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THE DECOMPOSITION OF SUBSTITUTED BENZOYL PEROXIDES IN THE PRESENCE OF DIMETHOXYBENZENES

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Abstract—Benzoyl peroxides, particularly those containing electron withdrawing substituents, undergo rapid decomposition in the presence of *m*-dimethoxybenzene, *p*-dimethoxybenzene, 2,5-di-t-butyl-1,4-dimethoxybenzene, and 2,5-dimethyl-1,4-dimethoxybenzene. Reactions are first order in peroxide and dimethoxy benzene, increasing in the order given. Identified products are the acids corresponding to the peroxide and esters involving ring substitution, ring substitution with elimination of a t-Bu group, and benzylic substitution. It is proposed that reaction involves a rate-determining charge transfer transition state leading to radical ion pairs which collapse to products. No free radicals have been detected.

The chemistry of organic peroxides has provided a rich mine for several generations of chemists and still appears far from exhausted. Of the host of reactions which have been observed, one of the most interesting and puzzling is the fast decomposition of diacyl peroxides in the presence of a variety of molecules which can be thought of either as easily-oxidized electron donors, or as potential nucleophiles because of the presence of available π- or unshared electron pairs. Examples include amines,[2] phenols,[3] a number of sulfur compounds,[4] halogen derivatives ranging from halide ions to alkyl iodides,[5] and electron rich olefins and aromatics.[6] Similar reactions are observed with peroxyesters,[3,7] sulfonyl peroxides, RSO_2–O–O-SO_2R,[8] and probably a few other classes of peroxides, and some of the most striking cases are intramolecular reactions in which the peroxide function and the reactive group are part of the same molecule.[5,9]

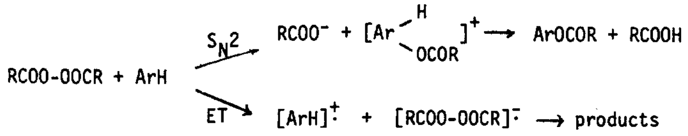
In general, the decompositions exhibit second order kinetics, first order in peroxide and first order in electron donor (the kinetics of the intramolecular cases are simple first order). Rates increase with the presence of electron-withdrawing groups on the peroxides and, in addition, cyclic peroxides such as phthaloyl[6a,10] and diphenoyl[11] peroxides show unusually high rates. Within a given group of electron donors, rates increase roughly with electron supplying substituents. With phenols as donors, at least, steric hindrance also appears important (the reactivity of 2,6-disubstituted phenols is greatly reduced).[3] Reaction-rates are usually solvent dependent, increasing with solvent polarity, thus implying relatively polar transition states.

The products of these reactions vary greatly depending on the electron donor, and are frequently complex and sometimes still ill-defined. In general, either the peroxide is reduced to the corresponding acid and the donor oxidized, or one or more fragments of the peroxide combine with the donor to yield a variety of products such as glycol esters or epoxides from olefins[6] and acyloxy aromatics from phenols and other electron-rich aromatics.[3,10] In a few cases, appreciable yields of free radicals are produced in these reactions, although it is not clear whether they are always formed in the initial reaction or arise from subsequent homolytic scission of a bond in a transient intermediate. The best known example of such radical formation is in the reaction of diacyl peroxides with tertiary amines such as dimethylaniline, which has long been used as an initiator for vinyl polymerization.[2] Finally, isotope labeling has shown that, in the few cases studied, the carbonyl oxygen from the diacyl peroxide undergoes little or no scrambling in products where the acyloxy group becomes attached to the electron donor.[12]

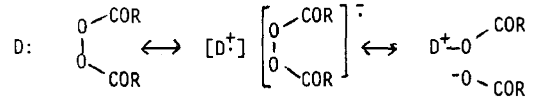
The possible mechanism of these reactions has received extensive discussion. There are two limiting models: simple electrophilic addition to the donor (or S_N2 displacement on peroxide oxygen) and electron transfer (ET), also called single electron transfer (SET) to yield a radical ion pair, e.g. for reaction with an electron rich aromatic.

