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Structural Effects on the Reactivity of Substituted Arylphosphines as Potential Oxygen-Scavenging Additives for Future Jet Fuels

Bruce Beaver* and Dan Rawlings

Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, PA 15282

P. Neta, Z. B. Alfassi,† and T. N. Das‡

Physical and Chemical Properties Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

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ABSTRACT

Efforts to develop oxygen-scavenging additives for future jet fuels (JP-900) are presented. Results from radiolytic experiments are used to develop structure-reactivity relationships for electron-transfer-initiated oxygenation (ETIO) of variously substituted arylphosphines. © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9:133–138, 1998

INTRODUCTION

To achieve the optimal performance capabilities demanded by the next generation of jet engines, significant improvement in jet fuel thermal stability is necessary. This objective has led the U.S. Air Force to initiate a JP-900 effort with the goal of producing a fuel thermally stable to 480°C (900°F) [1]. This objective is very challenging since it is a giant step beyond the current fuel precombustion temperature limit of 163°C (325°F) or the proposed temperature limit of JP-8 + 100 of 425°F [2]. In addition, a JP-900 fuel will have to achieve both oxidative and pyrolytic stability, properties that seem to be inversely related [3,4]. We define oxidative instability as deposit formation on engine surfaces shortly after the fuel reacts with its dissolved oxygen usually between 180°C and 220°C. We define pyrolytic instability as anaerobic deposit formation on engine surfaces usually after the fuel reaches temperatures near 480°C.

An economical way to provide JP-900 thermal oxidative stability specifications can be achieved by adding judiciously designed oxygen-scavenging additives to conventional jet fuels (JP-8). Our strategy is to develop additives that are thermally promoted to react with the oxygen dissolved in fuels and concomitantly produce innocuous products. These reactions must occur prior to the O_2-promoted degradation of the fuel. We have previously shown that the presence of triphenylphosphine in a JP-8 increases its thermal oxidative stability by 50% [5]. The factors involved in the design of such oxygen-scavenging additives have already been discussed at length [6].

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

†Permanent address: Ben-Gurion University, Beer Sheva, Israel.

‡On leave from: Bhabha Atomic Research Center, Trombay, India.

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Briefly, molecules that can be induced to undergo electron-transfer-initiated oxygenation (ETIO) should be amenable to oxygen-scavenging functions. We define the most simple case of ETIO as an oxygenation reaction in which the rate-limiting step involves an electron transfer from the substrate to molecular oxygen (or an activated form of oxygen). We have postulated that electron-rich molecules that have low oxidation potentials, such as various triarylphosphines [7], can be induced to undergo ETIO reactions [8]. Scheme 1 depicts our recent ETIO mechanistic proposal for the reaction of aryl phosphines at 150°C in oxygen-saturated dodecane in the presence of a phenolic antioxidant (BHT) [5].

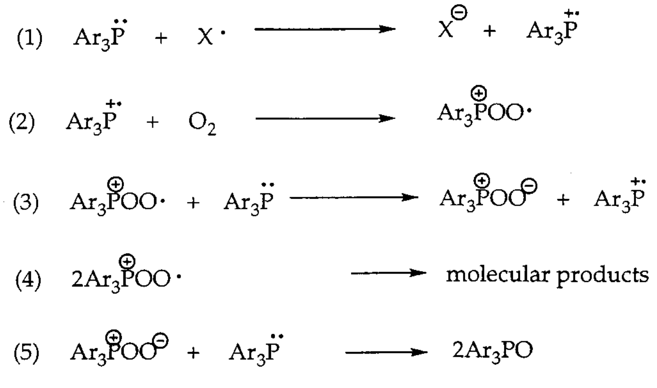
In Scheme 1, thermal initiation occurs, as in step **1** with an unspecified oxidant, via single-electron transfer (SET) to produce a reduced oxidant and a phosphine radical cation. Presumably, the unspecified oxidant is derived from dodecane hydroperoxides that form (low concentration) even in the presence of BHT [5]. Step **2** is the reaction of the phosphine radical cation with O_2 to yield an oxygenated phosphinium radical cation. Although we are unaware of any literature detailing the existence and nature of this species, it is anticipated that such a species would be a potent one-electron oxidant [9]. Thus, SET occurs between this oxidant and another phosphine to set up chain propagation in step **3.** Alternatively, oxygen atom transfer can occur as in step **3a,** followed by SET in step **3b.**

3a. $\mathrm{Ar_3\overset{+}{P}OO\cdot} + \mathrm{Ar_3P} \rightarrow \mathrm{Ar_3\overset{+}{P}O\cdot} + \mathrm{Ar_3PO}$

3b. $\mathrm{Ar_3\overset{+}{P}O\cdot} + \mathrm{Ar_3P} \rightarrow \mathrm{Ar_3PO} + \mathrm{Ar_3\overset{+\cdot}{P}}$

Steps **4** and **5** represent termination steps, of which there are other possibilities.

