Free-Radical Chemistry of Organophosphorus Compounds. V.[1,2] Reactions of Thiyl Radicals with Alkylphosphonites. Effects of Activation Energies and A Values on the α vs. β Scission Competition

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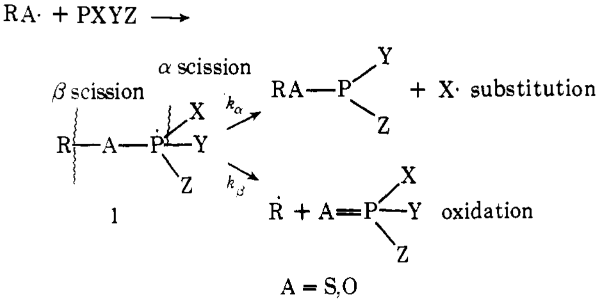
Abstract: The reactions of RS· with certain diethyl alkylphosphonites, $R'P(OEt)_2$, were studied as a function of temperature. Over a 100 °C range of temperatures the ratio of oxidation product to substitution product, i.e., $R'P(S)(OEt)_2/RSP(S)(OEt)_2$, was examined to establish values of $E_{sub} - E_{ox}$ and A_{sub}/A_{ox}. On reaction with $PhCH_2P(OEt)_2$ $E_{sub} - E_{ox}$ for a series of three RS· was: *i*-PrS·, 0.35 kcal/mol; *t*-BuS·, 0.48 kcal/mol; *p*-$MeC_6H_4CH_2S$·, 1.9 kcal/mol. Accompanying changes in A_{sub}/A_{ox} were minor. The reaction of *i*-PrS· with *t*-$BuP(OEt)_2$ had $E_{sub} - E_{ox}$ of 3.2 kcal/mol. Thus $E_{sub} - E_{ox}$ responds to structural changes in *both* RS· and $R'P(OEt)_2$. Arguments are presented in favor of a mechanism which involves formation of an intermediate phosphoranyl radical, $R'(RS)\dot{P}(OEt)_2$, which gives product via competitive α or β scission processes, the relative rates of which depend on the strengths of the C–P and C–S bonds undergoing scission. Excluded are mechanisms in which the initial configuration of $R'(RS)\dot{P}(OEt)_2$ or its rate of permutational isomerization *solely* control the α/β scission (substitution/oxidation) ratio.

Reaction of alkoxy and thiyl radicals with trivalent organophosphorus derivatives may give both oxidation and substitution products (eq 1). The ratios oxidation/substitution



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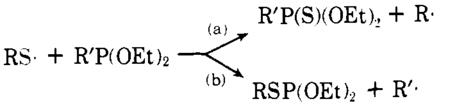
in these systems are strongly structurally dependent. We suggested earlier[3] that this competition be rationalized, to a first approximation, in terms of the effects of the strengths of the R–A and P–X bonds of the likely phosphoranyl radical intermediate (**1**)[4] on the α/β scission ratio. Since product studies at a single temperature neglect entropy factors, and thereby may lead to spurious conclusions, we have examined the temperature dependence of the oxidation/substitution ratio in the reaction of a series of thiyl radicals with certain alkylphosphonites, eq 2. The results of the

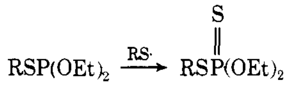


$$RS\cdot + R'P(OEt)_2 \begin{cases} \xrightarrow{(a)} R'P(S)(OEt)_2 + R\cdot \\ \xrightarrow{(b)} RSP(OEt)_2 + R'\cdot \end{cases} \tag{2}$$

work reported here strongly support the prior postulates and exclude possible explanations based *solely* on the configuration of the initially formed phosphoranyl radical or on the rate of its subsequent permutational isomerization.