A third and intermediate approach is to regard the transition state as a resonance hybrid of charge transfer and covalently bonded structures. Such a formulation is quite analogous to the mixture of ionic and polar structures proposed long ago to interpret "polar effects" in radical reactions[13] and implies that actually a whole spectrum of transition states are possible between the extremes of eqn (1).[14]

Another way of looking at the possible electron transfer process is in terms of potential energy surfaces and their cross-sections along coordinates associated with the stretching of the RCOO–OCOR bond and separation of peroxide P and donor D. Such a possible cross-section along the O–O bond length coordinate at a relatively large P-D separation is shown in Fig. 1. Curve A is a normal Morse curve for stretching of the O–O bond and



$$\text{RCOO-OOCR} + \text{ArH} \begin{array}{l} \xrightarrow{S_N2} \text{RCOO}^- + \left[\text{Ar}{\overset{\text{H}}{\underset{\text{OCOR}}{<}}}\right]^+ \longrightarrow \text{ArOCOR} + \text{RCOOH} \\ \xrightarrow{ET} [\text{ArH}]^{+\cdot} + [\text{RCOO-OOCR}]^{-\cdot} \longrightarrow \text{products} \end{array} \qquad (1)$$



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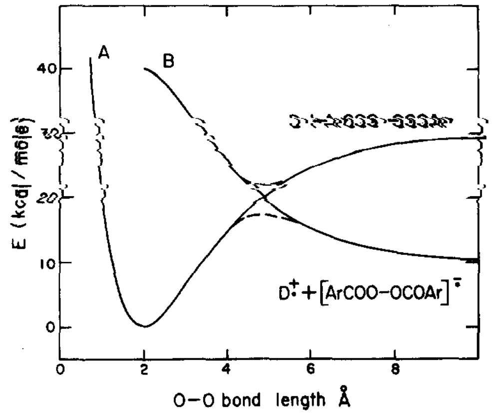


Fig. 1. Potential energy surfaces for charge transfer between peroxide and donor-cross-section along 0–0 bond stretch coordinate.

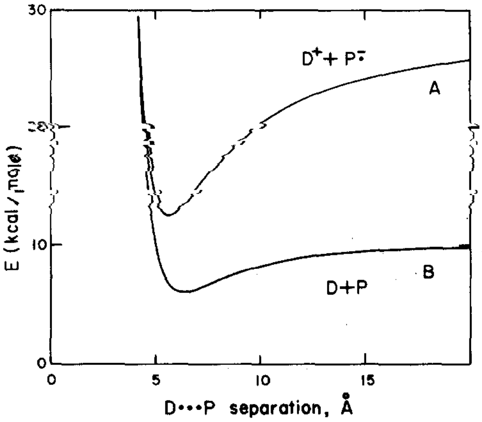


Fig. 2. Potential energy surfaces for charge transfer between peroxide and donor-cross-section along coordinate for peroxide-donor separation.

is drawn for an assumed bond-dissociation energy of 30 kcal/mole. Curve B, representing the system in which charge transfer has taken place, is constructed on the assumption that electron transfer to the unstretched peroxide is strongly endothermic, but that transfer after the O–O bond is an exothermic process, consistent with the fact that carboxylate anions can be oxidized at lower potentials than typical electron-rich aromatics. The curve between these points assumes that decrease in energy of the charge transferred species is proportional to the extent of O–O bond breaking. Where the two curves cross, *mixing of the two states will occur and the* "stretching" peroxide could cross over to the charge transferred state, although, at the actual transition state, charge transfer must be only partial.

So far, *our discussion is essentially that given by* Schuster for such systems,[10,15,16] and leads to the same conclusions, e.g. that activation barriers should be proportional to the oxidation protential of the donor, but could show proportionality constants significantly less than *unity*.

Fig. 2 illustrates a corresponding cross-section along the coordinate for D-P separation, and here our argument resembles that used by Kochi in discussing possible *electron transfer in the reactions of metal alkyls*.[17] We assume a weak interaction between peroxide and donor, and with a rather soft potential. The cross-section, Curve A, takes the depth of the well as 4 kcal and a potential of the form $1/r^6 - 1/r^3$. The potential determining the cross section B for the charge-transferred state should contain an additional term $-e^2/Dr$ due to electrostatic interaction. If D is taken as unity as has been done by Kochi,[17] such a term would be very large, 33 kcal for a separation of 5 Å. In practice, the charges are separated by polarizable portions of the molecules involved and the "effective" value of D may be larger. We have taken D as 4 giving a total well of -12 kcal. The relative positions of A and B depend on where we are on the 0–0 coordinate, and are here drawn for a point near the equilibrium 0–0 bond length, largely for clarity.

