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Laser Flash Photolysis and Time-Resolved ESR Study of Phosphinoyl Radical[†] Structure and Reactivity[§]

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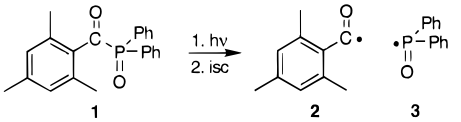
Abstract: The photochemistry of two phosphine oxides and the rate constants of reaction of their daughter radicals with several alkenes, halocarbons, and oxygen have been determined. Photolysis of (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide (**1**) and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (**4**) in each case affords a phosphinoyl and a benzoyl radical. The phosphinoyl radicals are readily detected by laser flash photolysis and exhibit absorption maxima at 325 and 450 nm for the diphenylphosphinoyl (**3**) and 2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphinoyl (**6**) radicals, respectively. The rate constants for reaction of the phosphinoyl radicals with alkyl halides, alkenes, and oxygen range from 10^4 to 10^9 M^{-1} s^{-1}. Radical **3** is 2−6 times more reactive than radical **6**. For example, **3** adds to methyl methacrylate with a rate constant of $(11 \pm 2) \times 10^7$ M^{-1} s^{-1} whereas **6** has an addition rate constant for the same reaction of $(2.3 \pm 0.3) \times 10^7$ M^{-1} s^{-1}. The rate constants for reaction with alkyl halides decrease with increasing C−X bond strength, while the rate constants for quenching by acrylates decrease with increasing methyl substitution on the β-carbon. The 2,6-dimethoxybenzoyl (**5**) and phosphinoyl (**6**) radicals derived from **4** are readily detected by time-resolved ESR (TR ESR); benzoyl radical **5** appears as a singlet and phosphinoyl radical **6** appears as a doublet of triplets (A(P) = 285 G, A(H) = 4.8 G). The CIDEP patterns of **5** and **6** indicate that the radicals are formed from α-cleavage of the triplet excited state of **4**. TR ESR has also proved useful in the direct detection of the polarized benzyl radicals formed from addition of phosphinoyl radicals **3** and **6** to styrene and 2,4,6-trimethoxystyrene. The lower reactivity of **6** compared to **3** is attributed to its more planar structure and lower degree of spin localization in a s-orbital on phosphorus.

Introduction

Acylphosphine oxides have attracted attention over the past few years,[1−16] partly due to their tremendous usefulness in industry[1,2] where their properties of visible absorption, high radical yield, and the colorless quality of their cured formulations[3] make them attractive photoinitiators. In addition, these species generate unique and highly reactive phosphorus centered radicals upon photolysis (eq 1).[4−6] The enhanced reactivity is attributed to the σ character of the phosphorus centered radical. Time-resolved ESR (TR ESR) experiments have shown that the diphenylphosphinoyl radical has a large ^{31}P hyperfine coupling constant (hfcc), $A(P) \approx 370$ G,[7−10] indicating that it is a σ radical with significant spin localization on phosphorus. The photophysics and photochemistry of acylphosphine oxides have been the subject of a number of studies and are now fairly well understood (see eq 1).[4−14]



1 **2** **3** (1)

A new class of related photoinitiators are the bis(acyl)-phosphine oxides[13,15,16] which incorporate the interesting potential to generate four radicals per precursor. Recent CIDNP studies have established α-cleavage from the triplet state as a reaction pathway.[13] However, little is known about the reactivity of the acylphosphinoyl radicals produced on their photolysis (eq 2).

Herein we report the first absolute bimolecular rate constants for the reaction of the benzoylphosphinoyl radical **6** with unsaturated compounds and halogen atom donor radical scavengers. We also report rate constants for reaction of the diphenylphosphinoyl radical **3** with the same scavengers. The results allow comparison of the reactivities of **3** and **6**. Finally, TR ESR experiments have been carried out which unequivocally

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[†] Also known as phosphonyl, phosphinyl, or phosphono radical.

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[§] Keywords: phosphinoyl radical, kinetics, laser flash photolysis, time-resolved ESR, photoinitiator.