Our current approach to the rational design of potential oxygen scavenger molecules relies heavily upon various radiolytic methods. These techniques allow us to make several important measurements necessary for developing structure-reactivity relationships. Based upon our current understanding of the mechanism of aryl phosphine oxygenation presented in Scheme 1, maximizing the rates of the propagation steps (steps **2** and **3**) should prove beneficial. In this manner, the kinetic chain length (KCL) should increase and thus provide more oxygen removal per initiation event. For radical chain reactions, gamma radiolysis techniques can be used to determine the magnitude of the KCL under various experimental conditions [10]. In addition, spectrophotometric pulse radiolysis provides a method for detecting the presence of reactive species, such as phosphine radical cations. We have previously used this technique to verify that O_2 can react with certain phosphine radical cations, step **2** in Scheme 1 [10]. Finally, we believe that spectrophotometric pulse radiolysis provides a method for estimating how the magnitude of k_3 will be affected by phosphine structure.



SCHEME 1

RESULTS AND DISCUSSION

The NIST Febetron [11] based pulse radiolysis apparatus was used to pulse an air-saturated CH_2Cl_2 solution of 1 mmol L^{-1} Ph_3P resulting in the formation of absorbance in the UV and visible range. The spectrum exhibits a strong peak at 330 nm and a substantial shoulder at 400–500 nm and has been ascribed to the radical cation, $Ph_3P\cdot^+$ [10]. This absorbance was formed in two steps: a substantial fraction was formed within <0.1 μs after the pulse, and the rest was formed by a gradual build-up over about 10 μs. This last step has been ascribed to the slower oxidation of Ph_3P by solvent-derived peroxyl radicals as shown:

$$\mathrm{Ph_3P + CHCl_2OO\cdot \rightarrow Ph_3P^{+\cdot} + CHCl_2OO^-} \qquad (6)$$

$$\mathrm{Ph_3P + CH_2ClOO\cdot \rightarrow Ph_3\overset{+\cdot}{P} + CH_2ClOO^-} \qquad (7)$$

From the dependence of the $Ph_3P\cdot^+$ absorbance, growth as a function of $[Ph_3P]$ a rate constant (k_{set}) is obtained. This rate constant is attributed to Reactions 3 and 4. This measurement is important because determining k_{set} for different phosphines will allow us to indirectly examine how k_3 changes with phosphine structure. This assumption is based upon a rough similarity in structure for an oxygenated phosphinium radical cation and a chlorinated peroxyl radical. Owing to inductive effects, both peroxyl radicals are very electron deficient and consequently undergo rapid SET with electron-rich molecules [9].

From the decay kinetics of $Ph_3P\cdot^+$ in deoxygenated, air-saturated, and oxygen-saturated CH_2Cl_2 solutions, the rate constant for the reaction of $Ph_3P\cdot^+$ with O_2 was determined to be $(7.3 \pm 1.4) \times 10^6$ L mol^{-1} s^{-1}. This k_2 value is about 100–400 times slower than those for the reactions of carbon-centered radicals with O_2 [12].

Similar experiments have been performed with several other phosphines to develop an understanding of the relationship between structure and oxidative reactivity. The optical absorption spectra of the triarylphosphine radical cations were found to be similar to that of $Ph_3P\cdot^+$, with small variations in peak position and molar absorptivity. Even the spectrum of the methyldiphenylphosphine radical cation (Figure 1) is quite similar to that of $Ph_3P\cdot^+$. The latter has λ_{max} at 330 nm [10], and the former has a slightly narrower peak with λ_{max} possibly 2–3 nm lower. This finding is rationalized by the pyramidal geometry of the phosphine radical cations, in which most of the unpaired spin density is localized on P, with only slight mesomeric interaction with the phenyl rings [10,13].