Regardless of the exact values of the parameters chosen, the consequences are clear. Considering Figs. 1 and 2 together, the lowest energy crossing point on the potential energy surface will occur when P and D are crowded together as closely as possible, and the resulting lowering of the charge transferred surface significantly decreases the requirement for stretching of the bond in the transition state.

These deductions may appear obvious, but they lead to further conclusions. As P and D are squeezed closer together, orbital overlap and mixing of states become increasingly important and the clean distinction between *ground and electron transferred states is blurred*. In fact, while the right hand side of curve B in Fig. 1 was drawn as leading to purely radical-ion pair intermediates, precisely the same sort of picture can be drawn for a *process going on to a covalently bonded intermediate*; i.e. the other alternative in eqn (1), by what we might call electrophilic substitution with a substantial charge-transfer contribution to the transition state; i.e. the situation depicted in eqn (2).

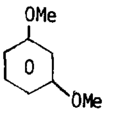
Since the transition states of these two processes are so similar, it seems to us unlikely that they can be distinguished by such probes as kinetics, kinetic isotope effects,[18] and correlations of rates with ionization or *oxidation potentials. Rather, the difference really* arises *after* the rate-determining step. If radical ion pairs are produced, rate- and product-determining steps are separated, and the best evidence for such pairs is the nature of the products formed and phenomena such as chemiluminescence which are difficult to account for by other mechanisms.[10,15,16]

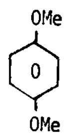
Which path is followed obviously depends on peroxide and donor structure, and, since we are dealing with fast, low activation energy processes occurring within the solvent cage, significant changes in reaction path may well occur within a given reaction series. In short, each specific reaction may occupy its own place within both a spectrum of possible rate-determining transition states and a range of subsequent reaction paths to final, isolated products.

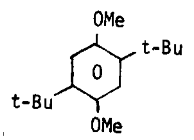
With this background, it appeared to us that a further study of the decomposition of various substituted benzoyl peroxides in the presence of electron-rich aromatics might clarify our picture of one group of these reactions, and this paper reports our results.

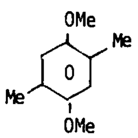
RESULTS

Kinetic studies. In inert solvents, rates of decomposition of substituted benzoyl peroxides vary only moderately with substituent or solvent, and may include a small amount of induced decomposition.[19,20] Data from the literature and some of our own appear in Table 1. Addition of cyclohexene, stilbene, or naphthalene has no significant effect on rate, but as shown in the Table *p*-dimethoxybenzene produces an appreciable acceleration, particularly with negatively substituted peroxides. Accordingly, we chose the dimethoxybenzenes below for further study.


m-DMB


p-DMB


DBDMB


DMDMB

Preliminary experiments showed that the accelerated decompositions were first order in both peroxide and donor (actually pseudo-first order in the presence of excess donor, with k's proportional to donor concentration). Further, since addition of methyl methacrylate has no significant effect on rate and leads to no detectable polymer, we conclude that induced decomposition is not a complication and no significant yields of radicals are produced.

Our complete kinetic study is summarized in Table 2, which includes both observed first order rate constants (k_1's) at the indicated donor concentrations, and, for those cases showing significant acceleration, second order rate constants (k_2's), calculated on the basis that the observed rate is the sum of contributions from the second order reaction and the normal decomposition. We have also made some measurements at other temperatures, and Table 3 lists the resulting activation parameters. For some of the more rapidly-reacting systems, these were used to extrapolate rates to 80° in Table 2.

