NaCl, and made alkaline with 1 N NaOH. The basic solution was then extracted with ether (2 × 10 mL), and the combined ether extracts were dried ($MgSO_4$). The excess solvent was evaporated under reduced pressure, and the crude product was purified by preparative GLC (5% SE-30 on ABS 80/90) to give 44 mg (32%) of the amine **17a** which was identical in all respects with the samples prepared by methods A and B.

11-Aza-1,2,3,4,4a,9,10,10a-octahydro-3,4a-propanophenanthrene (18). To a solution of alkene **17a** (225 mg, 1 mmol) in glacial acetic acid (8 mL) was added 10% Pt/C (200 mg), and the reaction mixture was stirred under hydrogen at room temperature and atmospheric pressure for 4 h. After removal of the catalyst by filtration, the mixture was carefully made alkaline with 4 N NaOH until pH 9 and then extracted with ether (4 × 20 mL). The combined organic layers were washed with saturated brine (10 mL) and dried ($MgSO_4$). Evaporation of excess solvent under reduced pressure afforded 193 mg (85%) of pure **18**. An analytical sample was obtained by preparative GLC (5% Carbowax 20M, firebrick): ^1H NMR δ 1.00–3.50 (complex, 17 H), 7.00–7.33 (m, 4 H); ^{13}C NMR δ 55.14, 134.29, 145.28; mass spectrum *m/e* 227, 185, 184 (base), 171, 170; exact mass 227.1680 (calcd for $C_{16}H_{21}N$, 227.1674). The hydrogen bromide salt was recrystallized from 2-butanone, mp 238–239 °C dec.

Acknowledgments. We wish to thank the National Institutes of Health (GM 25439) and the Robert A. Welch Foundation for their generous support of this work. We would also like to thank Dr. Franz Scheidl of Hoffmann-La Roche, Inc., for performing several of the combustion elemental analyses.

Electron-Transfer-Initiated Reactions of Organic Peroxides. Reaction of Phthaloyl Peroxide with Olefins and Other Electron Donors[1]

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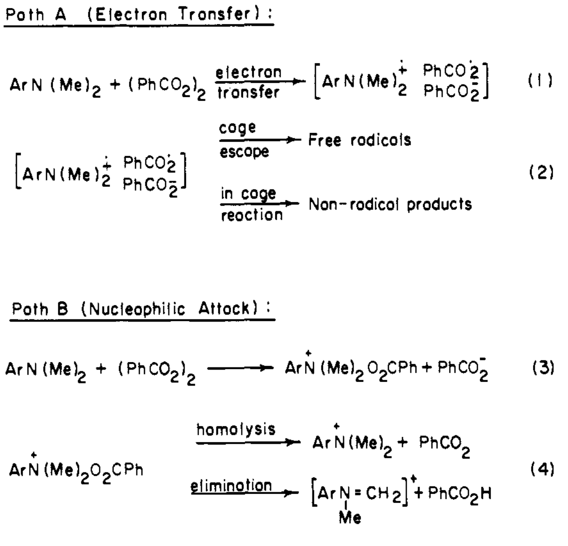
Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. *Received December 10, 1979*

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.

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. Over the years, evidence has accumulated in support of another, less widely recognized, 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. The general sequence of events for these reactions is electron transfer followed by reaction of the odd-electron intermediates to give eventually, by coupling, disproportionation, or a second electron transfer, even-electron products. This sequence has been found to predominate in a group of chain reactions generally described by the $S_{RN}1$ mechanism.[3,4]

The reactions of organic peroxides with reagents capable of serving as one- or as two-electron donors have served as a focus for much of the debate over the role played by electron transfer. The reaction of benzoyl peroxide (BPO) with amines is 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.[5] 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[6] and substituted amines.[7] Horner's postulate

Scheme I



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(1) Some of these results were reported in a preliminary communication: K. A. Horn and G. B. Schuster, *J. Am. Chem. Soc.*, **101**, 7097 (1979).

(2) Fellow of the Alfred P. Sloan Foundation, 1977-1979, and the Dreyfus Foundation, 1979-1984.

(3) J. F. Bunnett, *Acc. Chem. Res.*, **11**, 413 (1978).

(4) G. A. Russell, R. K. Norris, and E. J. Panek, *J. Am. Chem. Soc.*, **93**, 5839 (1971).

