J. Am. Chem. Soc. **1998,** *120,* 11773−11777 11773

Phosphinoyl Radicals: Structure and Reactivity. A Laser Flash Photolysis and Time-Resolved ESR Investigation

Steffen Jockusch and Nicholas J. Turro*

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027

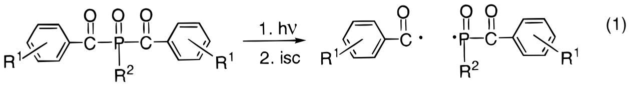
Received July 13, 1998

Abstract: The photochemistry of a series of bis(acyl)phosphine oxides and the rate constants of the reactions of their phosphorus radicals with *n*-butylacrylate, thiophenol, bromotrichloromethane, oxygen, and methyl viologen have been investigated by laser flash photolysis. The results were compared to a mono(acyl)phosphine oxide ((2,4,6-trimethylbenzoyl)diphenylphosphine oxide). The variation in reactivity of the different phosphorus radicals was correlated with the degree of radical localization and s-character on the phosphorus atom, as reflected by the ^{31}P hyperfine coupling constant, which was measured by time-resolved ESR. High ^{31}P hyperfine splitting is observed for high degree of spin localization in a σ-orbital. It was shown that typical radical reactions (addition to monomers and oxygen, and atom abstractions) correlate well with the ^{31}P hyperfine coupling. An inverse correlation was observed for electron-transfer reactions (reduction of methyl viologen), were a higher p-character of a localized orbital enhances the reaction.

Introduction

Bis(acyl)phosphine oxides have attracted attention in recent years because of their superior characteristics as initiators in photochemical curing processes involving free radical polymerization.[1−5] In particular, these photoinitiators are of interest, since their optical absorption extends well into the visible region allowing for the curing of pigmented formulations.[3,4] Moreover, the long-wavelength absorption, which is due to the aroyl−phosphinoyl chromophore, is destroyed during the photoreaction. The resulting bleaching allows a progressively deeper penetration of the incident light into the coating layer, which enables the curing of thick layers.[4]

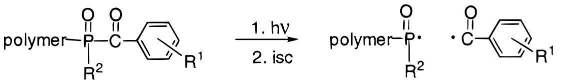
At the molecular level upon irradiation, bis(acyl)phosphine oxides undergo α-cleavage with high efficiency ($\Phi_\alpha \approx 0.6$)[6] to produce a benzoyl−phosphinoyl radical pair (see eq 1).[1−4] In a previous paper we showed that the α-cleavage typically occurs from a short-lived triplet state.[6] As a result of the very fast cleavage, competing bimolecular triplet quenching (e.g., reaction with oxygen), which would lower the yield of radicals, is generally not significant.



(1)

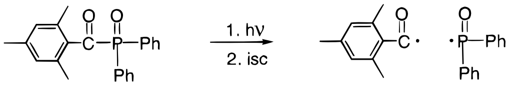
1 **2** **3**

Bis(acyl)phosphine oxides are highly effective photoinitiators since they can produce four radicals, each of which is an efficient initiator. For example, after addition of the (acyl)phosphinoyl radical (**3**) to a double bond, a mono(acyl)phosphine oxide unit is formed, located at one end of the growing polymer. This moiety can undergo a second α-cleavage reaction and form another benzoyl and phosphinoyl radical (see eq 2).[7]



(2)

Mono(acyl)phosphine oxides also undergo rapid α-cleavage from the triplet state to produce radicals (eq 3).[6,8−10] For more than a decade mono(acyl)phosphine oxides have been widely used as photoinitiators in free radical polymerization.[11−14] The photophysics and photochemistry of mono(acyl)phosphine oxides, which are similar to those of the bis(acyl)phosphine oxides, have been the subject of a number of studies and are now fairly well understood (see eq 3).[6,8−11,15−17]



(3)

1a **2a** **3a**

In this paper we describe a systematic study of the photochemistry of a series of bis(acyl)phosphine oxides (**1b**−**e**) and

---

(1) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.* **1996**, *118*, 6477.

(2) Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 7367.

(3) Leppard, D.; Dietliker, K.; Hug, G.; Kaeser, R.; Koehler, M.; Kolczak, U.; Misev, L.; Rist, G.; Rutsch, W. *Radtech '94 North Am.* **1994**, 693.