Product studies. Investigation of the products of some of the faster reactions in acetonitrile showed them to be quite complex, but that their major components separated by TLC were the acid corresponding to the peroxide and esters derived from peroxide and donor. The structure of the esters, however, determined by a combination of NMR and MS analysis, varied strikingly with the donor. *p*-DMB yielded the expected substitution product, while with DBDMB, a t-Bu group was eliminated. A small amount of the "normal" substitution product is evidently also formed, since the mass spectra of the fraction containing the above ester from *m*-chlorobenzoyl peroxide showed a small peak at $m/e = 404$, the value for the parent peak of the normal product. It should be noted that, while the product in (4) is written with the ester group in the place of the lost t-Bu group, spectral data do not, in fact, eliminate other isomers. This point is discussed further below.

The reaction of DMDMB yields a third type of ester as the major product, with a structure which could be clearly differentiated from the normal product by NMR and MS spectra.

Competitive bromination. For comparison with what is considered to be a classical example of an electrophilic substution, we have examined the competitive bromination of *m*-DMB and *p*-DMB in acetic acid for comparison with the rate data in the previous section. Results are summarized in Table 4. As expected, *m*-DMB reacts preferentially, the relative reactivities being *m*-DMB/*p*-DMB = 20.

DISCUSSION

We believe that our rate and product studies together provide strong evidence, both for electron transfer in the rate-determining transition state of these reactions, and also for a separation of rate- and product-determining steps.

The order of donor effectiveness, *m*-DMB < *p*-DMB < DBDMB < DMDMB is that of increasing ease of 1-electron oxidation insofar as it is known. The oxidation potential for *m*-DMB is 1.38V, and *p*-DMB is 1.34V;[21]

Table 1. Decomposition rates of substituted benzoyl peroxides at 80°. All k's $\sec^{-1} \times 10^5$

	Substituent				
Solvent	p-OCH_3	none	p-Cl	m-Cl	p-NO_2
benzene	8.40	2.70	1.45	1.33	2.18
acetophenone[a]	15.6	4.32	3.83	2.85	4.33
acetonitrile	21.3	5.07	3.25	3.58	5.07
benzene + 1M cyclohexene	9.20	3.75	1.93	2.62	9.80
benzene + 1M stilbene	8.08	3.15	--	2.50	4.63
benzene + 1M naphthalene	8.13	3.15	1.80	2.05	2.27
benzene + 1M p-DMB[b]	14.3	6.00	8.22	20.2	126

a) Data from ref. (20). b) p-dimethoxybenzene.

Table 2. Decomposition of substituted benzoyl peroxides in the presence of dimethoxy benzenes at 80°, all k's × 10^5

			Substituent				
Donor	Solvent		p-OCH_3	none	p-Cl	m-Cl	p-NO_2
none[a]	benzene	k_1	8.40	2.70	1.45	1.33	2.18
	acetonitrile	k_1	21.3	5.07	3.25	3.58	5.05
m-DMB[a]	benzene	k_1	11.2	2.96	4.03	4.53	14.1
		k_2	--	--	2.58	3.20	11.9
	acetonitrile	k_1	18.0	4.92	7.15	10.5	31.8
		k_2	--	--	3.90	6.9	26.7
p-DMB[a]	benzene	k_1	14.3	6.00	8.22	20.2	126
		k_2	--	3.30	4.97	16.6	121
	acetonitrile	k_1	20.4	9.00	14.9	83.8	436
		k_2	--	3.93	11.6	80.2	431
DBDMB[b]	acetonitrile	k_1	18.1	12.9	81.2	142[c]	952[c]
		k_2	--	31.3	312	568[c]	3810[c]
DMDMB[b]	acetonitrile	k_1	70.1	180	--	1580[c]	5068[c]
		k_2	195	700	--	6320[c]	20300[c]

a) 0.04M peroxide, 1M donor. b) .01M peroxide, 0.25M donor.

c) extrapolated from lower temperatures.