(5) L. Horner and E. Schwenk, *Angew. Chem.*, **61**, 411 (1949); L. Horner and E. Schwenk, *Justus Liebigs Ann. Chem.* **566**, 69 (1950); L. Horner and K. Scherf, *ibid.*, **573**, 35 (1951); L. Horner and C. Betzel, *ibid.*, **579**, 175 (1953); L. Horner, *J. Polym. Sci.*, **18**, 438 (1955).

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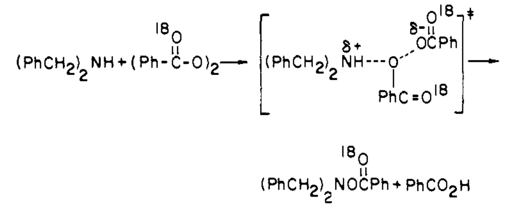
is shown as path A in Scheme I.

Not long after Horner's proposed sequence appeared, Walling and Indictor[8] 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 products. 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 I.

The debate over the mechanism of the reaction of amines with BPO was seemingly convincingly resolved by the classic isotope tracer experiments of Denney and Denney.[9] Dibenzylamine and benzoyl peroxide, labeled specifically with oxygen-18 in the carbonyl oxygens, give *o*-benzoyldibenzohydroxylamine, containing 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 5). Indeed, faced with this result,

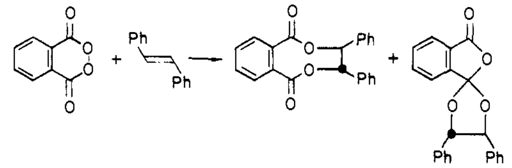


(5)

Horner[10] 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,[11] rests upon the assumption that the formation of a benzoyloxy radical (eq 1) before formation of the hydroxylamine product would scramble the labeled and unlabeled oxygen atoms. McBride's recent investigation of the structure of the benzoyloxy radical by EPR spectrometry in a crystalline matrix at low temperature shows that the unpaired electron is in an orbital of σ symmetry.[12] It is possible that during the short lifetime of Horner's radical ion pair 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.[13-21]

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).[22] In the course of our investigation of the CIEEL mechanism, we have demonstrated that radical ion intermediates are formed by electron transfer to a 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 and 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 an important role in the nonluminescent reactions of many compounds capable of serving as electron donors with easily reduced organic peroxides. We chose to investigate, as a possible example of such a process, the reaction of phthaloyl peroxide (**1**) with simply substituted olefins and with other electron donors.

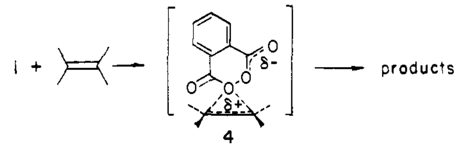
Phthaloyl peroxide was prepared and characterized by Greene,[23] and this synthesis initiated a detailed investigation of the reactions of this peroxide with a variety of olefins for which *trans*-stilbene will serve as a typical example. Thermolysis of **1** and *trans*-stilbene in CCl_4 at 80 °C was found to give two adducts, the cyclic phthalate **2** and the phthalide **3** (eq 6).[24] This reaction was



1 2 3

(6)

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[25] revealed that the magnitude of the bimolecular rate constant of these reactions depends 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[26] examined by oxygen-18 tracer methods the extent of exchange between the carbonyl and peroxide oxygens of **1** and the phthalate **2**. This study showed that about 11% of the label that was originally in the carbonyl oxygens of **1** is incorporated in the ether oxygens of **2**. These results led Greene to postulate a mechanism for the reaction of olefins with **1** that proceeds by a two-electron path. The transition-state structure for this reaction was represented as the complex of olefin and peroxide (**4**). It was suggested that this complex rearranged through additional intermediates to the observed products (eq 7).



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(7)

We have examined the reaction of **1** with a series of one- and two-electron donors. The kinetics, products, and solvent dependence of these reactions are entirely consistent with a one-electron transfer path quite similar to that proposed by Horner[5] for the reaction of amines with BPO. Moreover, we have unambiguously identified by nanosecond pulsed laser spectroscopy odd-electron intermediates in the reaction of **1** with excited-state electron donors. The correlation of the reaction kinetics for the ground- and excited-state donors indicates that both the excited- and the ground-state reactions proceed by the same mechanism.

Results and Discussion

Products. Our investigation of the chemistry of phthaloyl peroxide is centered upon an analysis of the products and kinetics of its reaction with a series of compounds that are classically considered to be neutral, acidic, or basic but are also capable of serving as single electron donors. For example, *N,N'*-diphenyl-

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(6) L. Horner and H. Junkermann, *Justus Liebigs Ann. Chem.* **591**, 53 (1955).

