzidine and peroxide concentrations. These results indicate clearly that the reaction is first order in each component. Similarly, the reaction of  $\lambda$  and trans-dianisylethylene was followed by conventional uv-spectrometry with excess olefin, and found to be first order in each component. The reaction of  $\lambda$  with trans-stilbene in benzonitrile was followed iodometrically and was found also to be first order in each component.

The results of the kinetic investigation for the systems examined are shown in Table 1. The bimolecular rate constant,  $k_2$ , varies greatly with the

structure of the reagent and somewhat with the nature of the solvent. Of course, the correlation of the magnitude of  $k_2$  with some feature of the structure of the reactant will provide insight into the nature of the interaction between the reagent and phthaloyl peroxide. One possible correlating parameter is the nucleophilicity of the reactant. Unfortunately, it is difficult to conceive of a meaningful way to compare quantitatively the nucleophilicity of, say, hydroquinone and tetracene. However, it is expected that, in a classical  $S_N2$  sense, the hydroquinone should be by far the more reactive of the pair. Our results indicate that this is not the case in their reaction with phthaloyl peroxide. In benzonitrile solvent the measured bimolecular rate constant for the reaction of tetracene with  $\lambda$  is 58 times greater than for that of hydroquinone. This observation is inconsistent with the notion of the operation of a simple nucleophilic displacement reaction.

A parameter that does correlate the observed bimolecular rate constants remarkably well over all of the compounds we have investigated, and in both solvents studied, is the one electron oxidation potential of the reactant (hereinafter referred to as the donor). The relationship between the natural log of the observed rate constant and the oxidation potential, measured by cyclic voltammetry, for THF solvent is shown in Figure 2. A similar plot is obtained for rates measured in benzonitrile solution. The major source of uncertainty in defining the correlation of Figure 2 is in the estimation of the oxidation potential. The magnitude of the slope of the line in Figure 2,  $-0.4/RT$  in THF and  $-0.51/RT$  in benzonitrile, is consistent with rate limiting, irreversible electron transfer as the key step in the reaction of phthaloyl peroxide with the various donors.<sup>30</sup>

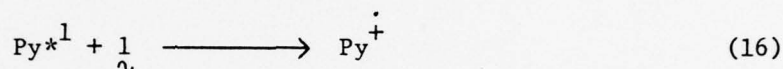
#### Laser Spectrometry:

It is widely recognized that electronic excitation dramatically changes the redox properties of reagents. Thus it is often observed that the  $S_{RN}1$  pathway can often be initiated by irradiation of the reaction mixture.<sup>31</sup> The pioneering

work of Weller and his associates has resulted in a clear understanding of the relationship between the electron donor (or acceptor) ability of electronically excited aromatic hydrocarbons and the thermodynamic and kinetic characteristics of their reactions.<sup>32</sup> Thus while pyrene ground state is a moderately reactive electron donor ( $E_{\text{ox}} = 1.36 \text{ V}$ ), pyrene excited singlet state ( $\text{Py}^*{}^1$ ) is a remarkably powerful reducing agent ( $E_{\text{ox}} = -2.00 \text{ V}$ ).<sup>33</sup> This change in reducing power is reflected in the reactivity of  $\text{Py}^*{}^1$ . Reaction of  $\text{Py}^*{}^1$  with an electron acceptor, say dicyanobenzene, has been observed to generate, at an approximately diffusion limited rate in acetonitrile, pyrene radical cation ( $\text{Py}^{\dot{+}}$ ) and dicyanobenzene radical anion ( $\text{DCB}^{\dot{-}}$ ).<sup>32</sup> Moreover, the rate of these electron transfer reaction has been shown to be a predictable function of the redox behavior of the system.

We examined the reaction of  $\text{Py}^*{}^1$  with peroxide  $\text{P}_2$  following pulse excitation with a 900 kw nitrogen laser. The laser excitation pulse has a peak width at half height of about 10 nsec. Thus we can probe the reaction solution at any time after this period. In Figure 3 is shown the transient absorption spectrum of a solution of pyrene and phthaloyl peroxide in acetonitrile recorded 140 nsec after the laser pulse. This spectrum is identical in all respects to the previously reported<sup>34</sup> spectrum of  $\text{Py}^{\dot{+}}$ , and indicates unambiguously that for this system electron transfer plays a major role in the reaction. It is important to note that the addition of phthaloyl peroxide to a solution of pyrene causes no measurable perturbation of the ground state absorption spectrum. The spectrum of the mixture is quantitatively the sum of the individual components. Moreover, the fluorescence emission spectrum of  $\text{Py}^*{}^1$  in the presence peroxide  $\text{P}_2$  is exactly that of  $\text{Py}^*{}^1$  itself. These observations indicate that there is no detectable complexation between pyrene and the peroxide either in the ground or the excited state, and that the chemistry must be understood in terms of locally excited states.

We are able not only to determine the product of the reaction of  $\text{Py}^{*1}$  with  $\frac{1}{\nu}$  but can measure the rate of reaction and the yield of  $\text{Py}^{\dot{+}}$  as well. By monitoring the rate of decay of the fluorescence of  $\text{Py}^{*1}$  at various concentrations of  $\frac{1}{\nu}$ , as is shown in Figure 4, we can extract the magnitude of the bimolecular rate constant. In this case the reaction is diffusion limited,  $k_2 = 1.67 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ , as it is expected to be from the Weller treatment. The yield of cage escaped  $\text{Py}^{\dot{+}}$  was measured by calibrating the intensity of the laser beam with a Gentek joule meter and correlating that with the optical density of the  $\text{Py}^{\dot{+}}$  absorption after all of the  $\text{Py}^{*1}$  has reacted, but before there has been significant decay of the  $\text{Py}^{\dot{+}}$ . In acetonitrile solution this measurement indicates that ca. 50% of the initially formed  $\text{Py}^{*1}$  eventually appears as  $\text{Py}^{\dot{+}}$ ; eq 16.