Rate constants for oxidation of various phosphines by peroxyl radicals, k_{set}, and for reaction of the phosphine radical cations with O_2, k_2, also have been determined and compared (Table 1). The results indicate similar k_{set} values for Ph_3P and $MePh_2P$, suggesting that inductive effects, at least from a methyl group, are not that important in this rapid electron-transfer reaction. The 4-methoxy group appears to exert some electron-donating effect to slightly enhance k_{set}. The 2-methoxy group does not exert such an effect and appears to decrease k_{set} slightly. On this basis,the enhancement of k_{set} found for phosphines with 2,6-dimethoxy substitution must be ascribed mainly to through-space 2*p*-3*d* overlap effects [14], which are strongest in such compounds. The largest k_{set} is found for tris(2,4,6-trimethoxyphenyl)phosphine, where both resonance and through-space effects are operative. It should be pointed out that the variations in k_{set} shown in Table 1 are all within less than one order of magnitude. This is due to the high rate constants for these reactions. Similar structural effects on the slow initiation reaction (Reaction 1 in Scheme 1) are likely to result in much greater selectivity, that is, in variations in rate constants of several orders of magnitude. This might have a dramatic effect on the efficiency of these phosphines as oxygen-scavenging additives in jet fuels.

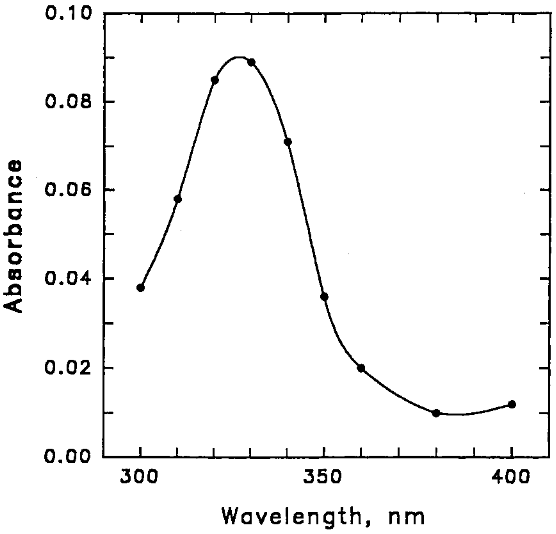


FIGURE 1 Optical absorption spectrum of methyldiphenylphosphine radical cation. Recorded by pulse radiolysis of CH_2Cl_2 solutions containing 1×10^{-3} mol L^{-1} $MePPh_2$ under air, 10 μs after the pulse.

The magnitude of k_2 (Table 1) also is affected by structure. The most dramatic effect is exerted by the 2,6-dimethoxy groups, which slow down the reaction beyond the measurable level; that is, the observed second-order decay of the radical cations is not affected by the presence and the concentration of O_2 [15]. The effect of the methoxy groups may be due to resonance effects that stabilize the phosphine radical cation and thus decrease its rate of reaction with O_2. In addition, steric effects may retard oxygen addition in the case of 2,6-dimethoxy substitution, although such effects are not seen in the quaternization of these phosphines [16]. Replacement of one phenyl with a methyl group results in a large enhancement of k_2. This result is surprising in view of the small differences found in the k_{set} values for Ph_3P and $MePh_2P$ and in the spectra of their radical cations. The larger k_2 may be due to a decreased steric encumbrance for the phosphorus atom and/or may indicate more localized spin density on P (beyond the estimated 85% localized spin density on P in $Ph_3P\cdot^+$) [13].

We have previously shown that gamma radiolysis of Ph_3P in CH_2Cl_2 solutions leads to a chain reaction, consistent with steps **2** and **3** in Scheme 1 (or **2**, **3a**, and **3b**). In this study we extend our previous work by a comparison of Ph_3P with additional phosphines, and we examine the effect of a polar solvent, DMSO, upon the relative oxidation yields. These comparisons are shown in Table 2 and Figure 2.