(4) Rutsch, W.; Dietliker, K.; Leppard, D.; Koehler, M.; Misev, L.; Kolczak, U. In *XXth International Conference in Organic Coatings Science and Technology*; Athens, 1994; p 467.

(5) Rutsch, W.; Dietliker, K.; Leppard, D.; Koehler, M.; Misev, L.; Kolczak, U.; Rist, G. *Prog. Org. Coat.* **1996**, *27*, 227.

(6) Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11495.

(7) Dietliker, K.; Leppard, D.; Jung, T.; Koehler, M.; Valet, A.; Kolczak, U.; Rzadek, P.; Rist, G. *RadTech Asia 97 Conf. Proc.* **1997**, 292.

(8) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141.

(9) Baxter, J. E.; Davidson, R. S.; Hageman, H. J.; McLauchlan, K. A.; Stevens, D. G. *J. Chem. Soc., Chem. Commun.* **1987**, 73.

(10) Koptyug, I. V.; Sluggett, G. W.; Landis, M. S.; Turro, N. J.; Bentrude, W. G. *J. Phys. Chem.* **1996**, *100*, 14581.

(11) Schnabel, W. In *Laser in Polymer Science and Technology: Applications*; Fouassier, J. P., Rabek, J. F., Eds.; CRC: 1991; Vol. 2, p 95.

(12) Jacobi, M.; Henne, A. *J. Radiat. Curing* **1983**, *10*, 16.

(13) Jacobi, M.; Henne, A. *Polym. Paint Colour J.* **1985**, *175*, 636.

(14) Dietliker, K. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J.-P., Rabek, J. F., Eds.; Elsevier Applied Science: New York, 1993; Vol. II, p 155.

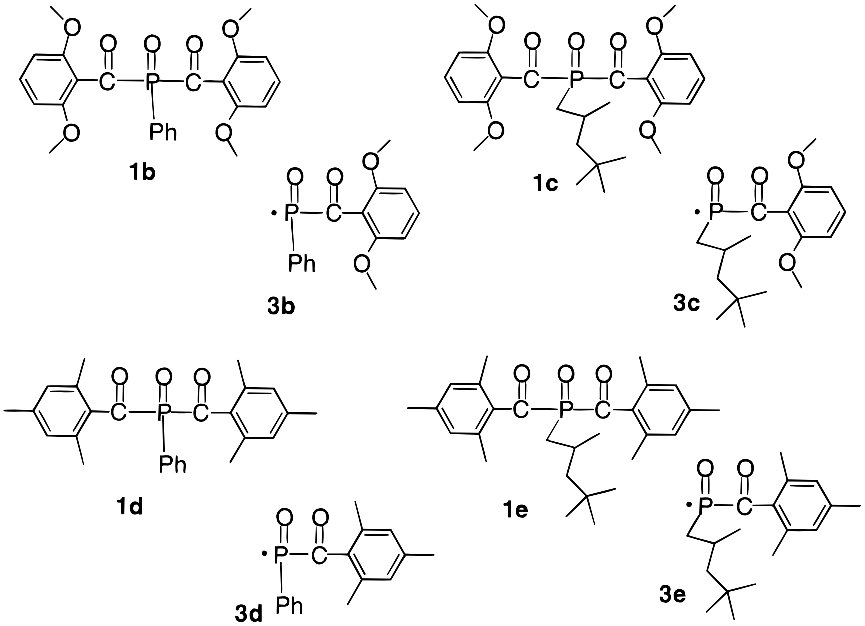
(15) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148.

(16) Turro, N. J.; Khudyakov, I. V. *Chem. Phys. Lett.* **1992**, *193*, 546.

(17) Kajiwara, A.; Konishi, Y.; Morishima, Y.; Schnabel, W.; Kuwata, K.; Kamanchi, M. *Macromolecules* **1993**, *26*, 1656.