Results

As seen in Table I the reactions of $PhCH_2P(OEt)_2$ with three thiyl radicals (*i*-PrS·, *t*-BuS·, and *p*-$CH_3C_6H_4CH_2S$·) were studied along with those of *i*-PrS· with two alkylphosphonites, $PhCH_2P(OEt)_2$ and *t*-$BuP(OEt)_2$. In this way both the effects of R· stability with constant R′ and vice versa could be investigated. Product ratios were measured as a function of temperature over the temperature range 0–100 °C or 20–100 °C. Use of an excess of RSH ensured that initial $RSP(OEt)_2$ was cleanly converted to the stable, oxygen-insensitive *O,O*-diethyl *S*-alkyl phosphorodithioate (eq 3) and that R· was rapidly trapped as RH. The latter prevented any of the known[5] potential side reaction 4 or the readdition of free R·′ to $RSP(OEt)_2$ from occurring. Reactions were run to total consumption of $R'P(OEt)_2$ and gave excellent product balances. (See Experimental Section for details.)



$$RSP(OEt)_2 \xrightarrow{RS\cdot} RSP(=S)(OEt)_2 \tag{3}$$

$$R\cdot + R'P(OEt)_2 \xrightarrow{-R'\cdot} RP(OEt)_2 \longrightarrow RP(S)(OEt)_2 \tag{4}$$

Plots of ln [(substitution)/(oxidation)] vs. $1/T$ gave the values of $E_{sub} - E_{ox}$ and A_{sub}/A_{ox} listed in Table I from which the k_{ox}/k_{sub} ratios shown were calculated. Errors (linear regression analysis) are at the 95% confidence level. Cases 1 and 2 compare results obtained by direct measurement of the product phosphorodithioate (case 1) with those obtained by use of the toluene peak as a measure of the amount of substitution which occurs (case 2). Agreement is excellent.

Figure 1 is the plot of log k_α/k_β vs. $1/T$ for case 1 which utilizes 49 experimental points, given as an example of the quality of the plots obtained.

Discussion

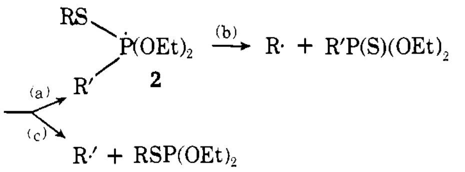
It should first be noted that within the series of reactions of $PhCH_2P(OEt)_2$ with three RS· there is a systematic variation in $E_{sub} - E_{ox}$; that is $E_{sub} - E_{ox}$ increases in the order *i*-PrS· < *t*-BuS· < *p*-$CH_3C_6H_4CH_2S$·. If the plausible assumption is made that E_{sub} is near constant since $PhCH_2$· is displaced in each case, then E_{ox} decreases in the order of increasing R· stability, i.e., *i*-Pr < *t*-Bu· < *p*-$CH_3C_6H_4CH_2$·. Likewise, a comparison of cases 1 and 2 with case 4 in which E_{ox} is likely unchanged shows an apparent increase in E_{sub} of about 3 kcal/mol when the less stable *tert*-butyl radical is the product of substitution instead of the benzyl species. *Thus, the competition between the enthalpies of oxidation and substitution in these reactions is apparently influenced by the stabilities of the radicals formed in both processes.*

Table I. E_a and A-Factor Effects on the Competition between Oxidation and Substitution in the Reaction RS· + $R'P(OEt)_2$

Case	RS·	R′	$E_{sub} - E_{ox}$[a]	A_{sub}/A_{ox}	r[b]	k_{ox}/k_{sub} (60 °C)
1	i-PrS[c]	$PhCH_2$	0.36 ± 0.01[f]	0.81	0.994	2.12
2	i-PrS[d]	$PhCH_2$	0.34 ± 0.02[g]	0.79	0.955	2.15
3	t-BuS[d]	$PhCH_2$	0.48 ± 0.06[h]	0.44	0.976	4.74
4	p-$MeC_6H_4CH_2S$[d]	$PhCH_2$	1.9 ± 0.1[i]	1.3	0.993	13.2
5	i-PrS[e]	t-Bu	3.2 ± 0.2[j]	5.4	0.995	22.9

[a] 95% confidence limit. [b] Correlation coefficient. [c] Based on GLC measurements of i-$PrSP(S)(OEt)_2$ and $PhCH_2P(S)(OEt)_2$. [d] Based on toluene and $PhCH_2P(S)(OEt)_2$. [e] Based on i-$PrSP(S)(OEt)_2$ and t-$BuP(S)(OEt)_2$. [f] 49 total points; temperatures 0, 20, 40, 60, 80, 100 °C; digital electronic integrator. [g] 54 total points; temperatures 0, 20, 40, 60, 80, 100 °C; electronic digital integrator. [h] 46 total points; temperatures 0, 20, 40, 60, 80, 100 °C; electronic digital integrator. [i] 33 total points; 0, 20, 40, 60, 80, 100 °C; disk integrator. [j] 36 total points; temperatures 20, 40, 60, 80, 100 °C; electronic integrator.