Figure 2 shows that the radiolytic yield for oxidation of $MePh_2P$ in CH_2Cl_2 at a low dose rate is at least eight times higher than that of Ph_3P at all concentrations examined and that the two compounds exhibit a similar dependence of G value on the square root of the concentration, suggesting a simi-

TABLE 1 Rate Constants Measured by Pulse Radiolysis of Phosphines in CH_2Cl_2

Phosphine	*k(set)*($\times 10^8$ *L mol*$^{-1}$ *s*$^{-1}$)^a	*k2*($\times 10^6$ *L mol*$^{-1}$ *s*$^{-1}$)^a
Triphenyl	2.6 ± 0.4	7.3 ± 1.4
Tris(p-methoxyphenyl)	3.9 ± 0.6	1.3 ± 0.3
Tris(o-methoxyphenyl)	1.7 ± 0.3	0.8 ± 0.3
Tris(2,6-dimethoxyphenyl)	5 ± 1	$\leq 0.1^b$
Tris(2,4,6-trimethoxyphenyl)^c	13 ± 2	$\leq 0.1^b$
Methyldiphenyl	2.7 ± 0.4	180 ± 30

[a] The rate constants are given with their estimated combined standard uncertainties.
[b] The second-order decay was not affected by the presence of O_2.
[c] We find that this phosphine is unstable in CH_2Cl_2. Presumably, this very nucleophilic phosphine is quaternized slowly at room temperature. In order to work with this phosphine, we prepared solutions and pulsed them within 5 minutes.

TABLE 2 Radiolytic Yields (G values in μmol J^{-1})^a for Oxidation of Phosphines (2 mmol L^{-1}) in Various Solvent Systems under Air

Phosphine	*$CHCl_3$*	*DMSO* (*10% $CHCl_3$*)^b	DMSO (*2.5% $CHCl_3$*)^b	*DMSO*
Triphenyl	83	17	13	11
Tris(4-methoxyphenyl)	120	28		21
Tris(2-methoxyphenyl)	15	7		14
Tris(2,6-dimethoxyphenyl)	23	75		17
Tris(2,4,6-trimethoxyphenyl)	40	70	59	24
Methyldiphenyl	187	25	17	

[a] The dose rate was 0.74 Gy s^{-1}. The relative standard uncertainty for the experimental G values is estimated to be generally around 10%.
[b] Volume fraction.

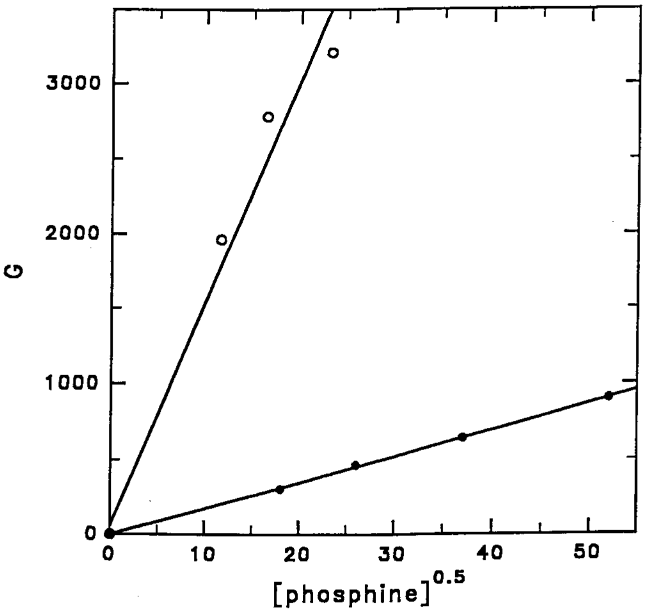


FIGURE 2 Dependence of the initial radiolytic oxidation yield (G, in μmol J^{-1}) of Ph_3P (●) and $MePPh_2$ (○) on the square root of the initial concentration of the phosphine (in μmol L^{-1}), irradiated in air-saturated CH_2Cl_2 solutions with a dose rate of 0.0062 Gy s^{-1}.

lar chain reaction mechanism. Table 2 shows that $MePh_2P$ is oxidized more efficiently than Ph_3P also when irradiated in $CHCl_3$ and in a DMSO/$CHCl_3$ mixture, although in these cases, which were examined at a much higher dose rate, the differences are smaller. The longer chain for $MePh_2P$ may be due to the higher value of k_2 for this compound, but we cannot rule out the possibility that it is due also to the other propagation reaction (**3** or **3a,b**) being faster. Although k_{set} values for Ph_3P and $MePh_2P$ in CH_2Cl_2 were found to be similar, the rate of propagation (k_3, Scheme 1) may be different for these two compounds since the oxidant in Reaction 3 is also changed for the two compounds (from $Ph_3P^+OO\cdot$ to $MePh_2P^+OO\cdot$).