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(15) R. V. Hoffman and R. Cadena, *J. Am. Chem. Soc.*, **99**, 8226 (1977).

(16) S. U. Vul'fson, O. L. Kaliya, O. L. Lebedev, and E. A. Luk'yanets, *Zh. Obshch. Khim.*, **46**, 179 (1976).

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(19) W. A. Pryor and W. H. Hendrickson, Jr., *J. Am. Chem. Soc.*, **97**, 1580 (1975).

(20) W. A. Pryor and W. H. Hendrickson, Jr., *J. Am. Chem. Soc.*, **97**, 1582 (1975).

(21) W. A. Nugent, F. Bertini, and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 4945 (1974).

(22) G. B. Schuster, *Acc. Chem. Res.*, **12**, 366 (1979).

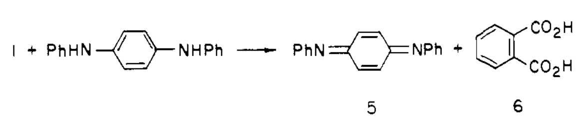
(23) Phthaloyl peroxide was prepared first by Russell [K. E. Russell, *J. Am. Chem. Soc.*, **77**, 4814 (1955)] and then by Greene [F. D. Greene, *ibid.*, **78**, 2246 (1956)].

(24) F. D. Greene, *J. Am. Chem. Soc.*, **78**, 2250 (1956).

(25) F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **80**, 3432 (1958).

(26) F. D. Greene, *J. Am. Chem. Soc.*, **81**, 1503 (1959).

p-phenylenediamine reacts rapidly with **1** to give in 88% yield the diimine **5** and phthalic acid (**6**) (eq 8). This reaction is a net



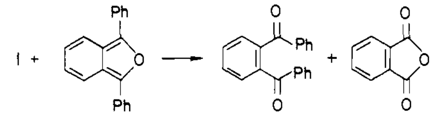
(8)

5 6

two-electron oxidation of the amine. From an analysis of the products, it is not possible to distinguish between simultaneous two-electron transfer (nucleophilic attack) and two sequential one-electron transfers. Similarly, the reaction of **1** with hydroquinone gives the two-electron oxidation product benzoquinone in high yield (eq 9). The products of the reaction of **1** with

(9)

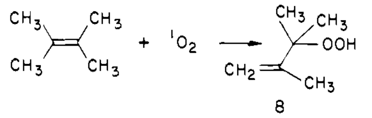
1,3-diphenylisobenzofuran (**7**) are identified as *o*-dibenzoylbenzene and phthalic anhydride (eq 10). These products result presumably



(10)

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 **7** is of special interest because it, among other reactions, has been used to support the conclusion that the thermolysis of **1** leads to the generation of singlet oxygen (${}^1O_2$).[27] 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 **8** in high yield[28] (eq 11). We examined the products of the



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(11)

reaction of **1** with tetramethylethylene, and **8** is not among them. Moreover, we showed that hydroperoxide **8** is stable to the reaction conditions employed. Thus, it appears that the previous report[27] of detectable formation of ${}^1O_2$ from thermolysis of **1** is incorrect.

As noted above, Greene[25] examined the products and the kinetics of the reaction of **1** and a series of olefins in CCl_4 solution. We have extended that investigation to benzonitrile solutions. In general, the reaction rate is accelerated in benzonitrile, and there is a slight loss of stereospecifically, but the nature of the reaction products is 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 infrared 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.[29] We should point out, however, that our analysis of the reaction kinetics (see below) indicates that the complexity of the reaction of **1** with these aromatic hydrocarbons is the result of multiple reaction paths for some intermediates 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 are particularly revealing. For all of the cases we examined, the basic reaction between the peroxide and reactant was clearly second order. Because of the wide range of reactivity we investigated, a variety of techniques was used to measure the reaction rate. For example, the reaction of **1** 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 concentrations. These results indicate clearly that the reaction is first order in diamine. Similarly, the reaction of **1** with *trans*-dianisylethylene was followed by conventional UV spectrometry with excess olefin and found to be first order in each component. The reaction of **1** with *trans*-stilbene in benzonitrile was followed iodometrically and was found also to be first order in each component.

