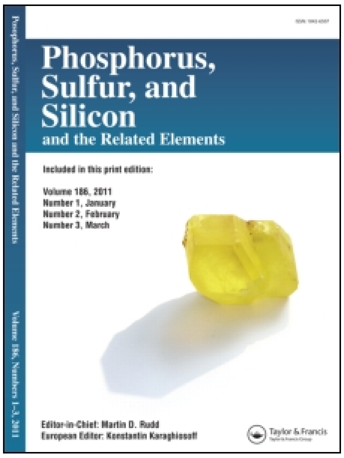


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

POSSIBLE EVIDENCE FOR A NEW MECHANISM FOR REACTION OF TRIMETHYLPHOSPHINE WITH DIOXYGEN

H. D. Burkett[a]; W. E. Hill[a]; S. D. Worley[a]
[a] Department of Chemistry, Auburn University, Alabama, U.S.A.

To cite this Article Burkett, H. D. , Hill, W. E. and Worley, S. D.(1984) 'POSSIBLE EVIDENCE FOR A NEW MECHANISM FOR REACTION OF TRIMETHYLPHOSPHINE WITH DIOXYGEN', Phosphorus, Sulfur, and Silicon and the Related Elements, 20: 2, 169 — 172

To link to this Article: DOI: 10.1080/03086648408077626

URL: http://dx.doi.org/10.1080/03086648408077626

Phosphorus and Sulfur, 1984, Vol. 20, pp. 169–172
0308-664X/84/2002–0169/$18.50/0

POSSIBLE EVIDENCE FOR A NEW MECHANISM FOR REACTION OF TRIMETHYLPHOSPHINE WITH DIOXYGEN

H. D. BURKETT, W. E. HILL* and S. D. WORLEY*

Department of Chemistry, Auburn University, Alabama 36849, U.S.A.

(*Received December 17, 1983; in final form February 28, 1984*)

Evidence is presented suggesting that the mechanism for reaction of trimethylphosphine with dioxygen proceeds through $Me_3\dot{P}O_2^{\bullet}$ as an intermediate. A mechanistic scheme is proposed to explain the products observed and the spectroscopic data obtained.

INTRODUCTION

The reactions of trialkylphosphines with dioxygen have been shown to produce R_3PO, $R_2P(O)OR$, $RP(O)(OR)_2$, and $P(O)(OR)_3$ in solution.[1] Neat samples of $P(n\text{-}C_4H_9)_3$ reacted with dioxygen to give only R_3PO, $R_2P(O)OR$, and R_2POR. A free radical mechanism involving $R^{\bullet}$, $RO^{\bullet}$, and $RO_2^{\bullet}$ was proposed, and the suggestion was made that dioxygen reacts with a hydrocarbon radical rather than at phosphorus—the key intermediates being the formation of the trivalent species R_2POR, $RP(OR)_2$, and $P(OR)_3$. The nature of the initiation process was not identified. Kinetic studies of the reactions initiated by azobisisobutyronitrile (AIBN) are consistent with a free radical mechanism, and the suggestion was made that impurities could provide the initiation step for the reactions in the absence of AIBN.[2]

In contrast to the reactions of tertiary phosphines, dialkaylphosphines react with dioxygen in solution or neat to give only dialkylphosphine oxides.[3] These reactions also showed the characteristics of free radical reactions (e.g. inhibition by hydroquinone), but it was believed that the reactions were initiated by the formation of $R_2\dot{P}(H)O{-}O^{\bullet}$.

We now report the results of a study of the gas phase reaction of PMe_3 with dioxygen and suggest a possible mechanism which is consistent with that proposed for dialkylphosphines.

RESULTS AND DISCUSSION

Trimethylphosphine (10 torr) and dioxygen-16 (30 torr) were mixed in a gas infrared cell and the reaction monitored by infrared spectroscopy over a period of two days. In addition to the usual infrared bands for trimethylphosphine an infrared band at

---

*Author to whom all correspondence should be addressed.

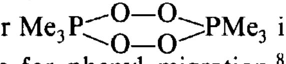
1060 cm^{-1} characteristic of the ν(P)OC vibration in $Me_2P^{16}OMe$ was observed.[4] If mixtures of $^{18}O_2$ (15 torr) and $^{16}O_2$ (15 torr) were used, an additional band at 1034 cm^{-1} assigned to $Me_2P^{18}OMe$ was also observed. No other changes in the infrared spectrum were apparent.