Since  $\text{Py}^{*1}$  reacts with peroxide  $\frac{1}{\nu}$  with a rate at the diffusion limit, information about the actual rate of the electron transfer is not easily available. To obtain meaningful kinetic data, and thereby forge a link between the ground and excited state reactions, it is necessary to decrease the reducing power of the donor excited state. This may be done by increasing the oxidation potential of the donor ground state, or by decreasing the electronic excitation energy of the donor excited state. We accomplished the required decrease in donor reducing power by employing anthracene triplet ( $\text{AN}^{*3}$ ). The oxidation potential of  $\text{AN}^{*3}$  is -0.47 V. We can monitor the rate of reaction of  $\text{AN}^{*3}$  with  $\frac{1}{\nu}$  by following the triplet-triplet absorption of  $\text{AN}^{*3}$ , or by following the rate of growth of the absorption due to anthracene radical cation ( $\text{AN}^{\dot{+}}$ ). As described above for pyrene, we measured the rate and the products of the reaction of  $\text{AN}^{*3}$  with peroxide  $\frac{1}{\nu}$ . The major product of this reaction is the anthracene radical cation. Unfortunately, the absorption spectrum of  $\text{AN}^{\dot{+}}$  and  $\text{AN}^{*3}$  overlap in the region where  $\text{AN}^{*3}$  absorbs. Moreover, there are two sources of  $\text{AN}^{\dot{+}}$  in this system. The first is the reaction of

anthracene excited singlet ( $AN^*1$ ) with peroxide  $\lambda$ . This reaction gives  $AN^+$  essentially instantaneously ( $\sim 15$  nsec) on the time scale of the triplet reaction. The second source, as mentioned above, is the reaction of  $AN^*3$  with  $\lambda$  which give rise to  $AN^+$  at the same rate that  $AN^*3$  reacts. These complications forced us to determine the rate constant for consumption of  $AN^*3$  by  $\lambda$  at low conversion where the concentration of  $AN^*3$  is much greater than that of  $AN^+$ . We also determined the rate of the reaction of  $AN^*3$  with  $\lambda$  by following the appearance of  $AN^+$  at 725 Nm where there is no overlap problem. The derived bimolecular rate constants obtained by these two complimentary techniques are within experimental error of each other and are reported in Table 1. Similarly, we have determined that 9-acetylanthracene triplet reacts with  $\lambda$  to give the corresponding cation radical and we have measured the rate of this reaction as well. These experiments show conclusively that electron transfer from the excited triplet donors is the major reaction, and that the rate of the reaction, as predicted by the Weller treatment, is slower than the diffusion limited value.

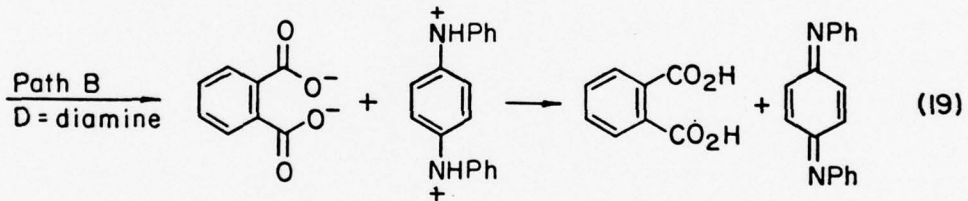
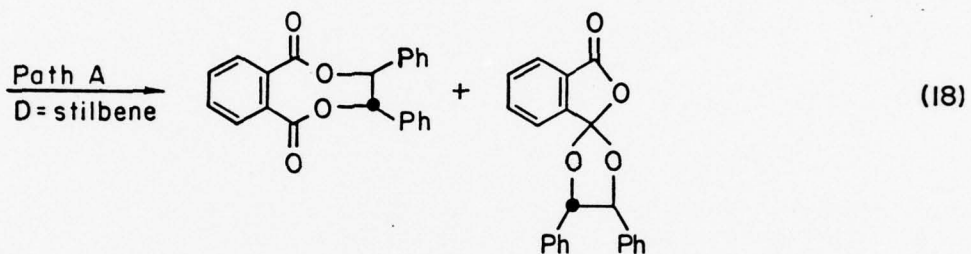
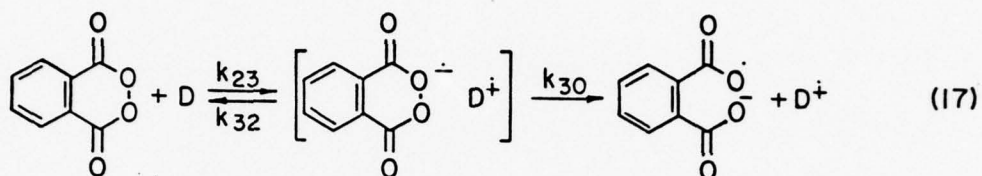
Mechanism:

The major objective of this work was to delineate the mechanism for the reaction of phthaloyl peroxide with compounds capable of reacting as one electron donors or as nucleophiles. The results of this investigation are entirely consistent with the electron transfer mechanism outlines in Scheme 3, in which Path A describes the case where the donor (D) cation radical adds to the phthalate radical anion, and Path B describes the circumstance where a second electron is transferred after the rate limiting step.

Support for this mechanism comes from the study of the reaction products, the observed kinetics and the detection of odd electron intermediates by the laser pulse spectrophotometric techniques. Among the most telling results of the product study is the observation of two electron oxidation products from the diamines and from hydroquinone. The reaction rate constants for these substrates depend upon the first oxidation potential. Thus odd electron intermediates are

indicated. Instead of forming adducts, as is the case with olefins, the phthalate radical anion is trapped as phthalate dianion by those substrates that are capable of undergoing facile two electron oxidation.

Scheme 3



As was observed by Greene for olefins, and by us for the amines, phenols, and aromatic hydrocarbons, the reactions follow second order kinetics. The dependence of the observed bimolecular rate constant on the structure of the donor reveals considerable information about the mechanism of this reaction. As is noted above, the one electron oxidation potential is a reliable predictor of the reactivity for all of the systems we have investigated. This correlation apparently holds over the variety of functional groups we have studied. Importantly, the dependence of the bimolecular rate constant on oxidation potential appears to hold for electronically excited donors as well as ground state donors.