In $CHCl_3$, phosphines with tris(2,6-dimethoxyphenyl) substitution have smaller G values compared to Ph_3P. However, the k_{set} values for this substitution pattern suggest an enhancement in the rate of radical cation formation compared to Ph_3P. Therefore, we suggest that the lower G values with tris(2,6-dimethoxyphenyl) substitution is due to their low values of k_2. However, we cannot rule out the possibility that k_3 also is lower for these compounds (as discussed earlier).

The G values in DMSO are lower than those in $CHCl_3$ because of lower efficiency in the initiation steps, that is, lower yields of primary oxidizing species and production of weaker oxidants as compared to those in $CHCl_3$. Most intriguing, however, is the finding that the G values for the tris(2,6-dimethoxyphenyl) substitution pattern is ~4-fold higher than that for Ph_3P; that is, the relative behavior of these compounds is reversed from that found in $CHCl_3$. Presumably, this difference is due to a solvent effect. We suggest that in $CHCl_3$ the behavior of the tris(2,6-dimethoxyphenyl) substitution pattern is consistent with stabilization of the transition state for formation of the phosphine radical cation by operation of through-space 2*p*-3*d* overlap [14]. However, in $CHCl_3$, through-space stabilization of the phosphine radical cation may sterically inhibit the subsequent reaction with O_2. On the other hand, in DMSO, after the radical cation is formed, strong solvation by DMSO might be more effective than through-space overlap effects, and consequently, the steric environment of the radical cation might be open enough for more efficient reaction with O_2. In an attempt to obtain evidence for this suggestion, we monitored the decay of the radical cation in DMSO/$CHCl_3$ by pulse radiolysis as a function of O_2 concentration, but we found k_2 to be too slow to measure. This means that k_2 is lower than 1×10^5 L mol^{-1} s^{-1} in both solvents but does not rule out the possibility that it is significantly lower in $CHCl_3$ than in DMSO/$CHCl_3$. Further studies are underway to explain this solvent effect, but for the present work, we are more concerned with the mechanism in nonpolar solvents that are more representative of the fuel environment.

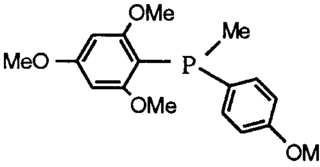
For this purpose, we have compared the relative rates of oxygenation of two phosphines with that of PPh_3 under conditions more similar to those likely to be experienced in a jet engine. Thus, tris(2-methoxyphenyl)phosphine and $MePh_2P$ where heated at 150°C in O_2-saturated dodecane in the presence of one equivalent of BHT. Analogously, with the radiolytic data, tris(2-methoxyphenyl)phosphine was less reactive and $MePh_2P$ more reactive than PPh_3. Their rates of oxygenation are 8.2×10^{-6}, 2.9×10^{-5}, and 1.2×10^{-5} mol L^{-1} min^{-1}, respectively.

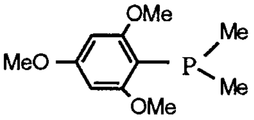
CONCLUSIONS

Most likely, a phosphine much more reactive with O_2 than $MePh_2P$ will be required to achieve successful O_2-scavenging additives for JP-900. If so, then our radiolytically developed structure-reactivity data suggest the following phosphine structural features might prove beneficial:

1. The presence of a 2,4,6-trimethoxyphenyl group will probably facilitate the formation of the phosphine radical cation in a rapid SET reaction as proposed for step **3** in Scheme 1.
2. The reaction of the phosphine radical cation with O_2 seems to be very sensitive to steric constraints. Our data suggest the presence of at least one methyl group would be very beneficial.

Our future work in this area will be directed at preparing and testing our hypotheses with the following phosphines:





EXPERIMENTAL

Phosphines were purchased from Aldrich Chemical Corp., while solvents (highest grade available) were from Mallinckrodt and were used as received [11]. Experimental details have been published previously [8,10].

ACKNOWLEDGMENT

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[15] In Ref. [10], we reported a larger k_2 value for tris(2,4,6-trimethoxyphenyl)phosphine. Unfortunately, we did not notice the instability of this phosphine in CH_2Cl_2 (see footnote in Table 1 and Ref. [16]).

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