Table 3. Activation parameters for peroxide decompositions

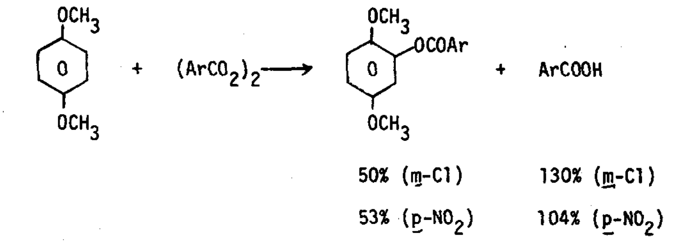
Substituent	Donor	Solvent	log A	E_a (kcal/mole)
m-Cl	--	acetophenone[a]	14.35	30.7
	p-DMB	benzene	9.52	21.3
	p-DMB	acetonitrile(AN)	8.84	19.4
	DBDMB	AN	9.01	18.9
	DMDMB	AN	8.56	17.3
p-NO_2	--	acetophenone[a]	14.37	30.3
	p-DMB	benzene	8.81	19.2
	p-DMB	AN	8.69	18.0
	DBDMB	AN	8.72	17.5
	DMDMB	AN	8.54	16.1

a) data from ref. (20).

Table 4. Competitive bromination of *m*-DMB and *p*-DMB[a]

	Rel. yield	Partial rate factor
2-Br-1,4-dimethoxybenzene	1.0	1.0
4-Br-1,3-dimethoxybenzene	18.2	36.4
2-Br-1,3-dimethoxybenzene	1.44	5.87
5-Br-1,3-dimethoxybenzene	.63	2.52

a) .05 of each + .005 M Br_2 in acetic acid, analysis by glc.



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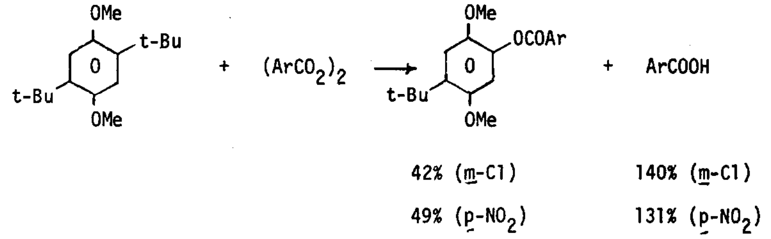

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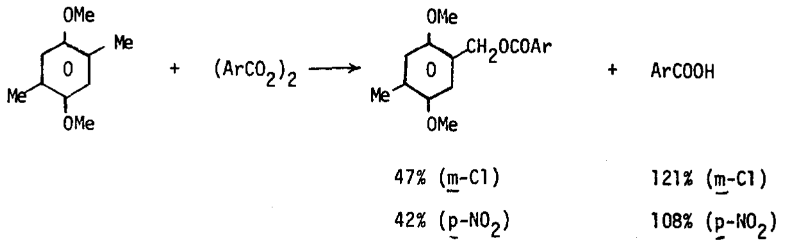


(5)

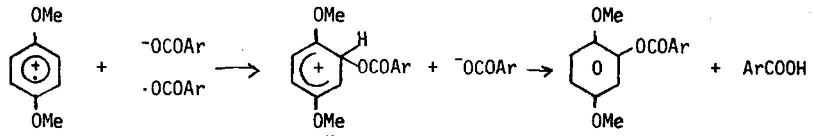
and, judging from data on phenols and alkylaromatics, alkyl substitution should lower oxidation potentials even further. On the other hand, for *m*-DMB *vs* *p*-DMB, the order is the reverse of that which would be expected for simple electrophilic substitution in which the 2, 4, and 6 positions of *m*-DMB should be activated by two *o*- or *p*-methoxyls, and the data on bromination in Table 4 shows clearly that this expectation is correct.

The increase in rate with solvent polarity and the introduction of electron-withdrawing groups on the peroxide are also consistent with electron transfer, but less diagnostic, since parallel effects would be expected for a two-electron process. For DMDMB log k_2 vs σ gives a good Hammett plot, $\rho = 1.8$. The other donors do not provide enough points for significant plots; but, from Table 2, there is no large change or significant trend in $k_2(p\text{-NO}_2)/k_2(m\text{-Cl})$ with change in donor structure. Actually, the sensitivity observed is rather small, either for electrophilic substitution or for a transition state in which charge transfer was more than partial.