10.1021/ja982463z CCC: $15.00

Scheme 1. Structure of the Bis(acyl)phosphine Oxides (**1b**−**e**) and Associated Phosphinoyl Radicals (**3b**−**e**)



reactions of their phosphinoyl radicals (**3b**−**e**) with a series of different substrates, including unsaturated monomers, oxygen, atom donators, and an electron acceptor. The results were compared with the diphenylphosphinoyl radical (**3a**) generated from a mono(acyl)phosphine oxide (**1a**). The structure of the bis(acyl)phosphine oxides and phosphinoyl radicals investigated are shown in Scheme 1.

Experimental Section

Materials and Solvents. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (**1a**) (BASF) was recrystallized from diethyl ether. Bis-(2,6-dimethoxybenzoyl)-phenylphosphine oxide (**1b**), bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide (**1c**), bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (**1d**), and bis(2,4,6-trimethylbenzoyl)-2,4,4-trimethylpentylphosphine oxide (**1e**) (Ciba Specialty Chemicals) were recrystallized from ethanol. Thiophenol (Aldrich Gold Label), 1-octanethiol (Aldrich), methyl viologen (Aldrich), bromotrichloromethane (Aldrich Gold Label), *n*-butylacrylate (Polysciences, Inc.), 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, 8 ns) from a Continuum Surelite I Nd:YAG laser and a computer-controlled system which has been described elsewhere.[18] Solutions of the phosphorus photoinitiators were prepared at concentrations such that the absorbance was ~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. Quenching rate constants with oxygen were measured as follows: Mixtures of oxygen and nitrogen of precisely known composition were prepared using a mass flow gas controller−mixer system in connection with an Oxygen Analyzer 2566 (Illinois Instruments). A gas splitter system diverted a small fraction of this flow through the sample in a fine stream of bubbles. Particular care was taken to keep the temperature of the sample cell constant at 24 °C during the bubbling by using a water circulator bath, to ensure a constant oxygen concentration in the sample solutions.

Time-Resolved ESR Experiments. TR-ESR experiments employed the pulses (355 nm, ca. 8 mJ/pulse, 8 ns) from a Continuum Surelite I Nd:YAG laser, a Bruker ER 100D X-band ESR spectrometer, and a PAR boxcar averager and signal processor (models 4420 and 4402). Argon-saturated solutions were flown through a quartz flow cell (~0.3 mm thick) in the rectangular cavity of the ESR spectrometer. Further details are described elsewhere.[19,20]

Results

Laser Flash Photolysis. Laser flash photolysis (355 nm excitation) of the phosphorus photoinitiators **1** affords readily detectable transient absorption spectra (see Figure 1) which decay on the microsecond time scale with mixed kinetics and have been assigned to the phosphinoyl radicals **3**.[6,8,15] The transient absorption spectra of **3a**[8,15] and **3c**[6] have been published earlier. All (acyl)phosphinoyl radicals (**3b**−**e**) show strong absorptions centered at about 450 nm. The radicals **3b** and **3d**, also show a transient absorption at about 330 nm. This additional absorption band is caused by the phenyl substituents on the phosphorus. In contrast, the radicals **3c** and **3e**, which possess alkyl substituents on the phosphorus, do not show the strong absorption at 330 nm. The benzoyl radicals **2a**−**e** do not interfere with the kinetics since they possess only a very weak absorption in the area where the phosphorus radicals absorb.[21,22] It was possible, however, to detect selectively by time-resolved IR[15] the benzoyl radicals **2a**, which were generated by laser flash photolysis of **1a**.

Time-Resolved ESR (TR-ESR). Laser flash photolysis (355 nm excitation) of argon-saturated acetonitrile solutions of the bis(acyl)phosphine oxides **1b**−**e** affords TR-ESR spectra shown in Figure 2. The spectra display absorptive doublets at low and high field relative to $g = 2$ due to the (acyl)phosphinoyl radicals **3** and broad absorptive lines near $g = 2$, assigned to benzoyl radicals **2**, whose small couplings are not resolved. In the case of the radicals **3c** and **3e**, the doublet of the phosphorus radical is split further into a doublet of triplets, caused by the

---

[18] McGarry, P. F.; Cheh, J.; Ruiz-Silva, B.; Hu, S.; Wang, J.; Nakanishi, K.; Turro, N. J. *J. Phys. Chem.* **1996**, *100*, 646.