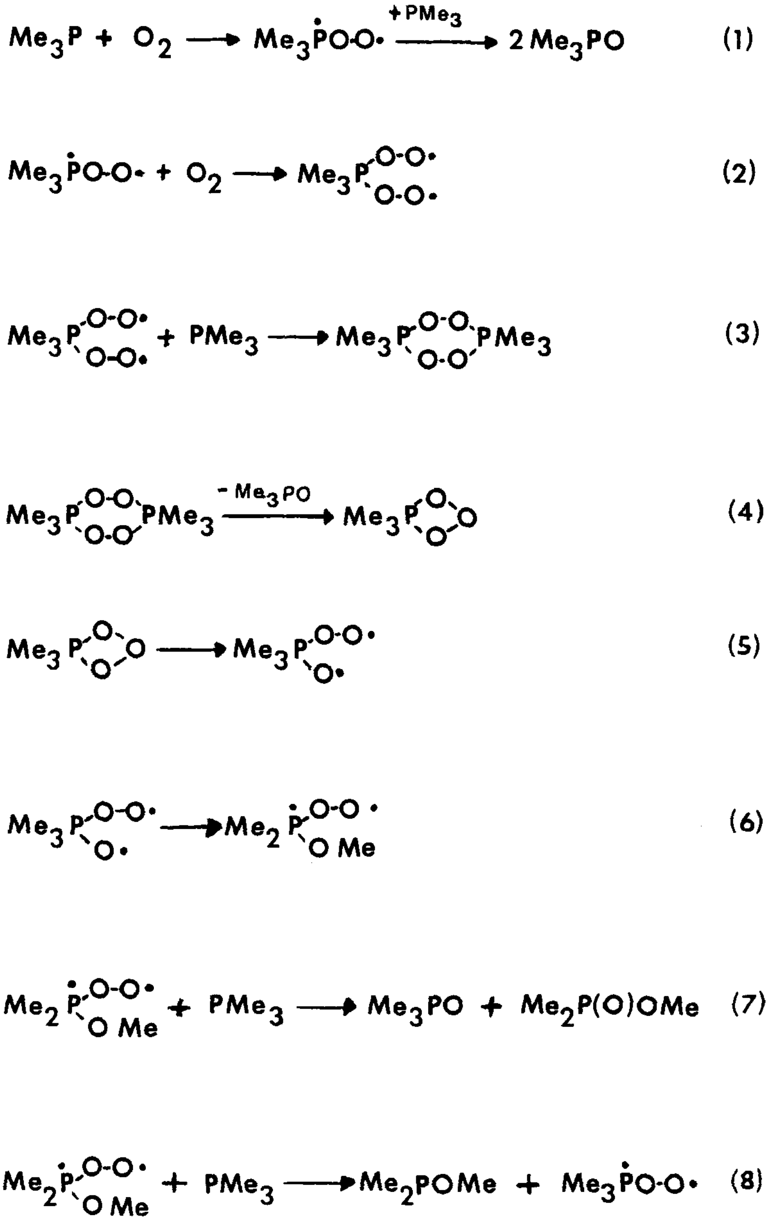
Mass spectral analyses of the mixture of PMe_3 with $^{16}O_2$ at low pressure (40 torr) gave a peak at m/e 124 albeit in low relative abundance assignable to a $Me_3P^{16}O_3^+$ species. This could not be due to $P(OMe)_3$ or $MeP(O)(OMe)_2$ since neither species was observed by ^{31}P nmr of either the gas or solid products under these conditions. If one of these species were responsible for the m/e 124 ion in low abundance because of low volatility, it would almost certainly have been detected in the ^{31}P nmr of the dissolved products of the gas-phase reaction. Other fragments assigned to species containing three oxygens were observed at m/e 109 (assigned to $Me_2PO_3^+$), m/e 94 (assigned to $MePO_3^+$), and m/e 79 (assigned to PO_3^+). Fragments containing two oxygen atoms were observed at m/e 108 ($Me_3PO_2^+$), m/e 93 ($Me_2PO_2^+$), and m/e 63 (PO_2^+).

Mixtures of PMe_3 with $^{18}O_2$ (ca. 40 torr) gave a species at m/e 130 assigned to $Me_3P^{18}O_2^+$. Fragments containing two oxygen-18 atoms were observed at m/e 112 ($Me_3P^{18}O_2^+$) and m/e 97 ($Me_2P^{18}O_2^+$).

The ^{31}P $\{^1H\}$ nmr of the gas mixture was obtained by condensing the gas into an nmr tube along with $CDCl_3$, and the tube was then sealed. The only species observed at −60°C was PMe_3 and small amounts of Me_2POMe ($\delta_P = -61.4$ and $+124$ ppm, respectively).[4,5]

If a gas mixture of PMe_3 and O_2 is made at a pressure of ca. 1 atm, reaction is observed in a matter of seconds as evidenced by the formation of a white non-volatile solid. The $^{31}P\{^1H\}$ nmr spectrum of this solid showed it to be a mixture of $Me_2P(O)OMe$ (20%) and Me_3PO (80%).[6] Infrared analysis of the solid confirmed these results.[7] The infrared spectrum of the volatiles again showed the presence of Me_2POMe, and the ^{31}P nmr at −60°C confirmed the presence of Me_2POMe as well as a trace amount of $MeP(O)(OMe)_2$.