Several precise mechanistic alternatives may be considered for these reactions. (1) Competing *concerted* sulfur transfer and R·′ displacement without formation of a discrete intermediate like **1** (eq 2). (2) Oxidation via intermediate **2** in competition with a *concerted, one-step, substitution* process:



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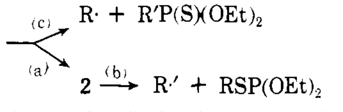
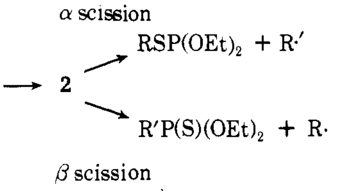
(3) Substitution via intermediate **2** in competition with a *concerted, 1-step oxidation* process:



$$\xrightarrow{(c)} R\cdot + R'P(S)(OEt)_2 \qquad \xrightarrow{(a)} \mathbf{2} \xrightarrow{(b)} R\cdot' + RSP(OEt)_2 \tag{6}$$

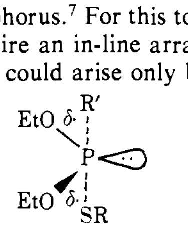
(4) Both oxidation and substitution via **2** with the *oxidation/substitution ratio determined by the relative rates of α and β scission:*



$$\longrightarrow \mathbf{2} \xrightarrow{\alpha\ \text{scission}} RSP(OEt)_2 + R\cdot' \qquad \mathbf{2} \xrightarrow{\beta\ \text{scission}} R'P(S)(OEt)_2 + R\cdot \tag{7}$$

Since ESR evidence is available[6] for the presence of a phosphoranyl radical similar to **2** when $CH_3S\cdot$ is generated in the presence of $(EtO)_3P$ or n-Bu_3P, we tend to discount alternative 1, although the ESR work does not *prove* the intermediacy of species like **2** in such reactions.

Furthermore, the substitution of $PhCH_2\cdot$ and t-Bu· by $Me_2N\cdot$ in cyclic phosphonites occurs with inversion of configuration about phosphorus.[7] For this to occur in a concerted fashion would require an in-line arrangement of R′ and RS, e.g., as in **3**. This could arise only by attack of RS· on



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pyramidal $R'P(OEt)_2$ opposite R′. The orientational requirement of **3** could confer upon the substitution process a reduced A value compared to that for oxidation which requires only that RS· attack toward the lone pair of pyramidal $(EtO)_2PCH_2Ph$ in order to give the known[8] retentive stereochemistry. Table I shows, however, the similarity of A_{ox} and A_{sub} in cases 1-4, a finding inconsistent with alternative 1.

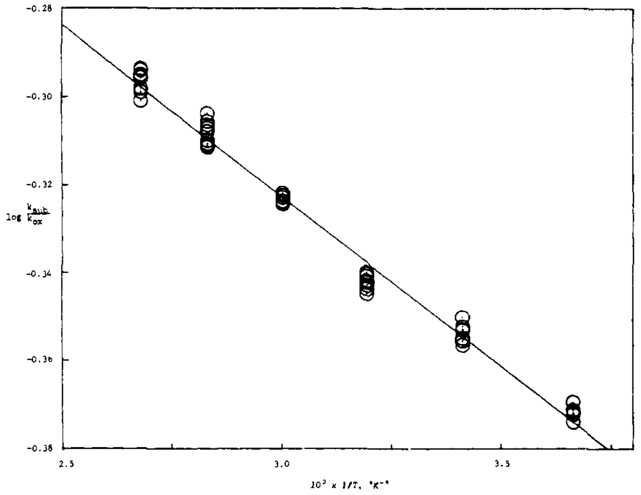


Figure 1. Temperature dependence of reaction 2, case 1 of Table I.