A simple linear extrapolation of the ground-state donor rate constants to the oxidation potential of  $AN^*$ <sup>3</sup> and 9-acetylanthracene triplet states predict a rate constant for reaction slightly faster than the diffusion limit. The rate constants that we observe are in fact somewhat less than diffusion controlled. This is not unexpected. In energy regions where  $\Delta G_{23}^0$  (the free energy change for the electron transfer) is close to zero, the Weller analysis<sup>32</sup> apparently accurately predicts the rate constant for the electron transfer reaction. Unfortunately, the electrochemical reduction of phthaloyl peroxide is irreversible, and thus it is not possible to obtain an accurate estimate of  $\Delta G_{23}^0$ . However, our attempt to measure the reduction potential of this peroxide indicate that it is similar to that of other diacyl peroxides, and thus probably falls within the range -0.1 and -0.5 V vs. SCE.<sup>35</sup> With this assumption, we can estimate the magnitude of the rate constant for the electron transfer reaction of the triplet donors with phthaloyl peroxide using Weller's method. Indeed, this analysis indicates that if the reduction potential of phthaloyl peroxide is -0.4 V, then the rate constants we observe for the triplet donors are within experimental error of the calculated values. This correlation of the reaction kinetics for the ground and excited state donors along with the unequivocal generation of odd electron intermediates from the excited state reaction constitutes strong evidence that the ground state reaction is proceeding by the electron transfer path.

An alternative approach to the understanding of the reaction of peroxide  $\downarrow$  with the various donors is to propose that these transformations proceed through a "charge-transfer complex" of some sort. However, this mechanism is not consistent with our data. In particular, if the formation of a charge-transfer complex preceded, or is, the rate determining step of the reaction, then it is expected that the rate of reaction would be related to the stability of the complex. We are not able to detect evidence of any complex in the electronic absorption spectra of phthaloyl peroxide with the donors we studied. However, in cases where these complexes can be detected, it is observed that their stabilities are not simply related to the redox behavior of their components.<sup>36</sup> Since, as pointed out above, the rate limiting step of our reaction

does follow the redox behavior of the components, it is unreasonable to propose an undetectable charge-transfer complex as an intermediate. Moreover, our observation that both singlet and triplet donors react at rates predictable by the electron transfer model indicates that complex formation, which should be much less favorable for the triplet, does not influence the rate of reaction.

Two experimental observations bear further discussion. First, the isotope tracer results reported by Greene indicate that about half of the oxygen of one carbonyl group of the peroxide is incorporated in the ether oxygens of the cyclic phthalate. At first glance, this observation seems inconsistent with our proposal of phthalate radical anion as an intermediate in the reaction. However, if, as seems likely, the benzoyloxy radical is a sigma radical, then any bonding interaction between the doubly occupied orbital of the carboxylate and the singly occupied orbital of the carboxy radical will lead to hindered rotation about the carbon-carbon bond connecting the carboxylate group to the ring. Of course, this rotation is required to interchange the oxygen atoms of the carboxylate. A similar three electron interaction can be used to account for the equivalence of the two oxygens of the benzoyloxy radical described by McBride.<sup>37</sup> Moreover, to the extent that the non-bonded orbitals of the carbonyl oxygens of the phthalate radical anion overlap with the sigma orbital of the peroxide, radical character will be transferred to the carbonyl oxygens. This notion is supported by a MINDO/3 calculation which puts considerable odd electron density on the carbonyl oxygens of the phthalate radical anion.<sup>38</sup> The first step in formation of the adduct is probably coupling of odd-electron centers (hence, the observed rearrangement in the norbornylene system).<sup>39</sup> Since our proposed model for the phthalate radical anion predicts some free electron density on the carbonyl oxygens, there may be some coupling to these positions. This coupling could lead to the observed apparent equivalence of carbonyl and peroxy oxygens.

The final point to be discussed is the apparent stereospecificity of the reaction. Evidently, closure of the second carbon-oxygen bond is faster than the rotation about the remaining carbon-carbon single bond of the olefin, since that rotation would lead to loss of stereochemistry. Also, ring closure is appar-

ently faster than rotation about the carboxylate-carbon bond since that rotation would lead to exchange of oxygen atoms. These observations are, of course, independent of the mechanism, and must be made for all but a concerted process, thus they cannot be used to distinguish between nucleophilic attack and electron transfer.

### Conclusions

The results of our study of the reaction of phthaloyl peroxide with a variety of reagents indicate that these processes proceed along a path initiated by an activated one electron transfer from the donor to the peroxide. Subsequent cleavage of the oxygen-oxygen bond of the reduced peroxide makes the electron transfer irreversible. The odd electron intermediates formed in these initial steps can add, as in the case of olefins, or undergo a second electron transfer as with the diamines, or diffuse into bulk solution as apparently occurs with the aromatic hydrocarbons. We feel that this mechanism easily accounts for all of the results we, and others, have accumulated while studying the reactions of phthaloyl peroxide. We note, however, that extrapolation of these conclusions to the reactions of other diacyl peroxides, in particular benzoyl peroxide, is not without some risk. Specifically, the oxygen-oxygen bond of phthaloyl peroxide is constrained to be in a relatively planar six membered ring. This structural feature may make this peroxide more easily reduced than, say, benzoyl peroxide. In the inevitable competition between nucleophilic attack and electron transfer, the one electron path will be accelerated by this ease of reduction. We are continuing to examine the structural features that encourage one electron processes between closed-shell reagent.

### Experimental

#### General:

<sup>1</sup>H NMR spectra were recorded on either a Varian Associated EM-390 or a Varian HR 220, with tetramethylsilane as internal standard. Mass spectra were obtained with Varian MAT CH-5 and 731 mass spectrometers. Infrared spectra were recorded on a Perkin Elmer 237B Infracord. UV and visible spectra were recorded on a

Cary 14 spectrometer. Elemental analyses were performed by J. Nemeth and Associates, Department of Chemistry, University of Illinois, Urbana. Melting points are uncorrected. Gas chromatography was performed on a Varian 2700 with flame ionization detector using a 2 meter 8.3% SE-30 column.