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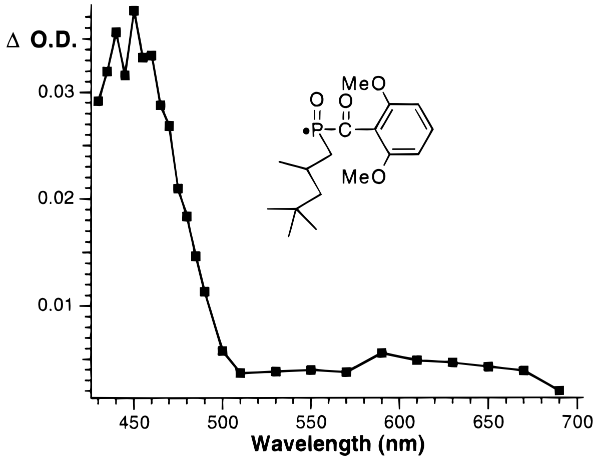
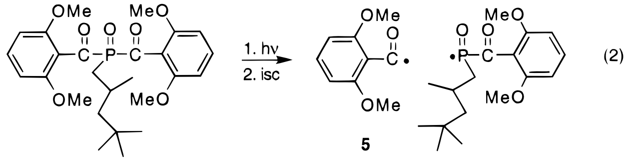


Figure 1. Transient absorption spectrum recorded 200−500 ns following 420 nm laser excitation of **4** in deoxygenated benzene solution at 23 °C.

identify the primary radicals **5** and **6** produced by photolysis of **4** and the adduct radicals formed by addition of **3** and **6** to styrenes.



4 **5** **6**

Results

Laser Flash Photolysis (LFP). LFP (355 nm excitation) of dilute hexane solutions of **1** affords a readily detectable transient absorption in the range 300−350 nm ($\lambda_{\max} = 325$ nm) along with a much weaker band in the range 400−450 nm.[6] Both absorptions decay on the microsecond time scale with mixed first- and second-order kinetics and are assigned to the diphenylphosphinoyl radical (**3**).[4−6] LFP (420 nm excitation) of dilute benzene solutions of **4** affords a transient absorption in the range 425−500 nm (see Figure 1) which decays on the microsecond time scale with mixed kinetics; this transient has been assigned (*vide infra*) to the 2,6-dimethoxybenzoyl-2,4,4-trimethylpentylphosphinoyl radical (**6**). Similar transient absorption spectra were recorded upon 308 and 355 nm excitation of **4**. The product of the extinction coefficient of **6** and the quantum yield for its formation, $\epsilon_{450}\phi$, was estimated to be ca. 2200 M^{-1} cm^{-1} in benzene solution by benzophenone actinometry.[17]

Addition of halocarbons, alkenes, or oxygen reduced the lifetimes **3** and **6** and resulted in clean pseudo-first-order decay kinetics. Bimolecular rate constants (k_q) for quenching of **3** and **6** were obtained from plots of the pseudo-first-order rate constants for decay of the transient absorption (k_{decay}) versus the concentration of added quencher according to eq 3, where k_o represents the first-order (estimated) rate constant for decay of the radicals in the absence of added quencher (see Figure 2). The bimolecular rate constants for quenching of phosphinoyl radicals **3** and **6** by alkenes and halocarbons are listed in Tables 1 and 2, respectively.

$$k_{\mathrm{decay}} = k_o + k_q[\mathrm{Q}] \qquad (3)$$

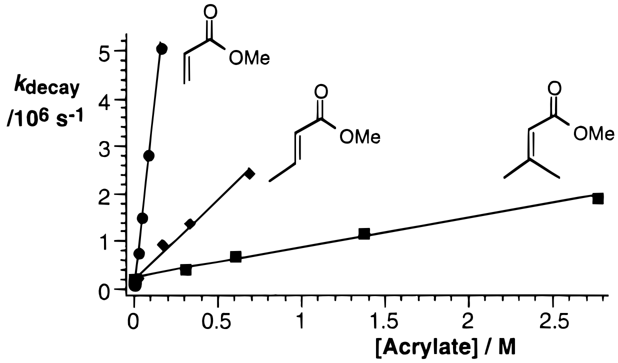
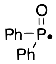
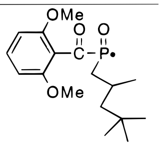


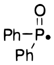
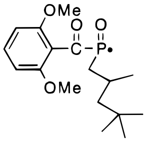
Figure 2. Plots of the pseudo-first-order decay rates (k_{decay}) of **3** versus acrylate concentration from LFP of deoxygenated solutions of **1** in hexane at 23 °C.