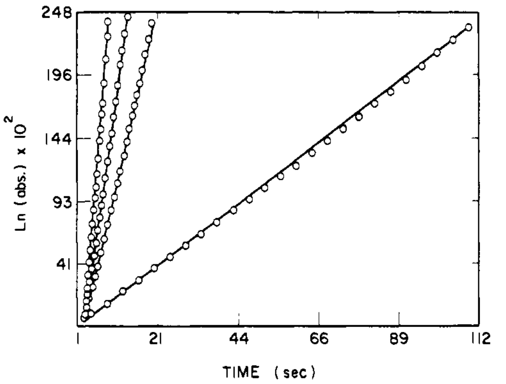

Figure 1. Kinetics of the reaction of phthaloyl peroxide with *N,N'*-diphenylbenzidine in THF. The initial concentration of the peroxide is 5.85×10^{-6} M, and the initial benzidine concentration varies from 5.93×10^{-5} M to 2.96×10^{-3} M.

Table I. Redox Properties and Bimolecular Rate Constants of Various Electron Donors

electron donor[a]	$E_{1/2}$, V vs. SCE[b]	k_2, $M^{-1}\,s^{-1}$ THF	k_2, $M^{-1}\,s^{-1}$ PhCN
pyrene (excited singlet)	−2.00		1.67×10^{10} [c]
anthracene (triplet)	−0.47		7.47×10^{8} [c,e]
anthracene (triplet)			7.27×10^{8} [c,f]
9-acetylanthracene (triplet)	−0.34		9.77×10^{7} [c]
N,N'-diphenyl-*p*-phenylenediamine	0.34		
N,N'-diphenylbenzidine	0.65[g]	533	*h*
7	0.79	89	548
tetracene	0.95[i]	8.1	57
trans-dianisylethylene	1.06[j]	2.86×10^{-2}	6.97×10^{-1}
hydroquinone	1.12[k]	3.5×10^{-1}	9.8×10^{-1}
p-methoxystilbene	1.22[l]		8.23×10^{-2}
2,5-diphenylfuran	1.29	3.4×10^{-2}	
trans-stilbene	1.51	*m*	5.37×10^{-4}

[a] All reactions were carried out at room temperature (25.0 ± 0.2 °C). [b] The oxidation potentials are taken from C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, 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. [e] Determined from the rate of growth of the $AN^{+}\cdot$ absorption at 725 nm. [g] Determined in THF with tetra-*n*-butylammonium perchlorate as the supporting electrolyte. [h] The diamine is not sufficiently soluble in benzonitrile for analysis. [i] A. J. Bard, K. S. V. Santhanan, J. T. Malov, J. Phelps, and L. O. Wheeler, *Faraday Soc. Discuss. Chem.* 45, 167 (1968). [j] Measured in acetonitrile with tetra-*n*-butylammonium perchlorate as the supporting electrolyte. [k] B. R. Eggins and J. Q. Chambers, *J. Chem. Soc., Chem. Commun.*, 232 (1969); V. D. Parker, *ibid.*, 716 (1969). [l] Determined from the absorption maximum of the charge-transfer spectrum of the olefin with TCNE. Cyclic voltammogram in acetonitrile indicates irreversible oxidation at 1.17 V vs. SCE. [m] Not determined due to interferences of the solvent with iodometric method.

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(27) K. D. Gundermann and M. Steinfatt, *Angew. Chem.*, **87**, 546 (1975).
(28) R. W. Denny and A. Nickon, *Org. React.* (*N.Y.*), **20**, 133 (1973).
(29) I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 2695 (1952).

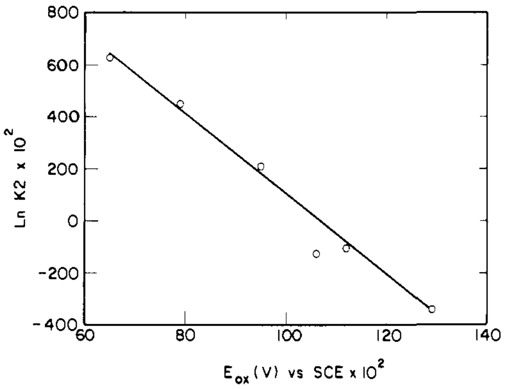

Figure 2. Correlation of the measured bimolecular rate constant (k_2) for reaction of various donors in THF solution with the one-electron oxidation potential. In order of increasing oxidation potential, the points are *N,N′*-diphenylbenzidine, 1,3-diphenylisobenzofuran, tetracene, *trans*-dianisylethylene, hydroquinone, and 2,5-diphenylfuran.