[19] Koptyug, I. V.; Ghatlia, N. D.; Sluggett, G. W.; Turro, N. J.; Ganapathy, S.; Bentrude, W. G. *J. Am. Chem. Soc.* **1995**, *117*, 9486.

[20] Lipson, M.; McGarry, P. F.; Koptyug, I. V.; Staab, H. A.; Turro, N. J.; Doetschman, D. C. *J. Phys. Chem.* **1994**, *98*, 7504.

[21] Huggenberger, C.; Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1980**, *84*, 3467.

[22] Fischer, H.; Baer, R.; Hany, R.; Verhoolen, I.; Walbiner, M. *J. Chem. Soc. Perkin Trans. 2* **1990**, 787.

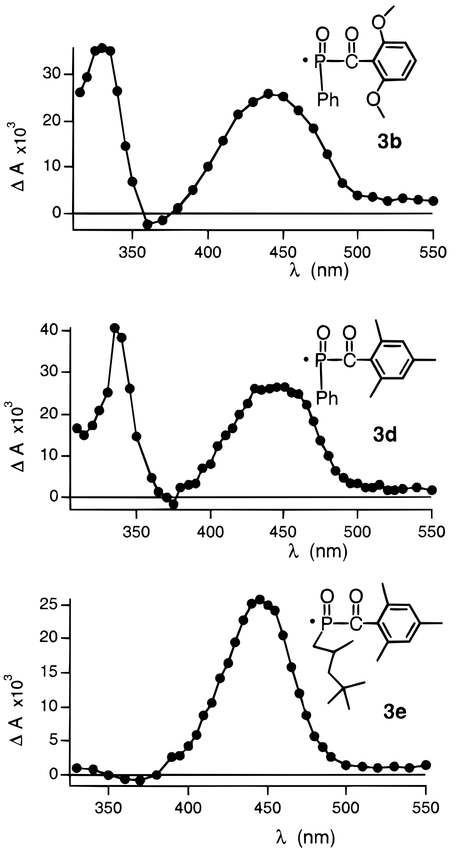
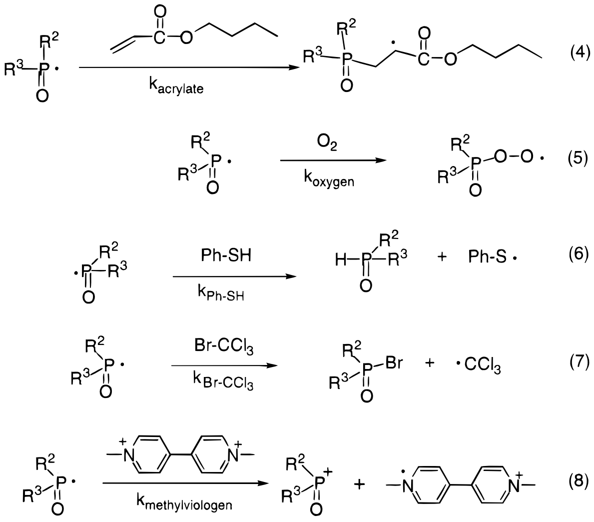


Figure 1. Transient optical absorption spectra recorded 200−700 ns following laser excitation (355 nm, 8 ns) of **1b**, **d**, **e** in argon-saturated acetonitrile solutions at 23 °C.

coupling of the two α-hydrogens of the alkyl chain (a_H = 4.6 G (**3c**) and a_H = 5.3 G (**3e**)).

There are some notable differences between the polarized spectra shown in Figure 2. In the case of **1d** and **1e**, all of the lines are clearly absorptive, due to the triplet mechanism polarization. The small distortion is due to the emission/absorption radical pair mechanism polarization from the geminate radical pair, which dominates at later observation times. This is expected to be observed due to the large phosphorus hyperfine coupling.[23] Conversely, the spectra of **1b** and **1c**, shown in Figure 2 are more dominated by a radical pair mechanism. The spectra in Figure 2 were recorded 300 to 400 ns after the laser flash. At an earlier time scale, the polarization by the triplet mechanism was clearly observed, which demonstrates that the radicals were formed from the triplet state of **1** by α-cleavage. Interestingly, the polarization by the triplet mechanism is much weaker for the methoxy substituted bis(acyl)phosphine oxides **1b** and **1c** compared to that for the methyl substituted compounds **1d** and **1e**. This effect was also observed by Baxter et al. for (2,6-dimethoxybenzoyl)- and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.[9]