Table 1. Bimolecular Rate Constants for Quenching of Phosphinoyl Radicals **3** and **6** by a Series of Acrylates, Acrylamide, Maleic Anhydride, and Styrene at 23 ± 2 °C[a]

	k_q / 10^7 $M^{-1}s^{-1}$	
Quencher	 **3**	 **6**
$H_2C{=}CH(Me)CO_2Me$	11 ± 2	2.3 ± 0.3
$H_2C{=}CH_2CO_2Me$	3.3 ± 0.2	1.1 ± 0.1
$MeCH{=}CH_2CO_2Me$	0.34 ± 0.05	0.014 ± 0.002
$Me_2C{=}CH_2CO_2Me$	0.062 ± 0.007	0.008 ± 0.001
$H_2C{=}CH_2CO_2NH_2$	1.8 ± 0.2	4.7 ± 0.2
maleic anhydride	3.6 ± 0.2	1.0 ± 0.2
$PhCH{=}CH_2$	6.0 ± 0.2[b]	4.5 ± 0.2

[a] Errors reported as twice the standard deviation from least-squares analysis of the data according to eq 3. [b] Data from ref 4.

Table 2. Bimolecular Rate Constants for Quenching of Phosphinoyl Radicals **3** and **6** by a Series of Halocarbons and Oxygen at 23 ± 2 °C[a]

	k_q / 10^6 $M^{-1}s^{-1}$	
Halocarbon	 **3**	 **6**
Cl_3CBr	830 ± 50	400 ± 100
$CH_2{=}CHCH_2Br$	6.8 ± 0.9	3.1 ± 0.3
$PhCH_2Br$	5.9 ± 0.1	1.1 ± 0.1
Cl_3CCl	1.43 ± 0.04	0.33 ± 0.02
$(CH_3)_3CBr$	0.40 ± 0.05	0.2[b]
$(CH_3)_2CHBr$	0.06[b]	0.01[b]
O_2	350 ± 20	230 ± 10

[a] Errors reported as twice the standard deviation from least-squares analysis of the data according to eq 3. [b] Estimated from the lifetime of **3** or **6** in neat deoxygenated halocarbon solution.

Time-Resolved ESR. Laser flash photolysis (355 nm excitation) of dilute acetonitrile solutions of **4** affords the TR ESR spectrum shown in Figure 3 consisting of an overall E/A* polarization pattern. The spectrum features a doublet of triplets due to the phosphinoyl radical **6** (A(P) = 285 G and A(H) = 4.8 G) and a broad absorptive singlet near centerfield ($g \sim 2$)

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[17] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry,* 2nd ed.; Marcel Dekker: New York, 1993.

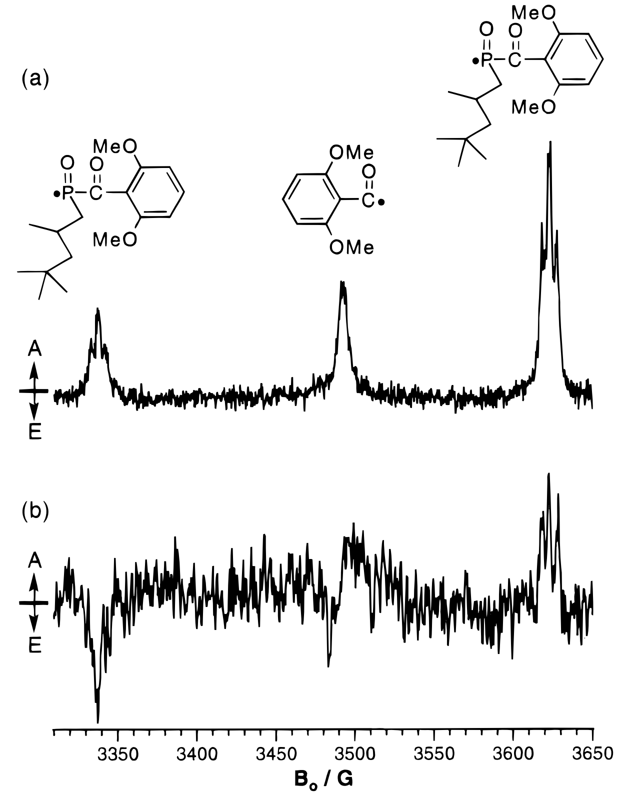
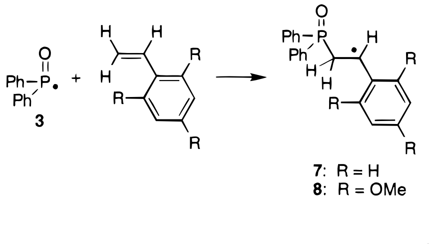