The results of the kinetic investigation for the systems examined are shown in Table I. 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, e.g., 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 **1** is 58 times greater than for 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 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 logarithm 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.[30]

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 be initiated by irradiation of the reaction mixture.[31] The extensive 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.[32] Thus, while pyrene ground state is a moderately reactive electron donor ($E_{\text{Ox}} = 1.36$ V), pyrene excited singlet state (Py^{*1}) is a remarkably powerful reducing agent ($E_{\text{Ox}} = -2.00$ V).[33] This change in reducing power is reflected in the reactivity of Py^{*1}. Reaction of Py^{*1} with an electron acceptor, e.g., dicyanobenzene, generates at an approximately diffusion-limited rate in acetonitrile pyrene radical cation (Py$^{+}\cdot$) and dicyanobenzene radical anion (DCB$^{-}\cdot$).[32] Moreover, the rate of these electron-transfer reactions has been shown to be a predictable function of the redox potentials of the system.

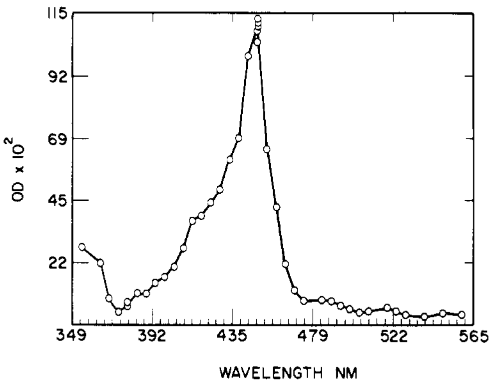

Figure 3. Absorption spectrum of Py$^{+}\cdot$ formed in a solution of pyrene and phthaloyl peroxide. The spectrum was recorded 140 ns after irradiation with a 10-ns wide pulse of light absorbed entirely by the pyrene.

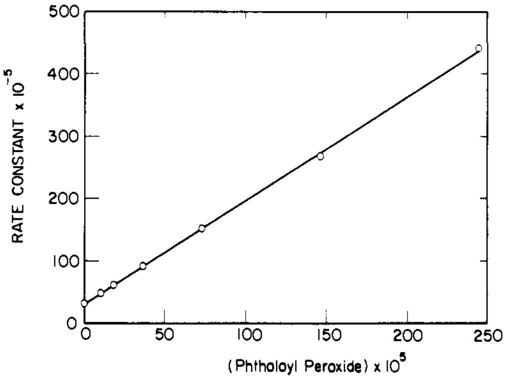

Figure 4. The observed fluorescence decay rate constant (k_{obsd}) for pyrene excited singlet at increasing phthaloyl peroxide concentration.

We examined the reaction of Py^{*1} with peroxide **1** following excitation with a 900-kW nitrogen laser. The laser excitation beam has a pulse width at half-height of about 10 ns. 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 ns after the laser pulse. This spectrum is identical in all respects with the previously reported[34] spectrum of Py$^{+}\cdot$ and indicates unambiguously that for this system electron transfer plays a major role in the reaction. 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 Py^{*1} in the presence of peroxide **1** is exactly that of the Py^{*1} itself. These observations indicate that there is no detectable complexation between pyrene and the peroxide either in the ground or in the excited state.

We are not only able to determine the product of the reaction of Py^{*1} with **1** but also can measure the rate of reaction and the yield of Py$^{+}\cdot$. By monitoring the rate of decay of the fluorescence of Py^{*1} at various concentrations of **1**, as is shown in Figure 4, we can extract the magnitude of this bimolecular rate constant. With Py^{*1}, the reaction is diffusion limited, $k_2 = 1.67 \times 10^{10}$ M^{-1}

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[30] G. B. Schuster, *J. Am. Chem. Soc.*, **101**, 5851 (1979). Use of the Polanyi relationship for electron-transfer reactions has been criticized recently: F. Scandola and V. Balzani, *ibid.*, **101**, 6140 (1979). However, the objection does not apply if the ΔG process refers to the hypothetical direct transfer of an electron from the donor to the acceptor at ground-state rather than transition-state geometry. This is the circumstance in our analysis, $\Delta G = E_{\text{Ox}} - E_{\text{Red}} - E_{\text{coul}}$. Thus, the state indicated by the ΔG process is never actually achieved during the reaction but is a reference state of the system that is useful in correlating k_2 with E_{Ox}.