Reactions of Phosphinoyl Radicals. The high reactivity (as measured by the second-order rate constant) of phosphinoyl radicals toward unsaturated compounds is one of the most desirable properties of phosphine oxide photoinitiators for radical polymerization.[2,4,5,11,17] Table 1 summarizes the bimolecular rate constants (k_{acrylate}) for the reaction of phosphinoyl radicals **3a**−**e** with *n*-butylacrylate (eq 4), obtained by laser flash photolysis.



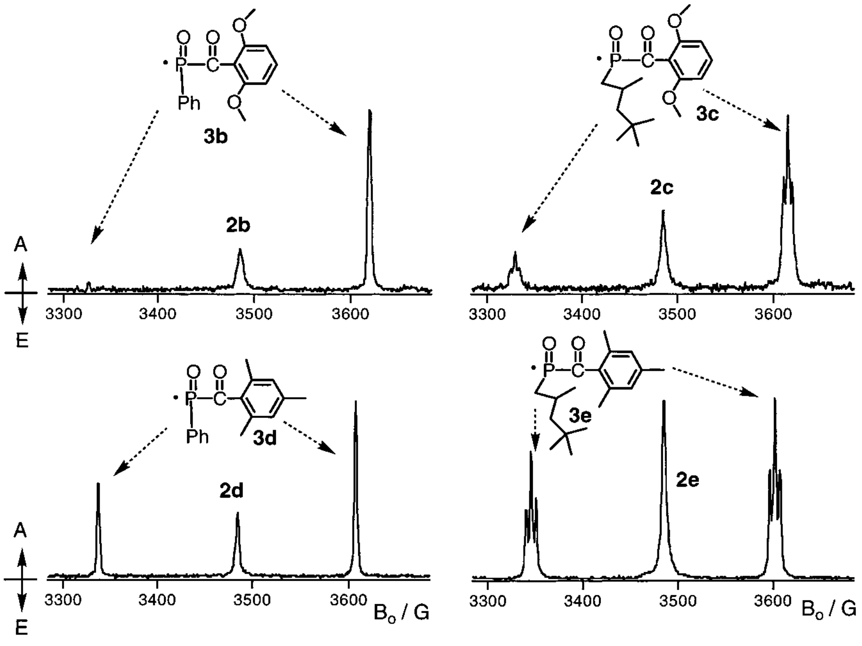


Figure 2. TR-ESR spectra recorded 300−400 ns following laser excitation (355 nm, 8 ns) of **1b**−**e** in argon-saturated acetonitrile solutions at 23 °C.

Table 1. ^{31}P Hyperfine Coupling and Bimolecular Rate Constants for Quenching of Phosphinoyl Radicals **3** by *n*-Butylacrylate, Thiophenol, Bromotrichloromethane, Oxygen, and Methyl Viologen in Acetonitrile Solution

	3a	**3b**	**3c**	**3d**	**3e**
^{31}P hyperfine coupling	369 G	294 G	286 G	270 G	255 G
$k_{\text{n-butylacrylate}}$ (M^{-1} s^{-1})	2.8×10^7	2.4×10^7	1.5×10^7	1.1×10^7	0.4×10^7
k_{PhSH} (M^{-1} s^{-1})	42×10^5	6.3×10^5		2.3×10^5	
k_{BrCCl_3} (M^{-1} s^{-1})	6.9×10^8	2.2×10^8	2.4×10^8	0.9×10^8	0.8×10^8
k_{oxygen} (M^{-1} s^{-1})	4.2×10^9	3.0×10^9	2.6×10^9	2.7×10^9	2.5×10^9
$k_{\text{methyl viologen}}$ (M^{-1} s^{-1})	$<10^6$	1.2×10^9	1.5×10^9	2.8×10^9	2.6×10^9