Figure 3. TR ESR spectra recorded (a) 50−250 ns and (b) 750−1050 ns following 355 nm laser excitation of **4** in deoxygenated acetonitrile solution at 23 °C.

assigned to benzoyl radical **5**. At early delay times (< 0.5 μs) all signals appear in absorption with the high field lines somewhat more intense (Figure 3a). Spectra recorded at longer delay times (> 0.5 μs) show an emissively polarized low field signal for **6**, while the high field line remains in absorption (Figure 3b). Similar spectra were obtained in benzene solution with 308 nm laser excitation.

The TR ESR spectrum recorded 50−250 ns following 308 nm laser excitation of **1** in benzene solution containing styrene is shown in Figure 4a. The main feature of the spectrum is the complex absorptive multiplet near centerfield assigned to benzyl radical **7** (eq 4). An absorptive doublet due to unreacted **3** (A(P) = 370 G) is present, while the singlet of **2** overlaps with **7** near centerfield. TR ESR spectra recorded at longer delay times show only polarized **7** with poorer signal-to-noise. The TR ESR spectrum recorded under similar conditions with 2,4,6-trimethoxystyrene as the radical trapping agent is shown in Figure 4b. Again, the unreacted radicals **2** and **3** are present in the spectrum recorded at early delay times (< 0.5 μs). The ^{31}P and ^{1}H hfcc's of **8** were determined by spectral reconstruction (see Figure 4c): A(P) = 48.70 ± 0.04 G, and $A(\mathrm{H}_\alpha) = A(2\mathrm{H}_\beta)$ = 14.12 ± 0.03 G.



3

7: R = H
8: R = OMe

(4)

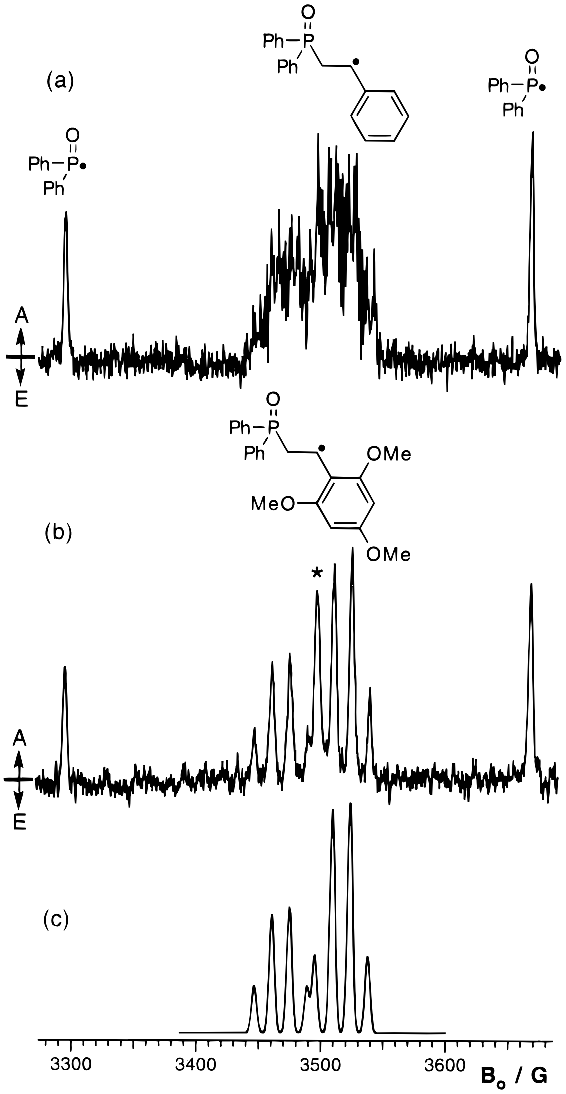


Figure 4. TR ESR spectra recorded 50−250 ns following 308 nm laser excitation of **1** in deoxygenated benzene solution at 23 °C in the presence of (a) 0.2 M styrene and (b) 0.06 M 2,4,6-trimethoxystyrene along with (c) the simulated TR ESR spectrum of radical **8** formed under these conditions. Radical **2** is designated with an asterisk in (b).