Solvents: Tetrahydrofuran (Aldrich, gold label) was distilled from Na/benzophenone under nitrogen. Benzonitrile (Eastman Kodak, aniline free) was distilled from  $P_2O_5$ . Acetonitrile (Aldrich, gold label) was distilled from  $CaH_2$  under nitrogen.

Methods for Kinetic Analyses: The kinetics for the reaction of phthaloyl peroxide with the electron donors was conducted by one of three methods: i) stop-flow techniques, ii) conventional uv-spectrometry or iii) iodometrically. The solutions for all kinetic runs were purged for 5 to 10 minutes with argon prior to use. The kinetics were pseudo-first order employing either excess peroxide or excess electron donor.

Kinetics by conventional UV-spectrometry were carried out in a 1 cm quartz cuvette. A 1.5 mL aliquot of phthaloyl peroxide solution was added to a 1.50 mL aliquot of the electron donor solution and mixed well in the sample cell. Then the disappearance of the electron donor was monitored as a function of time for approximately 10 to 12 half-lives.

Iodometric kinetics were carried out by recording the absorbance of the triiodide ion at 430 nm at periodic time intervals for two half-lives (the infinity absorbance was recorded after 10 half-lives) for 0.75 mL aliquot samples of the kinetic run employing the method of Benerjee and Budke.<sup>40</sup> To approximately 15 mL of a  $CHCl_3$ :acetic acid mixture (1:1) which has been purged with nitrogen gas for 1 m was added a 1.00 mL aliquot of a 50% KI solution. To this solution is added a 0.75 mL aliquot of the kinetic sample and the resulting solution is purged for 1 m with nitrogen and then diluted to a total volume of 25 ml with  $CHCl_3$ :acetic acid (1:1) solution.

Stop flow kinetics employed a stop-flow spectrophotometer designed by D. L. Knottinger.<sup>41</sup> The kinetics were monitored at the absorbance maxima of either the reagent (i.e. 1,3-diphenylisobenzofuran or tetracene) or the product (i.e. the oxidized products of N,N'-diphenyl-p-benzidine or hydroquinone) for 10 to 12 half-lives. The diimine of N,N'-diphenyl-p-benzidine is unstable under the reaction conditions but its disappearance is negligible over the period of investigation and becomes significant only at high benzidine concentrations.

Reaction of 1 with N,N'-diphenyl-p-phenylenediamine in THF at 25°C.

Gas chromatographic analysis of the reaction of phthaloyl peroxide ( $2.6 \times 10^{-4}$  moles) and N,N'-diphenyl-p-phenylenediamine ( $2.6 \times 10^{-4}$  moles) in 10 mL of THF indicates that the sole volatile products of the reaction are phthalic acid (98%) and the diimine 5 (88%) based upon the UV absorption spectrum. The diimine 5 was characterized by comparison with an authentic sample prepared by the method of Piccard,<sup>42</sup> as well as by its UV-visible absorbance spectrum  $\lambda_{\text{max}} = 445 \text{ nm}$  (THF).

Reaction of 1 with 1,3-diphenylisobenzofuran in THF at 25.0°C.

Examination of the carbonyl region of the infrared spectrum for the reaction of phthaloyl peroxide with 1,3-diphenylisobenzofuran in THF indicates phthalic anhydride and o-dibenzoylbenzene to be the sole carbonyl containing products of the reaction, no intermediate adducts were observed. G.C. analysis of the reaction of ( $1.298 \times 10^{-4}$  moles) phthaloyl peroxide with ( $1.284 \times 10^{-4}$  moles) of 1,3-diphenylisobenzofuran indicates that phthalic anhydride is formed in 78% yield and the yield of o-dibenzoylbenzene is 120%.

Reaction of 1 with Hydroquinone in Acetonitrile at 25°C.

Gas chromatographic analyses of the reaction of phthaloyl peroxide ( $3.10 \times 10^{-4}$  moles) and hydroquinone ( $3.33 \times 10^{-4}$  moles) in acetonitrile indicates that the volatile products of the reaction are benzoquinone (72%) and phthalic acid (58%). Since phthalic acid is slightly soluble in acetonitrile it's yield is based on a gravimetric determination.

Reaction of 1 with trans-stilbene in benzonitrile at 66.0°

The NMR analysis of the reaction mixture of phthaloyl peroxide ( $2.358 \times 10^{-4}$  moles) with trans-stilbene ( $2.441 \times 10^{-4}$  moles) indicates, after removal of benzonitrile by distillation, that the cyclic phthalate 2 and lactonic ortho-ester 3 are formed in a 1:3 ratio. Infrared analysis of the reaction mixture confirms that the sole carbonyl containing compounds of the reaction are 2 ( $1736\text{cm}^{-1}$ ) and 3 ( $1776\text{cm}^{-1}$ ). The NMR spectrum of the reaction mixture showed an aromatic multiplet centered at  $7.50\delta$ , a singlet at  $6.12\delta$  (assigned to the benzylic H's of 2) and a doublet of doublets centered at  $5.27\delta$  (assigned to the benzylic H's of 3).

Reaction of 1 with Tetracene in Acetonitrile at 25.0.

Thermolysis of phthaloyl peroxide ( $1.5 \times 10^{-4}$  moles) with tetracene ( $1.4 \times 10^{-4}$  moles) in acetonitrile resulted in the recovery of  $4.2 \times 10^{-4}$  moles (29%) of unreacted tetracene. The products of the reaction mixture indicated carbonyl group resonance at 1724, 1706, 1681, and  $1661\text{cm}^{-1}$ . Crystallization of the reaction mixture from  $\text{CCl}_4/\text{acetone}$  resulted in the isolation of 6 mg of a product with a carbonyl group resonance at  $1681\text{cm}^{-1}$  which had an elemental analysis of C, 79.16;H, 4.20 (calculated for a 1:1 adduct of tetracene with phthaloyl peroxide C, 79.58;H, 4.11).

Reaction of Tetramethylethylene (TME) with 1 in Benzonitrile

A solution of phthaloyl peroxide ( $7 \times 10^{-3}$  M) and TME ( $1 \times 10^{-1}$  M) was held at  $80^\circ$  in benzonitrile solution for 5 days. Examination of the reaction mixture by gas chromatography at periodic time intervals showed no detectable allylic hydroperoxide 8.