Alternatives 2 and 3 are unlikely ones in that *both* the oxidation and substitution activation energies in Table I respond to structural variation. In reaction 5 the rate of **2** formation should have little dependence on the nature of RS·, and the oxidation activation energy could be influenced by R· stability only if step (a) were rapidly reversible and followed by step (b) in a rate-determining role. Similarly, step (a) of reaction 6 would have to be reversible to account for the response of this scheme to changes in R·′. No experimental evidence is available concerning the reversibility of RS· additions to trivalent phosphorus. However, it seems unlikely that the two competing processes would occur one through an intermediate and one concertedly. In addition, it is known[9] that the second-order rate constant of RS· reaction with n-Bu_3P, $(EtO)_3P$, and Ph_3P is 10^8-10^9 at 60 °C. In these studies only oxidation was found. If reaction 6 obtains in the competitive oxidation/substitution reactions, then for case 5 the rate constant for step 6a would be at least 5×10^6. Assuming an A value of 10^9 for such a second-order process (likely a maximum in view of the above arguments about the stereospecificity of substitution) leads to an E_a of 3.5 kcal/mol. This requires that E_a for step 6a when R· is $PhCH_2$ be nearly zero and thus a near diffusion-controlled substitution process. Further the A_{sub}/A_{ox} ratio in comparing cases 2 and 5 responds just oppositely to what one expects for the replacement of a benzyl by a bulky *tert*-butyl.

For the above reasons we judge that alternative 4 most reasonably and economically depicts the mechanism of reaction of thiyl radicals with $RP(OEt)_2$. It can be estimated[3,4] from thermodynamic data that ΔH_r^0 (298 °C, g) for transfer of sulfur from t-BuS· to X_3P is favorable energetically by 28-29 kcal/mol. The energetics of this oxidation are depicted in Figure 2. It is less clear what the energetics of the substitution process should be. Most certainly the

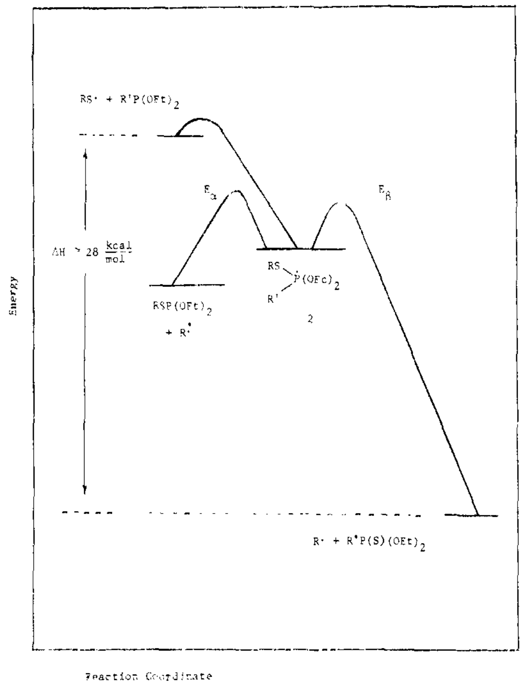


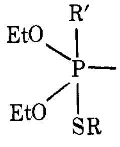
Figure 2. Energy diagram for reaction of RS· with $R'P(OEt)_2$.

strength of the P-S single bond formed is less than that for a P-O bond, but so far as we are aware no value is known. The energetics of P=O formation are favored over substitution in reactions of RO· with PX_3,[3,4] and we presume this to be true with RS·-PX_3 reactions. This also is shown in Figure 2. Only with reasonably stable R·', *t*-Bu, and $PhCH_2$· does substitution by RS· compete with oxidation, and with less stable R·', substitution may not be even thermodynamically a favorable process overall.

The observations of Table I then are readily explained within the context of Figure 2, and in Table I one may equate E_{sub} with E_α and E_{ox} with E_β. For the series of RS·, increasing R· stability is accompanied by a reduced E_a for β scission (E_β), the E_a for α scission (E_α) being presumed to remain essentially constant. We are unwilling to attach any particular importance to the small changes in A_α/A_β ($A_{\text{sub}}/A_{\text{ox}}$) observed in cases 1-4. Both scission processes have similar probabilities. The decrease in k_α seen in case 5 compared to cases 1 and 2 results from an increase in E_α (E_β for 1 and 4 presumed constant) which is somewhat offset by the increase in A_α/A_β. The cause of the latter effect is not apparent.