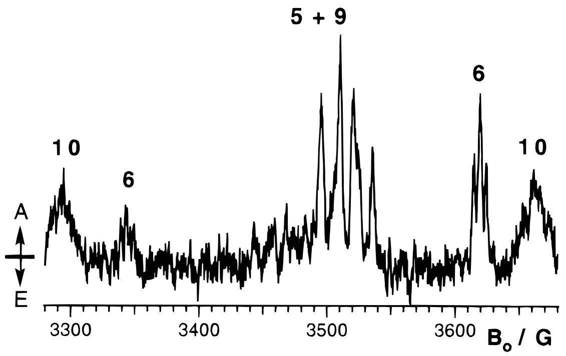
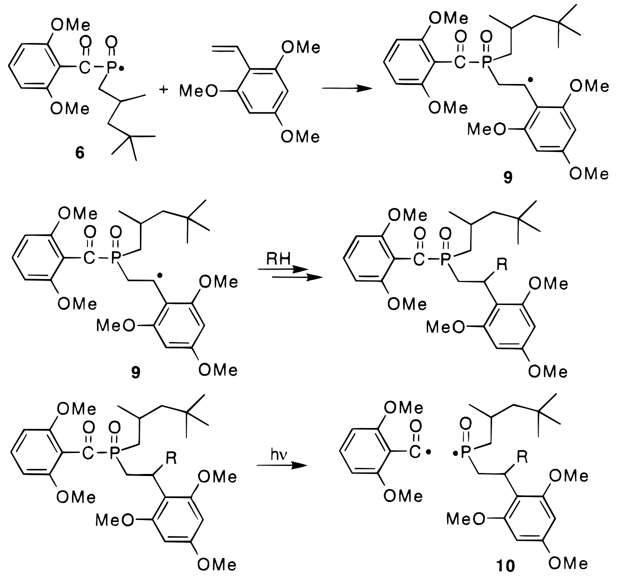


Figure 5. TR ESR spectrum recorded 150−450 ns following 355 nm laser excitation of **4** in deoxygenated benzene solution at 23 °C in the presence of 0.06 M 2,4,6-trimethoxystyrene.

The TR ESR spectrum recorded 150−450 ns following 355 nm laser excitation of a benzene solution of **4** containing 2,4,6-trimethoxystyrene is shown in Figure 5. The adduct radical (**9**) formed from addition of **6** to the styrene (see Scheme 1) appears as a multiplet near centerfield. The benzoyl radical (**5**) singlet overlaps the multiplet from **9**. The doublet of triplets from unreacted phosphinoyl radicals **6** (A(P) = 280 G, A(H) = 5 G) is present along with another doublet of multiplets (A(P) ≈ 370 G). The second phosphorus-containing radical is

Scheme 1



assigned to a secondary dialkylphosphinoyl radical **10**. Similar results were obtained using styrene as the radical scavenger.

Discussion

1. The Photochemistry of 4. The LFP and TR ESR studies of **4** are the first examples of *direct* detection of the radicals **5** and **6** formed upon photolysis. The CIDEP patterns in the TR ESR spectra indicate triplet cleavage of **4** (*vide infra*) in agreement with previous ^{31}P CIDNP studies[13] and similar to the reported photochemistry of **1**.[4,7–9]

Plausible candidates for the transient species detected at 450 nm following LFP of **4** (Figure 1) include the triplet excited state of **4**, benzoyl radical **5**, phosphinoyl radical **6**, a triplet biradical, or an enol.[18,19] The lifetime of the transient is shortened upon the addition of oxygen, alkyl halides, and acrylates without detectable decreases in the initial optical density at 450 nm. This indicates that the transient reacts rapidly with these reagents, but the yield of the transient is not affected by their presence. Clearly, high reactivity toward all three types of these reagents is unusual for triplet excited states, carbon-centered triplet biradicals, or enols, leaving radicals **5** and **6** as the most probable sources of the transient absorption. Benzoyl radicals are characterized by transient absorptions in the 350–390 nm range but are typically difficult to detect due to their low extinctions ($\epsilon \approx 150$ M^{-1} cm^{-1}).[20,21] However, the extinction coefficient for the 450 nm transient is estimated to be at least ten times larger ($\epsilon \geq 2200$ M^{-1} cm^{-1}). Thus, we assign the transient absorption centered at 450 nm to the benzoyl-substituted phosphinoyl radical **6**. This is further evidence that the main photochemical process is α-cleavage.