Several observations indicate that the transition states in these reactions must involve close approach of donor and peroxide and must have rather specific structures. The values of log A's from Table 3 (8–9) are small implying tight transition states. Most notable of all is the low reactivity of DBDMB vs DMDMB, implying significant sensitivity to steric hindrance, since substitution of t-Bu and Me groups in related compounds such as phenols produce essentially the same reduction in oxidation potential.[21]

Finally, we should note that there is spectral evidence for the formation of charge transfer complexes between *p*-nitrobenzoyl peroxide and *p*-DMB and its alkyl derivitives. Solutions of peroxide and donor develop an immediate yellow-brown color on mixing in the cold. Absorption spectra, however are not very informative since they show no clear charge-transfer peaks, but only a general shift of absorption to longer wavelengths, and further absorption increases slowly as reaction progresses. Accordingly, they were not investigated further.

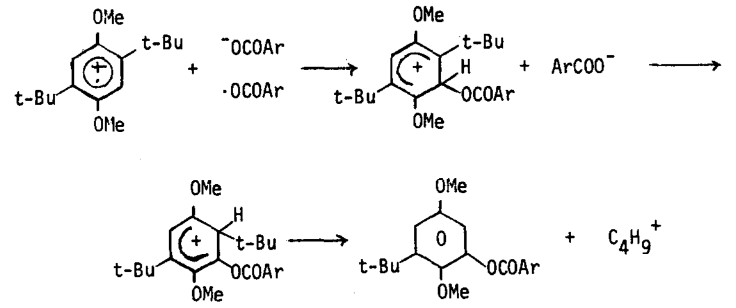
Taken all together, our kinetics appear consistent with a series of bimolecular reactions, all with similar transition states in which charge transfer is important, but in which peroxide and donor are closely associated. If this is granted, the striking changes in products with donor structure imply that the product-determining steps occur later, most probably via the collapse of some sort of radical ion pairs, although whether the bond in the peroxide is entirely broken at the product-determining step is not entirely clear. Assuming that it is, formation of "normal" ester might be written as



(6)

or an alternative scheme involving a radical- rather than an ion-pair intermediate. We prefer the former since complete trapping of such a radical pair within the solvent cage seems inprobable, and we have been unable to detect free radical production by these systems. In any case, the two types of possible intermediate should be in equilibrium via fast electron transfer, so our formulation implies that the ion pair is the more stable.

The loss of a t-Bu group from DBDMB is more ambiguous, particularly since the structure of the product is not unequivocal. As written, it could arise from ipso substitution or direct loss of a t-Bu cation from the radical ion, although the latter appears energetically unfavorable. Alternatively, if it has an isomeric structure, it would have to be the consequence of a proton shift, e.g.



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The benzylic ester found from DMDMB is a plausible product from an intermediate radical cation, since side-chain fragmentation of such species is well known. A plausible path is a fast radical disproportionation within the solvent cage to yield an intermediate ion pair.

This would again account for the lack of free radical production in the reaction, although proton transfer from radical cation to the carboxylate ion to give a radical pair could lead to the same final products.

One difficulty in formulating th exact paths by which products are formed is that the chemistry of radical cations in general is not well understood, although all the reactions we propose at least have plausible analogies. Our material balances for peroxide fragments are over 80%. Since most of the peroxide not accounted for as ester appears as the appropriate benzoic acid, we conclude that the additional products unaccounted for must be dimers or other oxidation products of the donor solvents.

Finally, our results may be compared with some of those in the literature for other donors and similar peroxides. For *p*-DMB-*p*-nitrobenzoyl peroxide in benzene, we obtain $k_2(45°) = 3.8 \times 10^{-5}$. For the parallel reaction with 4,4′-dimethoxystilbene, which has a significantly lower oxidation potential (0.90 V.), Greene reports 9.58×10^{-3}, and the rates of reaction of this donor with variations in solvent and peroxide structure parallel those reported here. The rates we observe also overlap those observed with phenolic donors. For phenol-benzoyl peroxide[3], $k_2(30°) = 5.7 \times 10^{-7}$. For DMDMB-benzoyl peroxide our extrapolated value (assuming the same log A as for *p*-nitrobenzoyl peroxide) is 1.9×10^{-5}. Again the lower rate for phenol is consistent with a higher reported oxidation potential (1.47 v).