Control experiments showed that the allylic hydroperoxide 8 was indefinitely stable under the reaction conditions, and that we could detect 8 at concentrations as low as  $5 \times 10^{-5}$  M.

Pulsed Nanosecond Laser Photolysis Apparatus

The pulsed-laser apparatus consists of a Moletron Model UV24 nitrogen laser having a 900 kw power rating at 20 Hz. The pulse width at half height was typically of 10 ns duration. The laser was focused to a 3 mm x 10 mm rectangle in the 1 cm sample cell. Power measurements, made at the sample table, varied generally between 2 and 7 mj/pulse. Laser pulse intensities were reproducible to  $\pm 5\%$ .

The probe beam was generated by a PRA Model ALH 2150 450 W xenon arc lamp

rectangle in the 1 cm sample cell. Laser pulse intensities were varied generally between 2 and 7 mj/pulse. Laser pulse intensities were reproducible to  $\pm 5\%$ .

The probe beam was generated by a PRA Model ALH 2150 450 W xenon arc lamp operated at 20 amps and pulsed with a 60  $\mu$ f capacitor charged to 350 V. The pulses were generally 140  $\mu$ s long. The total power of the probe pulse, measuring all wavelengths and integrated over the entire pulse, was determined to be  $0.46 \pm 30\%$  mj/pulse.

The probe light intensity and sample fluorescence were monitored using a Hamamatsu R928 photomultiplier tube with a  $50\Omega$  termination. The tube was wired with a nonlinear, four-dynode chain to avoid space charge problems and to prevent saturation at the high light intensities used to overcome photon statistical noise. The rise time of the detection system (to -300 mv) was measured to be ca. 2 ns using a 30 ps green pulse generated by an argon ion laser.

Spectral resolution was obtained using a PRA model 204B 0.25M monochromator which has a dispersion of 3.6 nm/mm. The measured absorption and fluorescence signals were processed on the Tektronix R7912 transient digitizer. All measurements of the nitrogen laser intensity were made using a Gentec joule meter Model ED-200 7010 with a calibration of 6.50 U/J when terminated in  $10^6$  ohm.

The sample cell used was a 1 cm square fluorescence cell which was fitted with a teflon stopcock and equipped with a small teflon-coated stir-bar.

#### Pyrene Excited Singlet-Phthaloyl Peroxide. Transient Absorption Spectrum

An acetonitrile stock solution of phthaloyl peroxide ( $2.51 \times 10^{-3} M$ ) containing pyrene ( $2.97 \times 10^{-5} M$ ) was prepared and kept at  $0^\circ C$ . The absorption spectrum of the transient intermediate in a nitrogen purged sample was measured 140 ns after the laser excitation. The intermediate showed no significant decay in 500 ns. Absorption data were obtained from 350 nm to 550 nm with a spectral resolution of generally better than 4 nm  $\lambda_{max}$  of the transient ( $CH_3CN$ ) = 450 nm.

#### Pyrene Excited Singlet - Phthaloyl Peroxide. Quenching Kinetics

The quenching rate constant ( $k_q$ ) for the reaction of phthaloyl peroxide with pyrene singlet in acetonitrile was measured. The pyrene concentration for each was  $5.12 \times 10^{-5} M$  while the concentration of phthaloyl peroxide varied between 0 and  $2.44 \times 10^{-3} M$ . All samples were nitrogen purged for 4 minutes prior to laser excitation. A plot of the derived first order rate constants versus phthaloyl peroxide concentration gave the desired quenching rate constant.

Anthracene Triplet - Phthaloyl Peroxide. Quenching Kinetics

A series of seven samples was prepared, each consisting of a 5 mL acetonitrile solution of anthracene ( $4.28 \times 10^{-4}$ ) with a concentration of phthaloyl peroxide between 0 and  $4.88 \times 10^{-3}$  M. The decay kinetics of the anthracene triplet produced by laser excitation of these samples were found to deviate from first order particularly in those samples where the concentration of phthaloyl peroxide was greater than  $1 \times 10^{-3}$  M. This deviation was found to be due to the growth of an absorption from anthracene radical cation at 425 nm, the maximum of the  $T_1 \rightarrow T_n$  absorption. This was confirmed by the observation of the growth of anthracene radical cation at 720 nm. The rate of growth of the radical cation was observed to have two components, as fast growth from anthracene<sup>\*1</sup> + phthaloyl peroxide and a much slower growth from anthracene<sup>\*3</sup> + phthaloyl peroxide. Thus the following method was used to obtain the quenching rate constant. Each of the eight samples in turn, was placed in the laser photolysis cell and photoexcited air saturated with the nitrogen laser (337 nm, ca. 3.5 mj/pulse). The optical density of the transient intermediate (monitored at 425 nm) was determined 1.45  $\mu$ s after the laser excitation (prompt anthracene radical cation). The sample was then nitrogen purged for 4 minutes and photoexcited. The decay of the anthracene triplet was then monitored with the R7912 transient digitizer. The optical density of the transient at 425 nm generated in each sample was measured twice while air saturated and the transient decay at 425 nm was measured twice while the sample was nitrogen purged. After correction for the prompt radical cation contribution was made, the observed rate constant for the anthracene triplet decay was determined. A least squares analysis of the derived first-order rate constants versus the concentration of added phthaloyl peroxide (less than  $1 \times 10^{-3}$  M) an estimate for the quenching rate constant,

Acknowledgement: We thank Mr. James Wehner for his valuable assistance with the pulsed laser photolysis. This work was supported in part by the Office of Naval Research and in part by the National Science Foundation. The laser facility was constructed with funds supplied by NSF.