CIDEP (chemically induced dynamic electron polarization) effects are dependent upon the initial multiplicity of the radical pair (RP) under observation.[22–24] Thus, TR ESR serves as an important tool for the identification of the spin multiplicity (singlet or triplet) of RP precursor excited states. The three most common mechanisms for the production of electron polarization in homogeneous solution are (i) the triplet mechanism (TM), the T_0-S mechanism, and (iii) the T_--S mechanism. The TM contributes to the initial CIDEP detected at early times following the laser flash due to the short triplet lifetime and rapid spin–lattice equilibration of the triplet sublevel populations. The TM leads to net absorptive (A) or emissive (E) polarization of both radicals preserving the binomial ratio of the line intensities. The sign of the TM polarization (A or E) is determined by the relative populations of the three triplet sublevels of the precursor. The T_0-S mechanism yields a symmetric E/A pattern (low field half of the spectrum in emission, high field half in absorption) for an initial triplet RP and an A/E pattern for an initial singlet RP. The relatively rare T_--S mechanism has been observed for RPs in highly viscous solvents,[25–27] in biradicals with chemically linked radical centers,[28–34] and for radicals possessing extremely large hfcc such as phosphinoyl radicals.[35–37] The T_--S mechanism leads to hyperfine-dependent net polarization causing emissive polarization of the low-field lines for an initial triplet RP.

The CIDEP pattern arising from photolysis of **4** (Figure 3) is very similar to that reported for **1**[7–9] and indicates that radicals **5** and **6** are derived from the triplet excited state of **4**. At early times following laser excitation ($\tau < 0.5$ μs, Figure 3a) all the lines are absorptively polarized due to contributions from the TM. However, the low field lines of **6** are significantly less intense than the high field lines due to an E/A contribution from the T_0-S mechanism. At longer times following laser excitation ($\tau > 0.5$ μs, Figure 3b), the TR ESR spectrum of **6** appears as a nearly symmetric E/A doublet of triplets due to T_0-S polarization. The T_--S mechanism, if operative, plays only a very minor role due to the relatively small ^{31}P hffc in **6** (A(P) = 285 G) as compared to alkoxyphosphinoyl radicals (A(P) ≈ 700 G) for which the T_--S mechanism has been conclusively documented.[35–37]

2. The Structure and Reactivity of Phosphinoyl Radicals. The high reactivity of phosphinoyl radicals toward unsaturated compounds[4,5,11,12] is one of the main advantages of acylphosphine oxide photoinitiators. However, phosphinoyl radicals are also highly reactive toward oxygen,[4] halocarbons, and hydrogen atom donors,[6] potential side reactions that could limit their effectiveness as photoinitiators. Thus, we have employed LFP to determine absolute rate constants for reactions of **3** and **6**

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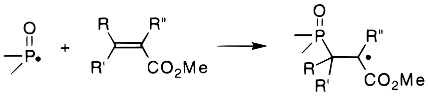
with a series of acrylates (eq 5; Table 1). We have also measured rate constants for reaction of **3** and **6** with several halocarbons (eq 6) and oxygen (Table 2). There are three important trends in the quenching rate constants. (i) The diphenylphosphinoyl radical (**3**) reacts more rapidly than the benzoyl-substituted phosphinoyl radical (**6**) with all the reagents except acrylamide. (ii) Increasing methyl substitution on the β-carbon of acrylates leads to decreasing rate constants. (iii) The rate constants for reaction with halocarbons correlate roughly with the C−X bond strength,[38] i.e., the rate constants decrease with increasing bond strength.



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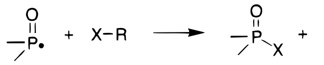
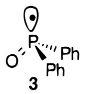


(6)

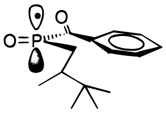
A qualitative steric effect on the addition rates of **3** to simple alkenes was noted in a TR ESR study.[39] Our rate constants, however, are the first systematic attempt to quantitate the steric effects on phosphinoyl radical additions to unsaturated compounds. Phosphinoyl radicals **3** and **6** react rapidly ($k_q \sim 10^5-10^8\ \mathrm{M^{-1}\ s^{-1}}$) with the unsaturated compounds listed in Table 1. Successive methyl substitution on the β-carbon of methyl acrylates leads to dramatic reductions in the quenching rate constants attributable to a steric effect on the addition reaction (eq 5). The rate constants for reaction of **3** with methyl acrylate and methyl methacrylate are in agreement with those determined previously by LFP.[4,5] The rate constants for quenching of **3** by methyl methacrylate determined by LFP, however, are ca. 4−7 times smaller than those determined by TR ESR ($1.6 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$).[11] The reason for the discrepancy was not previously addressed.[11] However, we note that TR ESR signal intensities are not always proportional to radical concentration due to the occurrence of one or more polarization mechanisms. Thus the rate constants determined by TR ESR may be less reliable than those determined by more direct techniques such as LFP.