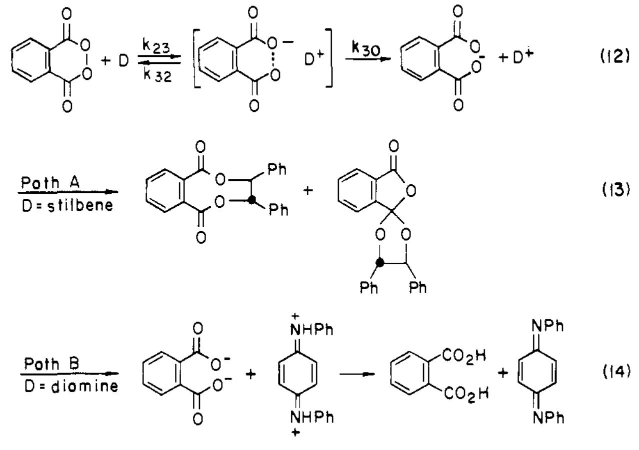
[31] R. A. Rossi and J. F. Bunnett, *J. Org. Chem.*, **38**, 1407 (1973).

[32] D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

[33] The oxidation potential of an electronically excited state may be estimated by simply subtracting the excitation energy from the ground-state oxidation potential.

[34] Z. H. Khan and B. N. Khanna, *J. Chem. Phys.*, **59**, 3015 (1973); T. Shida and S. Iwata, *J. Am. Chem. Soc.*, **95**, 3473 (1973).

Scheme II



s^{-1}, as it is expected to be from the Weller treatment. The yield of cage-escaped $Py^{+}\cdot$ was measured by calibrating the intensity of the laser beam and correlating that with the optical density of the $Py^{+}\cdot$ absorption after all of the Py^{*1} has reacted but before there has been significant decay of the $Py^{+}\cdot$. In acetonitrile solution, this measurement indicates that ca. 50% of the initially formed Py^{*1} eventually appears as $Py^{+}\cdot$.

Since Py^{*1} reacts with peroxide **1** at a rate limited by diffusion, information about the actual rate of the reaction 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 (AN^{*3}) which has an oxidation potential of -0.47 V. We can monitor the rate of reaction of AN^{*3} with **1** by following the rate of decay of triplet–triplet absorption of AN^{*3} or by following the rate of growth of the absorption due to anthracene radical cation ($AN^{+}\cdot$). As described above for pyrene, we measured the rate and the products of the reaction of AN^{*3} with peroxide **1**. The major product of this reaction is the anthracene radical cation. Unfortunately, the absorption spectra of $AN^{+}\cdot$ and AN^{*3} overlap in the region where AN^{*3} absorbs. Moreover, there are two sources of $AN^{+}\cdot$ in this system. The first is the reaction of anthracene excited singlet (AN^{*1}) with peroxide **1**. This reaction gives $AN^{+}\cdot$ essentially instantaneously (~15 ns) on the time scale of the triplet reaction. The second source, as mentioned above, is the reaction of AN^{*3} with **1** which gives rise to $AN^{+}\cdot$ at the same rate that AN^{*3} reacts. These complications forced us to determine the rate constant for consumption of AN^{*3} by **1** at low conversion where the concentration of AN^{*3} is much greater than that of $AN^{+}\cdot$. We also determined the rate of the reaction of AN^{*3} with **1** by following the appearance of $AN^{+}\cdot$ at 725 nm where there is no overlap problem. The derived bimolecular rate constants obtained by these two complementary techniques are within experimental error of each other and are reported in Table I. Similarily, we have determined that 9-acetylanthracene triplet reacts with **1** 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 to the peroxide is the major reaction path.

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 outlined in Scheme II, in which the species of eq 12 in square brackets could be the transition state; 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 donors are in agreement with the correlation of first oxidation potentials seen with the other donors. 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 a facile second electron transfer.

As was observed by Greene for olefins and by us for the amines, phenols, ethers, 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^{*3} and 9-acetylanthracene triplet states predicts 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 from the Weller analysis.[32] Unfortunately, the electrochemical reduction of phthaloyl peroxide is irreversible, and thus it is not possible to obtain an accurate estimate of $\Delta G_{23}°$ and thereby estimate k_2. However, even the simple linear extrapolation of the ground-state donor kinetic data to the oxidation potential of triplet anthracene and acetylanthracene gives a reasonably accurate estimate of the observed rate constant. Thus, the predicted k_2 for triplet anthracene is 3×10^7 times that observed for ground-state tetracene, and the observed k_2 is only about a factor of 17 less than that value. Part of the reason for the discrepancy may be due to the change in solvent from benzonitrile to acetonitrile neccesitated by technical considerations. Another part may be due to the expected breakdown in the free-energy relationship when the electron transfer is nearly thermoneutral. Similar curvature is seen also in proton-transfer reactions when the rate approaches the diffusion limit.[35] The correlation of the reaction kinetics for the ground- and excited-state donors along with the unequivocable generation of odd-electron intermediates from the excited-state reaction constitutes strong evidence that the ground-state reaction also is proceeding by the electron-transfer path.