Table 1

Electron Donor <sup>a</sup>	$E_{1/2}$ V vs SCE <sup>b</sup>	$k_2$ (M <sup>-1</sup> s <sup>-1</sup> )	
		THF	PhCN
Pyrene (excited singlet)	-2.00	---	$1.67 \times 10^{10}$ <sup>c</sup>
Anthracene (triplet)	-0.47	---	$7.47 \times 10^8$ <sup>c</sup>
9-Acetylanthracene (triplet)	-0.34	---	$9.77 \times 10^7$ <sup>c</sup>
N,N'-Diphenyl-p-phenylenediamine	0.34	---	---
N,N'-Diphenylbenzidine	0.65 <sup>e</sup>	533	---
$\lambda$	0.79	89	548
Tetracene	0.95 <sup>g</sup>	8.1	57
<u>trans</u> -Dianisylethylene	1.06 <sup>h</sup>	$2.86 \times 10^{-2}$	$6.97 \times 10^{-1}$
Hydroquinone	1.12 <sup>i</sup>	$3.5 \times 10^{-1}$	$9.8 \times 10^{-1}$
<u>p</u> -Methoxystilbene	1.22 <sup>j</sup>	---	$8.23 \times 10^{-2}$
2,5-Diphenylfuran	1.29	$3.4 \times 10^{-2}$	---
<u>trans</u> -Stilbene	1.51	---	$5.37 \times 10^{-4}$

- a) All reactions were carried out at room temperature ( $25.0 \pm 0.2^{\circ}\text{C}$ )
- b) The oxidation potentials are taken from C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems" Dekker, NY, 1970, unless otherwise noted.
- c) Laser studies were carried out in acetonitrile.
- d) This reaction was too fast to measure on the stopped flow apparatus available.
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- k) Not determined due to interference of solvent with iodometric method.

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Captions for Figures

Figure 1

Kinetics of the reaction of phthaloyl peroxide with N,N'-diphenylbenzidine in THF. The initial concentration of the peroxide is  $5.85 \times 10^{-6}$  M and the initial benzidine concentration varies from  $5.93 \times 10^{-5}$  M to  $2.96 \times 10^{-3}$  M.

Figure 2

Correlation of the measured bimolecular rate constant ( $k_2$ ) for reaction of various donors with the one electron oxidation potential. In order of increasing oxidation potential, the points are: N,N'-Diphenylbenzidine, 1,3-Diphenylisobenzofuran, Tetracene, trans-Dianisylethylene, Hydroquinone, 2,5-Diphenylfuran.

Figure 3

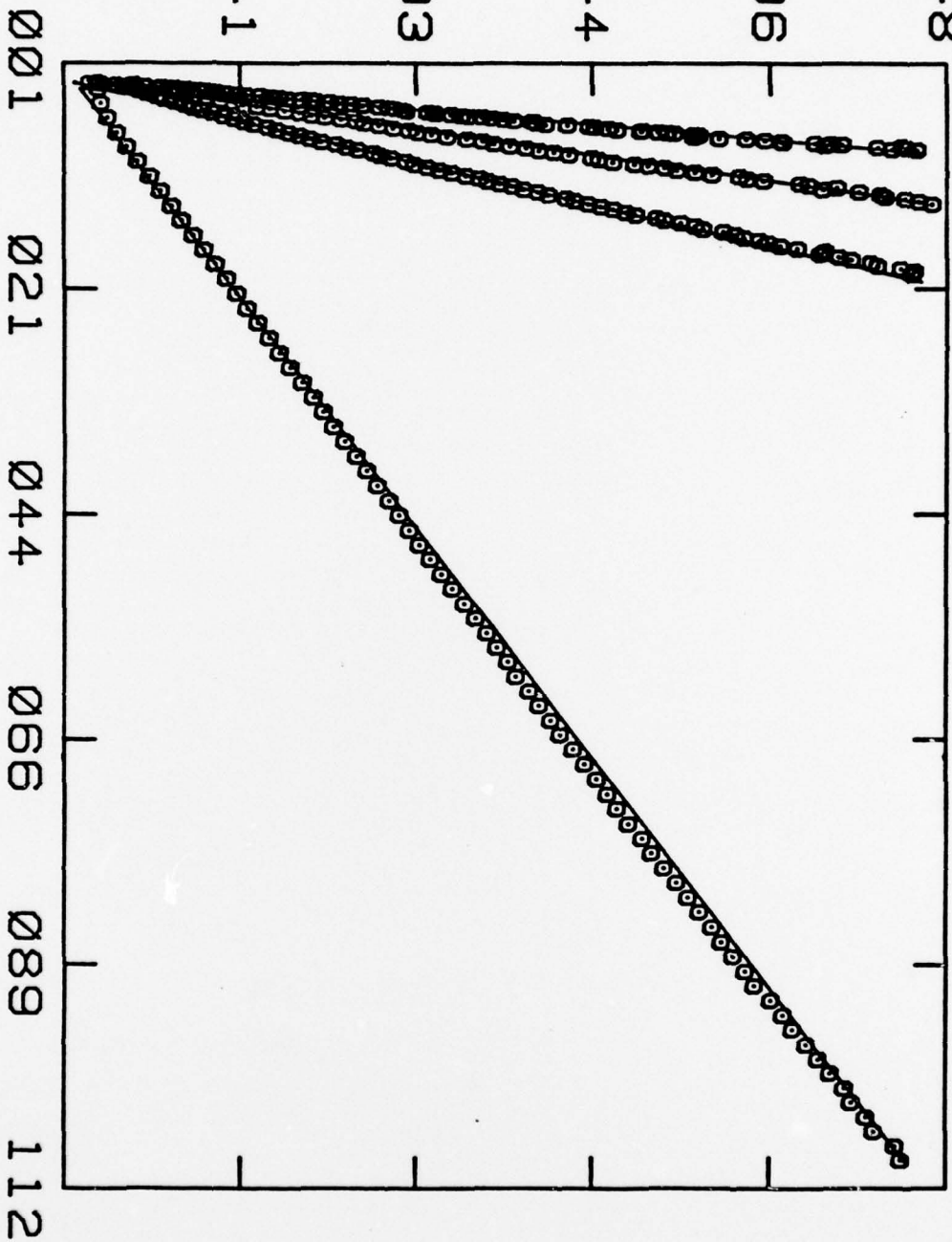
Absorption spectrum of  $\text{Py}^{\dot{+}}$  formed in solution of pyrene and phthaloyl peroxide. The spectrum was recorded 140 ns after irradiation with a 10 ns wide pulse of light absorbed entirely by the pyrene.