Polar effects are important in radical reactions. The rates of additions of highly nucleophilic or electrophilic radicals to unsaturated compounds correlate with the alkene electron affinity (or ionization potential) and may be susceptible to solvent effects.[40,41] The rate constants for quenching of **3** and **6** by methyl methacrylate are at least 30 times greater than the rate constants for quenching by methyl crotonate despite their expected similar electron affinities. Therefore, we conclude that steric effects are much more significant than polar effects in the addition of phosphinoyl radicals to alkenes.

The TR ESR studies provide key information linking the *structures and reactivities* of **3** and **6**. The high reactivity[4,5] of phosphinoyl radicals has been attributed to their nonplanar structure as a result of a high degree of s-character and spin localization phosphorus.[42−45] The lower ^{31}P hfcc of **6** compared to **3** indicates that it possesses a lower degree of s-character and a more planar structure resulting in lower reactivity toward unsaturated compounds and atom donor scavengers. The higher reactivity of pyramidal phosphinoyl radicals has been attributed to the relative accessibility of the localized spin to the radical trapping reagents.[5]



3



6

The red shifted electronic absorption of **6** compared to **3** suggests a significant difference in their structures.[46] The absorption spectrum of **3** shows strong UV absorption (300−340 nm) and a weaker visible Rydberg absorption (380−440 nm) similar to that of all α-phenyl substituted carbon and other group 14 centered radicals.[47] The possibility that the absorption spectrum of **6** shown in Figure 1 is simply the low energy Rydberg transition is ruled out by the high extinction. Thus, the visible absorption of **6** may be a π,π^* type absorption involving the benzoyl group. Such a transition would require a somewhat planar geometry to allow conjugation between the phosphorus p-orbital and the benzoyl group. The more pyramidal structure of **3** may preclude extensive delocalization of spin into the two phenyl rings causing the electronic transition to be higher in energy.

Further confirmation for the rapid addition of phosphinoyl radicals to alkenes was obtained from the TR ESR studies. Substituted benzyl radicals **7** and **8**, formed by the addition of **3** to styrene and 2,4,6-trimethoxystyrene (Figure 4), respectively, were readily identified. The E/A* polarization of **3** is transferred to the adduct radicals indicating that under these conditions the addition reaction (eq 4) is rapid enough to compete effectively with spin−lattice relaxation of **3**. The ESR spectrum of **7** is a complex multiplet; however, removal of the 2 ortho H's and the para-H by substitution with methoxy substituents leads to dramatic simplification of the corresponding spectrum and allows facile spectral reconstruction and extraction of the hfcc's of **8** ($A(\mathrm{P}) = 48.70$ G, $A(\mathrm{H}\alpha) = A(2\mathrm{H}\beta) = 14.12$ G). Slightly higher hfcc's ($A(\mathrm{P}) \sim 60-85$ G, $A(\mathrm{H}) \sim 16-25$ G) have been measured for the additions of **3** to simple alkenes.[39] This implies less spin localization on phosphorus in **8** due to significant spin delocalization into the phenyl ring.

The TR ESR spectra recorded following photolysis of **4** in the presence of the two styrenes clearly demonstrate the ability of bis(acyl)phosphine oxides to yield *four* radicals upon irradiation. For example, the expected adduct benzyl radical **9** was readily detected along with unreacted **5** and **6** (see Figure 5); however, the key feature was the appearance of a second doublet of multiplets with a larger ^{31}P hfcc. These signals are tentatively assigned to a dialkylphosphinoyl radical (**10**) generated by secondary photolysis of the product formed by scavenging of **9** (see Scheme 1).