Another factor which could affect the ease of either α or β scission is the configurational requirement for such a process. ESR studies of nonphenyl-substituted phosphoranyl radicals[10] have shown large (600-1200 G) isotropic phosphorus hyperfine splittings which have usually been interpreted in terms of a trigonal bipyramidal structure with odd electron equatorial. A very recent report[11] has pointed out that a trigonal bipyramidal geometry with electron pair equatorial and the odd electron distributed over the axial ligands may more accurately describe such species. The geometric considerations which follow apply to either electronic description.

The usual assumption in pentacovalent phosphorus chemistry is that groups enter and leave the trigonal bipyramid only in the apical position.[12] In other work[13] we have obtained evidence that the alkoxy radical enters the $(RO)_4P$· intermediate in at least a stereoselective manner and ESR results which lead to a similar conclusion for H· have appeared.[14] If RS· attacks $R'P(OEt)_2$ in such a way that the RS· enters the apical position of the intermediate phosphoranyl radical, and the electropositive odd electron (or pair) fifth ligand is equatorial as indicated by ESR,[10] then both **4** and **5** could be formed initially. Presumably **4**



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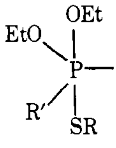

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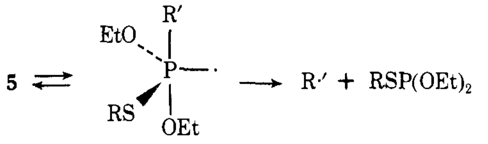
favors α scission, and the ratio **4**/**5** therefore would influence the k_α/k_β ratio. It is seen from Table I that a mechanism in which **4** gives only α scission and **5** only β scission cannot apply (unless the ratio **4**/**5** is influenced by RS and R' in a way that coincidentally parallels bond strengths). If **4** or **5** gives both α and β scission, then relative bond strengths would still contribute to α/β, and the role of initial **4**/**5** ratio would be hard to decipher. Clearly, *the ratio α/β is not solely controlled by the configurations of the initially formed intermediates and the statistics of their formation.*

A further consideration in these systems is the possibility that α scission is exclusively apical but that a permutation process[15] interconverts isomers in such a manner that R' can attain the apical position prior to α scission. (In other studies in RO· systems we have presented evidence that a pair-wise permutation (Musher[16] mode M_1) prior to β scission is not required.)[8,17] Such a possibility is shown in eq 8.



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Again the data of Table I do not rule out such a process having some role. However, if **5** → **6** does occur, then it must constitute a rapid equilibration step preceding a slower α scission[18] unless the effects of changing R' on $k_{5\to6}$ just happen to parallel R·' stability. *The ratio α/β does not depend on the rate of **5** → **6** alone.*

Experimental Section

Materials. The preparations of all reactant and product phosphorus compounds were described earlier.[3] Where necessary pure products for GLC sensitivity calibrations against internal standards were isolated by preparative GLC methods.

Kinetic Measurements. Pyrex reaction tubes were serum capped and flushed with nitrogen. Diethyl benzylphosphonite (~0.9 mmol) was transferred to the reaction tubes by means of a syringe and approximately 1.9 ml of nitrogen-flushed *o*-dichlorobenzene was added (molar concentration of phosphonite, ~0.3). The above solutions were equilibrated in a constant temperature bath for 30 min before 0.5 ml of mercaptan was added. After another 15 min, 0.005 mmol of azobisisobutyronitrile (AIBN) in 0.1 ml of *o*-dichlorobenzene was added, and the reaction tubes were heated for at least 10 decomposition half-lives of AIBN. Control reactions showed that the phosphonites were stable under these reaction conditions although the formation of some of the corresponding phosphonates (<3%) was noted after an extended period. Not more than 5% of the phosphonite underwent reaction with thiol before addition of AIBN. All reactions were shown to be inhibited strongly by addition of galvinoxyl. The above procedure was applied to α vs. β scission ratio measurements at 40, 60, 80, and 100 °C. Reactions at 0 and 20 °C were initiated by photolysis in Pyrex tubes using a Rayonet reactor with lamps giving peak power at 350 nm.