Figure 4

The observed fluorescence decay rate constant ( $k_{\text{obs}}$ ) for pyrene excited singlet at increasing phthaloyl peroxide concentration.

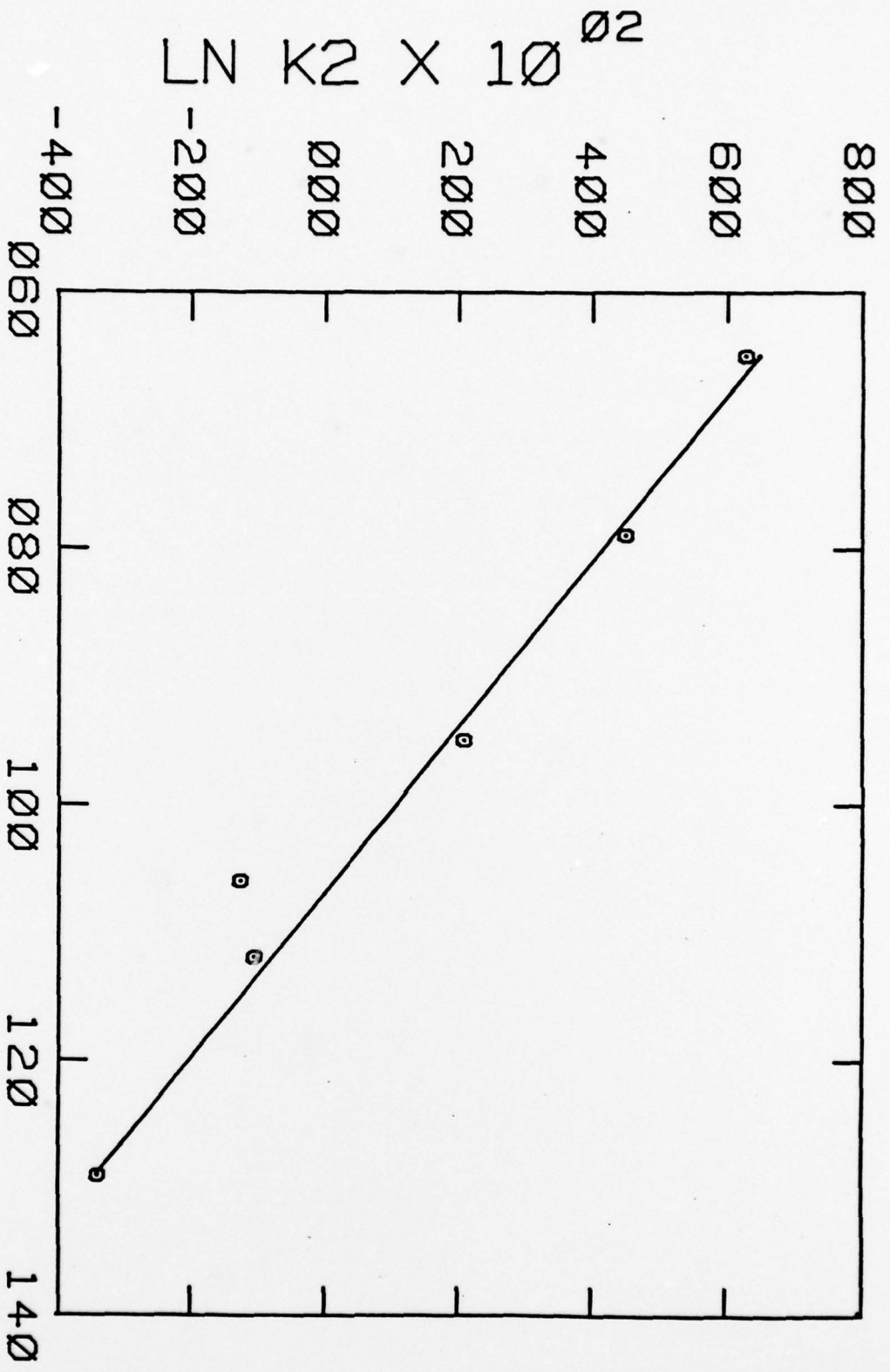
LN (ABS.) X 10<sup>02</sup>