Summary and Conclusions

The photochemistry of bis(acyl)phosphine oxide **4** involves α-cleavage from a triplet excited state to afford radicals **5** and **6** which are readily detectable by LFP and TR ESR. Phosphinoyl radicals **3** and **6** react rapidly with halocarbons, alkenes, and oxygen ($k = 10^4-10^9\ \mathrm{M^{-1}\ s^{-1}}$). The rate constants for

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reaction with acrylates decrease with methyl substitution on the β-carbon due to a steric effect on addition. The rate constants for halogen atom abstraction correlate roughly inversely with the strength of the C−X bond. In general, **6** is 2−6 times less reactive than **3** toward the same reagents. The lower reactivity, red-shifted absorption, and smaller ^{31}P hfcc of **6** compared to **3** is consistent with the former having a more planar geometry.

We finish with a word of caution with respect to extrapolating rate constants for initiation of polymerization to the ranking of the efficiency of photoinitiators in practical systems. The rate constant of addition of initiator radicals to monomer is an important, but not the only factor determining the ranking of photoinitiators in practical systems. For example, the possibility of side reactions (e.g., hydrogen atom abstractions, reaction with oxygen, radical-radical termination, etc.) may contribute to the overall ranking of a photoinitiator, and indeed rankings may reverse in different formulations.

Experimental Section

Materials and Solvents. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**1**) (BASF) was recrystallized from diethyl ether. Bis-(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (**4**) (Ciba-Geigy) was separated from its coinitiator, 2-hydroxy-2-methyl-1-phenylpropanone, by silica gel chromatography. Methyl acrylate, methyl methacrylate, methyl crotonate, and 3,3-dimethylacrylate were obtained from Aldrich and passed through activated alumina before use. Maleic anhydride (Aldrich), acrylamide (Aldrich), and styrene (Aldrich Gold Label) were used as received. 2,4,6-Trimethoxystyrene was synthesized by Wittig reaction of 2,4,6-trimethoxybenzaldehyde (Aldrich) and methyltriphenylphosphonium bromide (Aldrich).[48] Bromotrichloromethane, allyl bromide, benzyl bromide, and 2-bromopropane were used as received from Aldrich. 2-Methyl-2-bromopropane (Aldrich) was distilled before use. Benzophenone (Aldrich) was recrystallized from ethanol before use. Hexane (Fisher HPLC), acetone (Alfa spectrophotometric grade), benzene (Aldrich spectrophotometric grade), carbon tetrachloride (Aldrich spectrophotometric grade), and acetonitrile (Aldrich spectrophotometric grade) were used as received.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses (355 nm, ca. 8 mJ/pulse, 6 ns) from a Quanta Ray DCR II Nd-YAG laser or a Lambda Physik FL 3002 dye laser (Stilbene 420, 420 nm, ca. 2 mJ/pulse, 20 ns) pumped by a Lambda Physik Lextra 50 excimer laser (308 nm, ca. 80 mJ/pulse, 20 ns) and a computer-controlled system which has been described elsewhere.[49] Solutions of **1** or **4** were prepared at concentrations such that the optical density was ca. 0.3 at the excitation wavelength employed. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells. Fresh solutions were prepared at each quencher concentration. The rate constants for reaction of **3** and **6** with halocarbons and the acrylates were determined in hexane and benzene solution, respectively. The rate constants for reaction of **3** and **6** with maleic anhydride and acrylamide were measured in acetone solution due to their low solubility in hydrocarbon solvents. The oxygen quenching experiments were carried out in acetonitrile solution.

Time-Resolved ESR Experiments and Simulations. Time-resolved ESR experiments employed the pulses from an MPB Technologies AQX-150 excimer laser (308 nm, ca. 80 mJ/pulse, 20 ns) or a Quanta Ray DCR II Nd-YAG laser (355 nm, ca. 50 mJ/pulse, 6 ns), a Bruker ER 100D X-band ESR spectrometer, and a PAR boxcar averager and signal processor (Models 4420 and 4402). Argon saturated solutions were flowed through a quartz flow cell (1 mm thick) in the rectangular cavity of the ESR spectrometer. Further details are described elsewhere.[50−52] The ESR spectrum of **8** was simulated by assuming a single ^{31}P and three equivalent ^{1}H hfcc's. Simulations using different hfcc's for the α and β protons gave slightly different values for the α and β hfcc's, but the uncertainty far exceeds the differences in the two hfcc's. A Gaussian lineshape was employed since inhomogeneous line broadening arises from the other small hyperfine couplings. Since there is a mixture of several different types of polarizations, the intensities of the eight lines for **8** were freely adjusted. Note, however, that the intensities of both quartets are very close to a binomial 1:3:3:1 ratio.

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