In view of our results several points can be made. The reaction products observed by us for the gas phase reaction of PMe_3 with dioxygen are of the same class as those observed by Buckler for the neat reaction of PBu_3 with O_2.[1] However, the observation of a $Me_3PO_3^+$ species in the mass spectrum of the gas mixture suggests that a possible initiation process for the reaction different from that proposed by Buckler[1] may be involved. A mechanism consistent with the observations of Buckler and also our results is shown in Scheme 1. For the initiation step (1) we suggest the formation of $Me_3\dot{P}O_2^{\bullet}$, since other workers have shown that both tertiary[1,2] and dialkyl phosphines[3] all react via a radical pathway. The formation of $Me_2P(O)OMe$ could occur by methyl migration on $Me_3\dot{P}O_2^{\bullet}$ or  in a manner similar to the proposal of Itzstein and Jenkins for phenyl migration,[8] or it could occur through a termination step such as 7. Although ozonides similar to Me_3PO_3 have been shown to be very unstable and decompose to give trialkylphosphine oxides and singlet dioxygen,[9] we feel that a rearrangement such as that shown in step 6 would be competitive with decomposition in the gas phase for the specific case of methyl migration. The resulting diradical could then react with PMe_3 in a termination step to produce the two observed solid products Me_3PO and $Me_2P(O)OMe$ (step 7) or in



SCHEME 1

a propagation step to produce the primary gas product Me_2POMe and $Me_3\dot{P}O_2^{\bullet}$. Of course, Me_3PO could also be produced from a termination reaction of the $Me_3\dot{P}O_2^{\bullet}$ with PMe_3 as shown in step 1. This proposed mechanism does not utilize the methyl or methoxy radicals which would be primary species involved in propagation in a Buckler-type mechanism. However, we would emphasize that our proposed mechanism refers only to the gas-phase reaction of dioxygen and trimethylphosphine.

EXPERIMENTAL

Materials. Trimethylphosphine (Strem Chemical Company) was transferred to a previously dried glass vessel equipped with a Teflon stopcock in a nitrogen filled dry box. The phosphine was then degassed on a vacuum line using 3–4 freeze/thaw cycles. High purity oxygen was obtained from Matheson. $^{18}O_2$ (99.8%) was purchased from Alfa Inorganics, Inc.

Spectra. Infrared spectra were recorded on a Perkin-Elmer 580 or 983 Spectrophotometer equipped with a Perkin-Elmer Data Station using a vacuum-tight 10 cm cell having KRS-5 windows. ^1H nmr spectra were obtained on a Varian EM 390 spectrophotometer at 90 MHz, and ^{31}P nmr spectra were recorded on a Varian CFT 20 spectrophotometer at 32.1 MHz (in C_6D_6 or $CDCl_3$). Gas-phase products were condensed in a cooled nmr tube (at 77 K) which was then sealed on a vacuum line; solids were dissolved in solvent and loaded into nmr tubes in a dry box. Chemical shifts were measured relative to internal TMS and external 85% H_3PO_4. Mass spectral data were obtained on a DuPont 491-B mass spectrometer equipped with a Finnigan INCOS data station; gas aliquots were taken directly from the infrared cell.

Preparation of Gas Mixtures. Reactions were carried out at room temperature in preheated (at 10^{-6} torr) glass vessels. Trimethyl phosphine was expanded into the vessel (glass blub or IR cell), and dioxygen was added at various pressures greater than that of the phosphine.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of this work by the National Science Foundation (CHE-7920825), The Research Corporation, and a Grant-In-Aid from Auburn University.

REFERENCES

1. S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962).
2. M. B. Floyd and C. E. Boozer, *J. Am. Chem. Soc.*, **85**, 984 (1963).
3. M. M. Rauhut and H. A. Currier, *J. Org. Chem.*, **26**, 4626 (1961).
4. F. Seel and K. D. Velleman, *Chem. Ber.*, **105**, 406 (1972).
5. L. Maier, *Helv. Chim. Acta.*, **47**, 2129 (1964).
6. R. Wolff, *Z. Phys. Chem.* (*Leipzig*), **26**, 726 (1980).
7. V. W. D. Burhardt, E. G. Hohn and J. Goubeau, *Z. Anorg. Allg. Chem.*, **442**, 19 (1978).
8. M. V. Itzstein and I. D. Jenkins, *J. Chem. Soc., Chem. Commun.*, 164 (1983).
9. R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, **90**, 537 (1968).