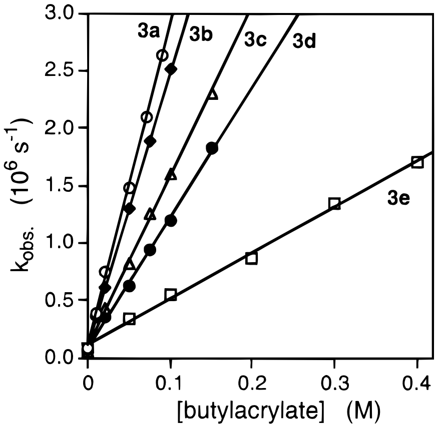


Figure 3. Pseudo-first-order decay rate constant (k_{obs}) of the radicals **3a**−**e** versus *n*-butylacrylate concentration; laser flash photolysis of argon-saturated acetonitrile solutions of **1a**−**e** ($\lambda_{\text{ex}} = 355$ nm) in the presence of different *n*-butylacrylate concentrations at 23 °C.

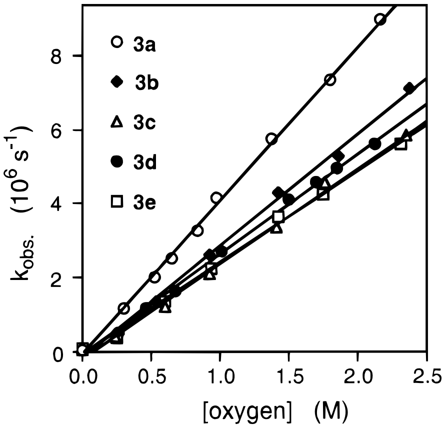


Figure 4. Pseudo-first-order decay rate constant (k_{obs}) of the radicals **3a**−**e** versus oxygen concentration; laser flash photolysis of acetonitrile solutions of **1a**−**e** ($\lambda_{\text{ex}} = 355$ nm) in the presence of different oxygen concentrations at 24 °C.

The pseudo-first-order treatment of the decay of the absorption of **3a**−**e** according to eq 9 yields the second-order rate

$$k_{\text{obs}} = k_0 + k_{\text{acrylate}}[\text{acrylate}] \qquad (9)$$

constants k_{acrylate}, where k_{obs} represents the observed pseudo-first-order rate constant at various concentrations of *n*-butylacrylate, and k_0 the first-order (estimated) rate constant for the decay of the radical in the absence of added quencher (see Figure 3).

An important common side reaction, which reduces the initiation efficiency of polymerization, is the addition of oxygen to the radicals **3a**−**e** (eq 5). The rate constants k_{oxygen} were obtained by pseudo-first-order treatment (see above, and Figure 4) and variation of the oxygen concentration by saturation of the acetonitrile solutions with oxygen nitrogen mixtures using 9.1 mM as saturation concentration at 1 atm partial pressure oxygen at 24 °C.[24] As expected for such organic radicals, all rate constants k_{oxygen} range from 2 to 3 × 10^9 M^{-1} s^{-1} (see Table 1).

Other common reactions which lower the initiation efficiency of polymerization are atom abstractions from materials that are required to be present in a photocuring formulation. To distinguish the reactivity between the different phosphinoyl radicals **3a**−**e** toward atom abstraction, we chose model compounds with high atom donor tendency. Thiophenol is often employed as standard hydrogen donor in laser flash photolysis, since the thiophenoxyl radical resulting from hydrogen atom abstraction can be directly detected by its absorption at around 450 nm (eq 6).[25] Laser flash photolysis of **1** yielded the radicals **3** whose lifetime was reduced upon addition of thiophenol. Synchronously with the decay of **3**, the growth of the thiophenoxyl radical at 450 nm was observed. Since the absorption of thiophenoxyl radicals interferes with the decay kinetic of **3b**−**e** at 400 to 480 nm, rate constants were only determined for the radicals **3a**, **b**, and **d**, which possess strong transient absorptions at 335 nm where the thiophenoxyl radical does not interfere. The results are summarized in Table 1. The radical of 1-octanethiol does not show an optical absorption in the visible range. Therefore, we attempted to employ 1-octanethiol as hydrogen donor to study the differences in reactivity of the phosphinoyl radicals **3a**−**e**. In the case of the diphenylphosphinoyl radical (**3a**), the rate constant for hydrogen abstraction was 7.1 × 10^5 M^{-1} s^{-1}, nearly 1 order of magnitude smaller than for the analogous reaction using thiophenol. For the other phosphorus radicals **3b**−**e**, no change in the decay kinetics of the radicals was observed with increasing 1-octanethiol concentrations. From the quencher concentrations utilized and considering the accuracy of decay kinetic measurements, we conclude that if hydrogen abstraction were to occur, the rate constant should be <10^5 M^{-1} s^{-1}.