An alternative approach to the understanding of the reaction of peroxide **1** 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.[36] 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 less

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(35) For a recent discussion, see: J. R. Murdoch, *J. Am. Chem. Soc.*, **102**, 71 (1980).

(36) R. S. Drago, *Struct. Bonding (Berlin)*, **15**, 73 (1973). For a recent example, see: S. Fukuzumi, K. Mochida, and J. K. Kochi, *J. Am. Chem. Soc.*, **101**, 5961 (1979).

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, the benzoyloxy radical is a σ radical, and any bonding interaction between the doubly occupied orbital of the carboxylate and the singly occupied orbital of the carboxyl radical, giving a weak three-electron bond,[37] 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. Moreover, to the extent that the nonbonded orbitals of the carbonyl oxygens of the phthalate radical anion overlap with the σ 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.[38] The first step in formation of the adduct from the radical ions is probably coupling of odd-electron centers (hence, the observed rearrangement in the norbornylene system).[39] 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 apparently somewhat faster than rotation about the carboxylate–carbon bond since rapid rotation would lead to exchange of oxygen atoms. These conclusions 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. The odd-electron intermediates formed in this initial step 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 e.g., 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 reagents.

Experimental Section

^{1}H NMR spectra were recorded on either a Varian Associates 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 and a 2-m 8.3% SE-30 column.

Solvents. Tetrahydrofuran (Aldrich, gold label) was distilled from sodium/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 kinetic analysis for the reaction of phthaloyl peroxide with the ground-state electron donors was conducted by one of three methods: (i) stop-flow techniques, (ii) conventional UV spectrometry, or (iii) iodometry. The solutions for all kinetic runs were purged for 5–10 min with argon prior to use. The reactions showed pseudo-first-order behavior employing either excess peroxide or excess electron donor.

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

Iodometric measurements were carried out by recording the absorbance of the triiodide ion at 430 nm at periodic time intervals for 2 half-lives; the infinity absorbance was recorded after 10 half-lives.[40] To approximately 15 mL of a $CHCl_3/CH_3COOH$ mixture (1:1) which had been purged with nitrogen gas for 1 min was added a 1.00-mL aliquot of a 50% KI solution. To this solution was added a 0.75-mL aliquot of the kinetic sample and the resulting solution purged for 1 min with nitrogen and then diluted to a total volume of 25 mL with $CHCl_3/CH_3COOH$ (1:1) solution. The absorbance at 430 nm, shown to be directly proportional to the concentration of **1**, was measured.

Stopped-flow measurements used a spectrophotometer designed by D. L. Krottinger.[41] 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 10–12 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 product from reaction of phthaloyl peroxide (2.6×10^{-4} mol) and *N*,*N*′-diphenyl-*p*-phenylenediamine (2.6×10^{-4} mol) in 10 mL of THF indicates that the only 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,[42] as well as by its UV–visible absorbance spectrum (λ_{max} 445 nm in 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 mixture of phthaloyl peroxide with 1,3-diphenylisobenzofuran in THF indicates phthalic anhydride and *o*-dibenzoylbenzene to be the major carbonyl-containing products. No intermediate adducts were observed. Gas chromatographic analysis of the products from reaction of 1.3×10^{-4} mol of phthaloyl peroxide with 1.3×10^{-4} mol of 1,3-diphenylisobenzofuran indicates that phthalic anhydride is formed in 78% yield, and the yield of *o*-dibenzoylbenzene, identified by its IR spectrum, is 100 ± 20%.

Reaction of 1 with *trans*-Stilbene in Benzonitrile at 66.0 °C. Analysis of the NMR spectrum of the reaction mixture of phthaloyl peroxide (2.4×10^{-4} mol) with *trans*-stilbene (2.4×10^{-4} mol) indicates, after removal of benzonitrile by distillation, that the cyclic phthalate **2** and lactonic orthoester **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 cm^{-1}) and **3** (1776 cm^{-1}). The NMR spectrum of the reaction mixture showed an aromatic multiplet centered at δ 7.50, a singlet at 6.12 (assigned to the benzylic H's of **2**), and a doublet of doublets centered at 5.27 (assigned to the benzylic H's of **3**).