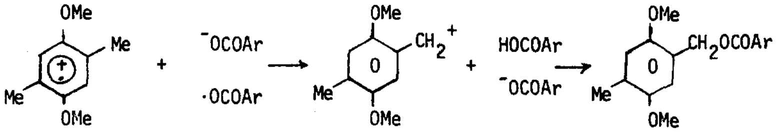
Alkyl and alkoxy phenols show considerably higher rates, and it appears that phenols and dimethoxybenzenes have comparable donor properties. Walling and Hodgdon[3] originally proposed that the phenol reactions involved nucleophilic attack by phenol oxygen on the peroxide bond, primarily because 0-deuterated phenols showed a small kinetic isotope effect, $k_H/k_D = 1.29–1.35$ and because rates were depressed in solvents which strongly hydrogen-bond to phenols. Denney and Denney,[12b] however, showed by isotope labeling experiments that the first bond between peroxide and phenol is probably to carbon. We now believe that these peroxide-phenol reactions probably involve electron transfer in "tight" transition states similar to those we have discussed here. As here, *o*-substitution reduces rates, suggesting steric hindrance, and products change drastically with structure, un- and *p*-substituted phenols undergo predominantly *o*-substitution, while 2,6-disubstitution leads to chiefly *p*-coupled products.

To summarize our position, there is certainly plausible evidence for "charge transfer" transition states in the systems we have reported here and many others in the literature. However, how much, and how closely reactants are bound in the transition state, remains something of a mystery. Just how and how quickly do the products of this rate-determining transition state pass on to products remains even more obscure. More data on both rates and products for a variety of donors are needed, as well as reliable oxidation potentials for a variety of donors measured under strictly comparable conditions, and a clearer view of the whole field of radical-ion chemistry.

EXPERIMENTAL

Materials. Peroxides were prepared from the corresponding acid chlorides and Na_2O_2,[19] recrystallized from toluene, and purity (>99%) determined by iodimetry. *m*-DMB and *p*-DMB were commerical materials. DBDMB was prepared by alkylating *p*-DMB with t-BuOH in acetic acid-oleum,[22] m.p. 102–2°; yield, 67%. DMBMB was prepared from 2,5-dimethylbenzoquinone in three steps by the method of Robinson and Basey,[23] m.p. 105–7°; overall yield, 71%.

Kinetic experiments were carried out under argon in thermostatted vessels and followed by iodimetric titration of aliquots. The data gave good first order plots, and the order in respect to donor was determined by varying initial donor concentration, Table 5 showing typical data. The effect of varying



(8)

temperature was determined for four systems, Table 6, the data yielding the activation parameters in Table 3. The absence of induced decomposition or scavengable radicals was checked for both *m*-Cl- and *p*-NO_2-benzoyl peroxide with *p*-DMB in benzene and DBDMB and DMDMB in acetonitrile in the presence of 0.05–0.20 M methyl methacrylate. There was no retardation of rate or formation of polymer.

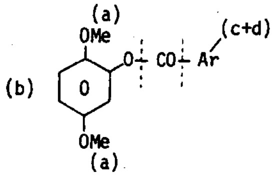
Table 5. Decomposition of 0.01 M *p*-nitrobenzoyl peroxide in acetonitrile in the presence of DBDMB (30°)

[DBDMB]	k_2 ($M^{-1}sec^{-1}$ x 10^4)
.05	5.57
.10	5.33
.15	5.33
.20	5.33
.25	5.33

Product studies were carried out by decomposing 0.2 mM of peroxide in 5 ml acetonitrile containing 1 mM donor at 25–45°. Solvent was removed and products separated by tlc on silica gel using hexane–ether mixtures for elution. Separations were carried out very conveniently using a Chromatron apparatus (Harrison Research Corp., Palo Alto, California) in which the silica gel is spread on a circular plate which is spun rapidly; the sample and then solvent are introduced at the center of the plate and successive fractions collected from the periphery. The major products separated were the acids corresponding to the preoxides and esters. Ester structures were determined by NMR and MS analysis using EM-390 and Varian 112-S instruments. The spectral assignments and other data are summarized in Chart 1. However, as noted earlier while only single esters were obtained from reactions with DBDMB, the data do not eliminate the possibility that they have the isomeric structures 1,4-di-methoxy-2-t-butyl-6-aroyloxybenzenes.