For halogen atom abstraction reactions, bromotrichloromethane was selected as substrate. Earlier studies showed that bromotrichloromethane is an efficient bromine donor compared to other donors.[2] The rate constants k_{BrCCl_3} of reaction 7 are listed in Table 1.

Besides addition reactions (eqs 4 and 5) and atom abstractions (eqs 6 and 7), electron-transfer reactions of phosphorus radicals are also possible. As a model for electron-transfer, methyl viologen, which possesses a high reduction potential ($E_{1/2} = -0.46$ eV in acetonitrile, SCE)[26] and is often used as a standard electron acceptor, was selected. The reduced form of methyl viologen, the paraquat radical cation (eq 8), possesses a strong optical absorption with a maximum at 608 nm.[27] Laser flash

---

(23) Buckley, C. D.; McLauchlan, K. A. *Mol. Phys.* **1985**, *54*, 1.

(24) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

(25) Bonifacic, M.; Weiss, J.; Chaudhri, S. A.; Asmus, K.-D. *J. Phys. Chem.* **1985**, *89*, 3910.

(26) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Mever, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1979**, *101*, 4815.

photolysis of **1b**−**e** yielded the radicals **3b**−**e**, whose lifetime was reduced upon addition of methyl viologen. Simultaneous with the decay of **3b**−**e**, the growth of the paraquat cation radical was observed at 600 nm. The rate constants for reaction 8, listed in Table 1, were obtained by pseudo-first-order treatment of the decay of the radicals **3b**−**e** (see above) by variation of the methyl viologen concentration. In the case of laser photolysis of **1a** in the presence of high methyl viologen concentration (0.6 mM), no change in the lifetime of **3a** and no production of paraquat cation radicals were observed. Estimating from the quencher concentrations used in these studies and the accuracy of decay kinetic measurements, if reaction 8 were to occur, the rate constant should be $< 10^6$ M^{-1} s^{-1}.

Discussion

Phosphinoyl radicals (**3**) possess a high reactivity toward unsaturated substrates. The radical **3a**, generated from the mono(acyl)phosphine oxide **1a**, shows the highest rate constant to *n*-butylacrylate, compared to the radicals **3b**−**e**, generated from the bis(acyl)phosphine oxides **1b**−**e** (see Table 1). But this does not necessarily imply or guarantee, that mono(acyl)-phosphine oxides will be better photoinitiators than bis(acyl)-phosphine oxides. In fact, the bis(acyl)phosphine oxides **1c** and **d** perform significantly better than **1a** in most industrially relevant applications.[7,28,29] This better performance of **1c** and **d** could be caused by the bathochromic shifted optical absorption of the bis(acyl)phosphine oxides compared to the mono(acyl)-phosphine oxide among other possible factors. In addition, the role of the radicals produced by initiator photolysis in the polymerization process is complex and involves also chain termination.

The rate constants of the different phosphorus radicals vary almost 1 order of magnitude toward a given substrate (see Table 1). Radical reactivity is often correlated with radical stability.[30,31] The latter in turn correlates inversely with localization of the radical or s-character of a localized orbital. However, since s-character and orbitals are theoretical concepts, an experimental parameter, which is expected to correlate with s-character, is required. Such a parameter is the ^{31}P hyperfine coupling, which correlates well with s-character in localized orbitals. The ^{31}P hyperfine coupling decreases in the order of **3a** > **3b** > **3c** > **3d** > **3e**. Similarly, the rate constants for acrylate addition (eq 4) decrease in the same order (see Table 1 and Figure 5). Thus, there is a strict correlation between reactivity (k) and ^{31}P hyperfine coupling. The high reactivity of the phosphinoyl radical **3a** has been attributed to a nonplanar structure which results in a high degree of s-character and spin localization on the phosphorus.[2,32−34] A decrease of s-character and increase of p-character (more planar structure and spin delocalization) causes a decrease of the ^{31}P hyperfine coupling and reactivity. Thus, for typical radical reactions, i.e., addition to olefinic monomers (eq 4), atom abstractions (eqs 6 and 7), and addition of oxygen (eq 5), a high degree of spin localization on the phosphorus would result in both high rate constants and a high value of ^{31}P hyperfine coupling. This is the case for the radicals **3a** and **3b**. For all reactions (eqs 4−7) the rate constants correlate well with the ^{31}P hyperfine coupling. Minor irregularities can be caused by small errors in the determination of the rate constants by laser flash photolysis.