The above reaction mixtures were analyzed under temperature-programmed conditions on a dual-column F & M 810 instrument equipped with thermal conductivity detectors. Aluminum columns, 6 or 7 ft by 0.25 in., packed with 20% SE-30 on 60–80 Chromosorb W regular, were used. The percentages of α and β scission products were determined by analysis of the products toluene (octane), *O,O*-diethyl *S*-isopropyl, *tert*-butyl, and benzyl phosphorodithioates (tridecane), and diethyl benzyl phosphonothionate (tridecane). The internal standards used for each analysis are given above in parentheses. Sensitivity calibrations in each case were carefully determined using a series of solutions in *o*-dichlorobenzene in which the weight ratio of compound to standard was varied from 0.5 to 2.0. A series of these standards was run before each set of analyses and with each column. In the reactions of *i*-PrSH with diethyl *tert*-butyl- and benzylphosphonites the peak for product phosphorodithioate was sufficiently well separated from other products to allow reliable quantitative analysis. Essentially identical results ($E_\beta - E_\alpha$) were obtained in the *i*-PrSH/PhCH$_2$(OEt)$_2$ reaction with either toluene or the phosphorodithioate. For the other two reactions, the amount of α scission product was determined by analysis for toluene. In all cases the formation of the appropriate phosphorodithioate was demonstrated by VPC analysis on several different columns of product mixtures doped with authentic phosphorodithioate. Accountability of starting phosphite in terms of α and β cleavage products was usually 90–95% but in some cases was as high as 98% or as low as 88%. In addition 1–3% of the diethyl benzylphosphonate was present among the products along with the apparent thio analogue of a 1–2% impurity present in all preparations of the benzylphosphonite. Thus accountability is in fact very near quantitative.

At each temperature, 3 to 8 samples were run. Quantitative results were then calculated from peak areas obtained by use of a Disc integrator or a Vidar Autolab Model 6300 Digital Integrator. Plots of ln k_α/k_β vs. $1/T$ using all points were subjected to linear regressions analysis. By this means the error in slope at a 95% confidence level and a correlation coefficient were obtained for each plot (Table I).

References and Notes

(1) For part IV see: W. G. Bentrude, J.-J. L. Fu, and P. E. Rogers, *J. Am. Chem. Soc.*, **95**, 3625 (1973).

(2) This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(16) J. I. Musher, *J. Chem. Ed.*, **51**, 94 (1974); *J. Am. Chem. Soc.*, **94**, 5662 (1972).

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Chemiluminescence and Energy Transfer in Systems of Electrogenerated Aromatic Anions and Benzoyl Peroxide

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Abstract: Studies of energy transfer for mixed systems of every binary combination of anthracene, fluoranthene, 9,10-diphenylanthracene (9,10-DPA), rubrene, and coronene, in which anions are generated in the presence of benzoyl peroxide (BPO), are explained in terms of homogeneous generation of triplet molecules which subsequently form cations through quenching interaction with BPO, this step then being followed by mixed electron transfer reactions which lead to a predominant anion and cation (in terms of concentration) which may undergo anion–cation annihilation. For "energy-sufficient" systems this annihilation step can lead to the formation of excited singlet molecules, while, for "energy-deficient" systems, triplet–triplet annihilation is the essential path through which excited singlet molecules are formed. In the mixed system coronene–9,10-DPA, we find that unlike all mixed systems reported in the literature, the luminescence observed is from the species with the higher singlet level (i.e., 9,10-DPA) and is rationalized in line with a mechanism we propose. In the nine other binary mixtures we have examined the emitting species is also in line with the prediction we make from our mechanism. Ecl from unmixed systems of aromatic hydrocarbon as well as heteroaromatics have also been studied. We have found quite generally that one does not have to invoke the direct generation of singlet molecules, as a result of homogeneous electron transfer reaction between an electrogenerated anion and the bulk oxidant (e.g., either BPO or its decomposition product, benzoate radical (Ph-CO$_2$·)), in order to rationalize excited singlet formation.

I. Introduction

In a recent preliminary publication,[2a] hereinafter referred to as part I, we discussed chemiluminescence and its mechanism for systems consisting of electrogenerated aromatic hydrocarbon anions and benzoyl peroxide dissolved in aprotic solvents. Our mechanism differed from that of Siegel and Mark,[2b] who proposed for similar systems of electrogenerated aromatic hydrocarbon anions with either 1,2-dibromo-1,2-diphenylethane (DPEBr$_2$) or 9,10-dichloro-