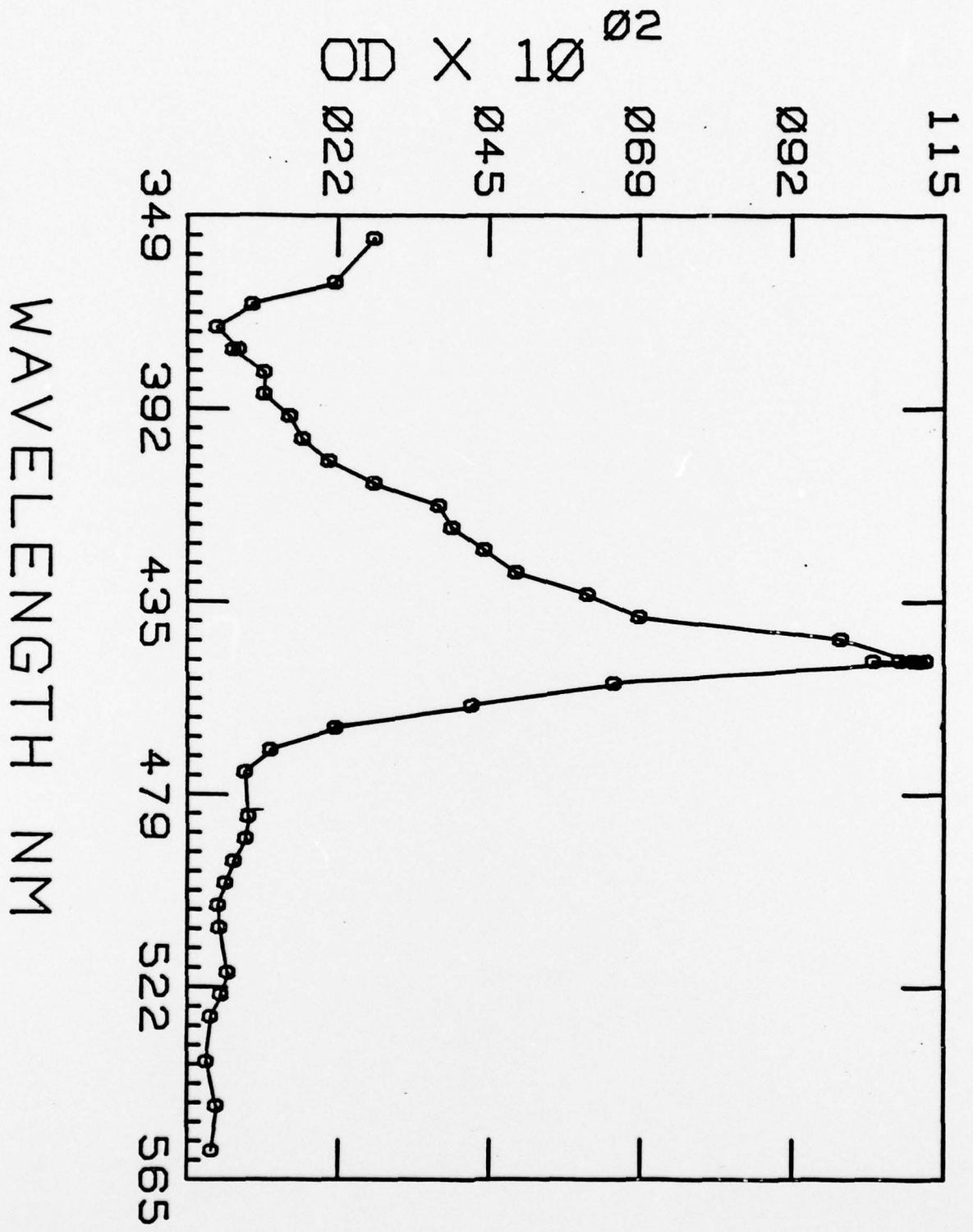
248  
196  
144  
093  
041



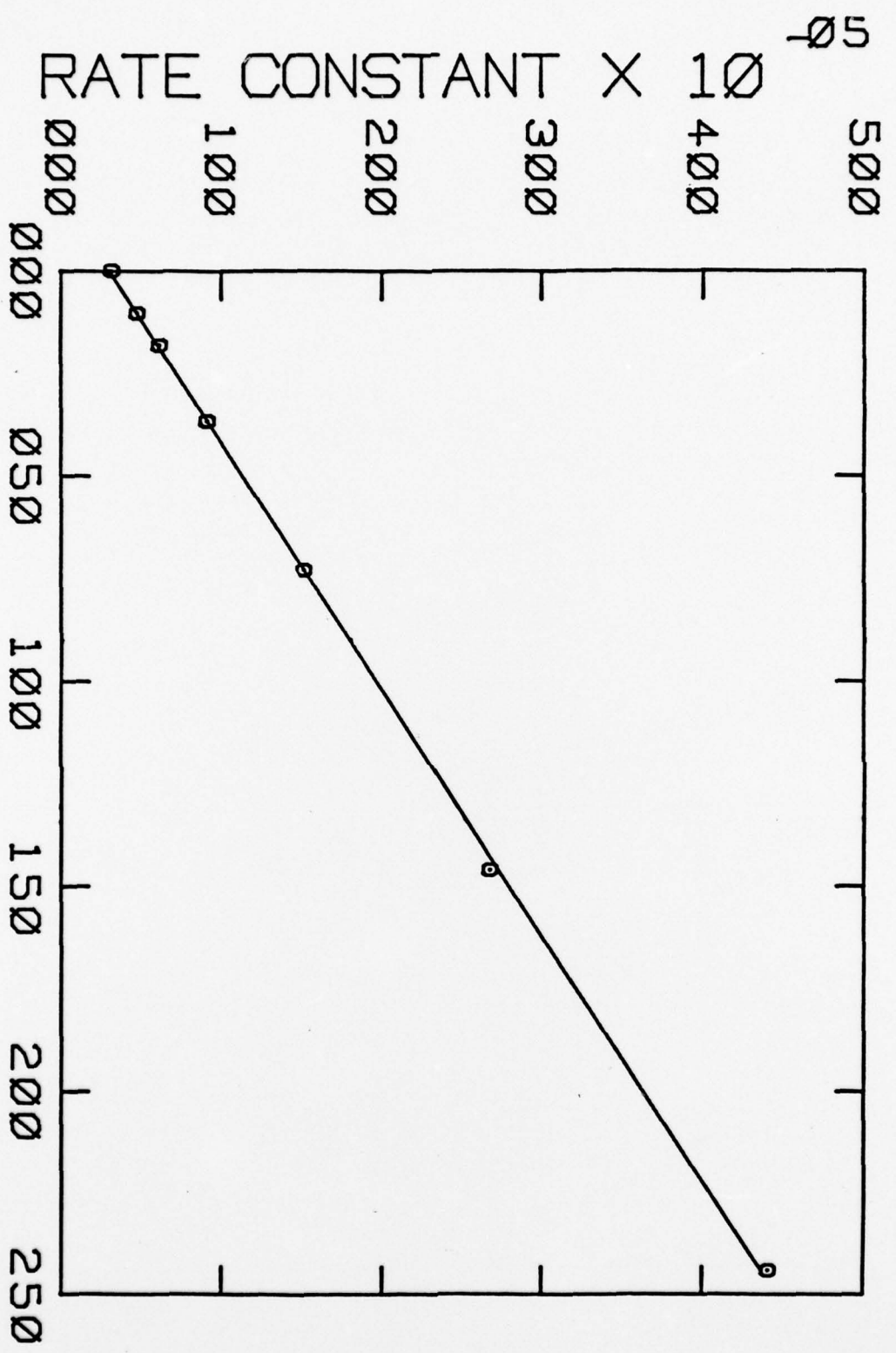
TIME (SEC)

OXID. POT. VS SCE X 10<sup>02</sup>





CONC. OF PP X 10<sup>05</sup>



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