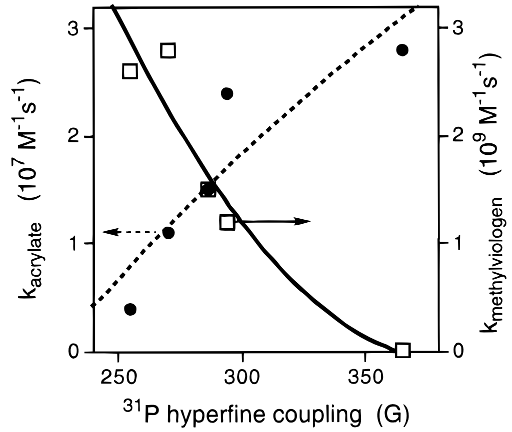


Figure 5. Reaction rate constants of phosphorus radicals with *n*-butylacrylate and methyl viologen versus ^{31}P hyperfine coupling.

In contrast to above situation, electron delocalization and enhanced p-character should improve the reactivity in electron-transfer reactions. Indeed, oxidation of phosphorus radicals **3b**−**e** by methyl viologen (eq 8) correlates inversely with the ^{31}P hyperfine coupling (see Table 1 and Figure 5). High rate constants were observed for radicals with low ^{31}P hyperfine coupling (higher degree of spin delocalization, more p-character). Under our experimental conditions, no reaction of radical **3a** with methyl viologen was observed, suggesting that the carbonyl α to the phosphorus in radicals **3b**−**e** is essential for the reaction.

Summary and Conclusion

Phosphinoyl radicals (**3**) generated by photolysis of acyl and bis(acyl)phosphine oxides, possess high rate constants of addition to acrylates. This high reactivity is the basis of their effectiveness as photoinitiators for free radical polymerization. The differences in the rate constants can be explained with different degrees of radical localization and s-character on the phosphorus atom. A physical parameter, which reflects this degree of radical localization, is the ^{31}P hyperfine coupling. It was shown that typical radical reactions (addition to monomers and oxygen, and atom abstractions) correlate well with the ^{31}P hyperfine coupling. An inverse correlation was observed for electron-transfer reactions (reduction of methyl viologen).

Acknowledgment. We thank the National Science Foundation and Ciba Specialty Chemicals for their generous support of this research and Dr. P. Lechtken (BASF, Germany) and Dr. M. Kunz (Ciba Specialty Chemicals) for samples of **1a** and **1b**−**e**, respectively. The authors thank Dr. M. Kunz (Ciba Specialty Chemicals) for comments on the manuscript.

JA982463Z

---

(27) Bockman, T. M.; Kochi, J. K. *J. Org. Chem.* **1990**, *55*, 4127.

(28) Jung, T.; Koehler, M. *J. Oberflaechentech.* **1998**, *38*, 26.

(29) Rees, M. T. L.; Russell, G. T.; Zammit, M. D.; Davis, T. P. *Macromolecules* **1998**, *31*, 1763.

(30) Kochi, J. K., Ed. *Free Radicals*; John Wiley & Sons: New York, 1973.

(31) Hay, J. M. *Reactive Free Radicals;* Academic Press: London, New York, 1974.

(32) Geoffroy, M.; Lucken, E. A. C. *Mol. Phys.* **1971**, *22*, 257.

(33) Kerr, C. M. L.; Webster, K.; Williams, F. *J. Phys. Chem.* **1975**, *79*, 2650.

(34) Bentrude, W. G. In *Free Radicals*; Kochi, J. K., Ed.; John Wiley & Sons: New York, 1973; Vol. 2; p 600.