Brominations. In order to provide GLC reference data, *m*-DMB and *p*-DMB were treated separately with Br_2 in AcOH and the isomeric products separated by TLC (Chromatron) and identified by NMR or comparison with authentic material. For the competitive bromination, 50 mM each of *m*-DMB and *p*-DMB were dissolved in 10 ml AcOH and 5 mM Br_2 in 12 ml

Chart 1[a].

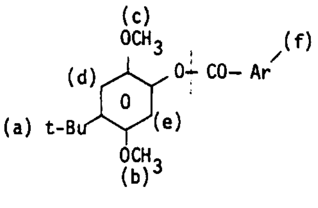


nmr

	m-Cl			p-NO2
(a)	s(6H)	3.87δ		3.83δ
(b)	m(3H)	6.85δ		6.95δ
(c)	m(2H)	7.63δ	s(4H)	8.55δ
(d)	m(2H)	8.30δ		

	p-Cl	p-NO2
ms:	294 (M+2)	303 (M)
	292 (M)	153, 150
	153, 139, 111	

m.p. 63-4° (m-Cl)
133-4° (p-NO_2)

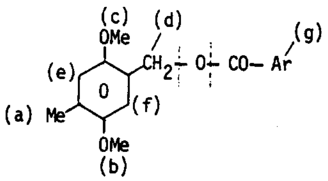


nmr

	m-Cl			p-NO2
(a)	s(9H)	1.40δ		1.40δ
(b)	s(3H)	3.85δ		3.80δ
(c)	s(3H)	3.90δ		3.87δ
(d)	s(1H)	6.77δ		6.79δ
(e)	s(1H)	7.05δ		7.05δ
(f)	2m(4H)	7.4-8.4δ	s(4H)	8.53δ

	m-Cl	p-NO2
ms:	350 (M+2)	359 (M)
	348 (M)	150
	139	

m.p. 113.5-114.5° (m-Cl)
153-4° (p-NO_2)



nmr

	m-Cl			p-NO2
(a)	s(3H)	2.20δ		2.26δ
(b)	s(3H)	3.85δ		3.90δ
(c)	s(3H)	3.88δ		
(d)	s(2H)	5.40δ		5.50δ
(e)	s(1H)	6.80δ		6.89δ
(f)	s(1H)	6.97δ		7.03δ
(g)	2m(4H)	7.6-8.2δ	s(4H)	8.46δ

	m-Cl	p-NO2
ms:	322 (M+2)	331 (M)
	320 (M)	181, 165, 150
	181, 139	

m.p. 68-68.5° (m-Cl)
121-123° (p-NO_2)

(a) Letters identify protons in NMR, dashed lines major MS fragments.

Table 6. Effect of temperature on peroxide decompositions[a]

		m-Cl-benzoyl perox.		p-NO_2 benzoyl perox.	
Donor	Solvent	T	k_1 $sec^{-1}x10^5$	T	k_2 $sec^{-1}x10^5$
p-DMB (1M)	benzene	80	24.9	80	126
		60	4.23	60	19.0
		40	.58	40	3.50
p-DMB (1M)	AN	60	16.1	60	97.7
		45	3.82	45	24.0
		30	.88	30	6.67
DBDMB (.25M)	AN	50	13.3	50	89.4
		40	7.62	40	36.6
		30	1.97	30	15.2
DMDMB (.25M)	AN	50	180	40	248
		40	82.4	30	97.6
		30	30.6	25	67.2

(a) 0.04M peroxide with DMB, .01M with DBDMB and DMDMB.

AcOH added slowly with stirring at room temp. Reaction was complete in a few mins and the products in hexane were washed with water and bicarbonate, dried, and the solvent removed. Analysis was by GLC using a 10 ft. 10% CW-20M column at 220°, and the isomers, which separated in the order 2-Br-*p*-DMB, 4-Br-*m*-DMB, 2-Br-*m*-DMB, 5-Br-*m*-DMB were assumed to have the same response factor. Results are listed in Table 4.

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