Reaction of 1 with Tetracene in Acetonitrile at 25.0 °C. Thermolysis of phthaloyl peroxide (1.5×10^{-4} mol) with tetracene (1.4×10^{-4} mol) in acetonitrile resulted in the recovery of 4.2×10^{-5} mol (29%) of unreacted tetracene. The products in reaction mixture have carbonyl group resonances at 1724, 1706, 1681, and 1661 cm^{-1}. Crystallization of the

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(38) We thank Professor A. J. Arduengo and Mr. P. Gelburd of this department for their assistance with these calculations.

(39) F. D. Greene and W. W. Rees, *J. Am. Chem. Soc.*, **82**, 890 (1960). It is possible, however, that the rearrangement occurs at the radical cation stage: T. Shono, A. Ikeda, J. Hayashi, and S. Hakozaki, *ibid.*, **97**, 4261 (1975); R. Brettle and J. R. Sutton, *J. Chem. Soc., Chem. Commun.*, 449 (1974).

(40) D. K. Banerjee and C. C. Budke, *Anal. Chem.*, 36, 792 (1964).

(41) D. L. Krottinger, M. S. McCracken, and H. V. Malmstadt, *Talanta*, **26**, 549 (1979).

(42) J. Piccard, *Chem. Ber.*, 46, 1843 (1913).

reaction mixture from CCl_4/acetone resulted in the isolation of 6 mg of a product with a carbonyl group resonance at 1681 cm^{-1}. Anal. Calcd for a 1:1 adduct of tetracene with phthaloyl peroxide: C, 79.58; H, 4.11. Found: C, 79.16; H, 4.20.

Reaction of Tetramethylethylene (TME) with 1 in Benzonitrile. A solution of phthaloyl peroxide (7×10^{-3} M) and TME (1×10^{-1} M) was held at 80 °C 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 5×10^{-5} M.

Pulsed Nanosecond Laser Photolysis Apparatus. The pulsed-laser apparatus consists of a Molectron 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 × 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 ±5%.

The probe beam was generated by a PRA Model ALH 2150 450 W xenon arc lamp operated at 20 A and pulsed with a 60-μF capacitor charged to 350 V. The pulses were generally 140 μs long. The total power of the probe pulse, measuring all wavelengths and integrated over the entire pulse, was determined to be 0.46 ± 30% mJ/pulse.

The probe light intensity and sample fluorescence were monitored by using a Hamamatsu R928 photomultiplier tube with a 50-Ω 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 by using a 30-ps green pulse generated by an argon ion laser.

Spectral resolution was obtained by 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 a Tektronix R7912 transient digitizer. All measurements of the nitrogen laser intensity were made by using a Gentec Model ED-200 7010 joule meter with a calibration of 6.50 V/J when terminated in 10^6 Ω.

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 (2.51×10^{-3} M) containing pyrene (2.97×10^{-5} M) was prepared and kept at 0 °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 to 550 nm with a spectral resolution of generally better than 4 nm.

Pyrene Excited Singlet–Phthaloyl Peroxide. Quenching Kinetics. The quenching rate constant (k_2) for the reaction of phthaloyl peroxide with pyrene singlet in acetonitrile was measured. The pyrene concentration for each was 5.12×10^{-5} M while the concentration of phthaloyl peroxide varied between 0 and 2.44×10^{-3} M. All samples were nitrogen purged for 4 min prior to laser excitation. A plot of the derived first-order rate constants vs. 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 (4.28×10^{-4} M) with a concentration of phthaloyl peroxide between 0 and 4.88×10^{-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 1×10^{-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, a fast growth from anthracene^{*1} and a much slower growth from anthracene^{*3}. Thus, the following method was used to obtain the quenching rate constant. Each of the seven samples, in turn, was placed in the laser photolysis cell and photoexcited while air saturated with the nitrogen laser (337 nm, ~3.5 mJ/pulse). The optical density of the transient intermediate (monitored at 425 nm) was determined 1.45 μs after the laser excitation (prompt anthracene radical cation). The sample was then nitrogen purged for 4 min 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 vs. the concentration of added phthaloyl peroxide ($<1 \times 10^{-3}$ M) gives an estimate for the quenching rate constant.

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