

PHOSPHORUS-CONTAINING COMPOUNDS

For each phosphorus-containing compound for which experimental kinetic data are available, the literature rate constants are listed. Phosphine [PH₃] and the other phosphorus-containing inorganic compounds for which experimental data are available are included for completeness. In the table associated with each reaction, the experimental techniques used are denoted by abbreviations listed in the table below. For example, use of a pulsed laser photolysis system to generate OH radicals with resonance fluorescence monitoring of OH radicals is denoted by PLP-RF.

List of abbreviations used in tables of rate data, under "*Technique*" column.

Abbreviation	Experimental Technique
DF	Discharge flow
PLP	Pulsed laser photolysis
RR	Relative rate
RF	Resonance fluorescence
EPR	Electron paramagnetic resonance

When relative rate methods (denoted in the "*Technique*" column by "RR") were used, the rate constant for the reference compound from the most recent review and evaluation is used to re-evaluate the rate constant for the compound in question (which therefore may be different from that cited in the original publication). For relative rate studies, the rate constant used for the reference reaction to place the measured rate constant ratio(s) on an absolute basis is noted, and is that recommended from this evaluation unless noted otherwise.

For absolute rate studies, the temperature-dependent rate expressions are also given (if cited), either as the Arrhenius expression $k = A e^{-B/T}$ (in which case no entry is given in the column labeled "*n*") or as the three-parameter expression $k = A T^n e^{-B/T}$. When rate constants have been measured over a range of temperatures, Arrhenius plots of $\ln k$ vs $1/T$ often exhibit curvature.¹⁻³ While an Arrhenius expression may be adequate over short temperature ranges, extrapolation outside of the temperature range for which the Arrhenius expression is valid is likely to result in significant errors in the predicted rate constant.

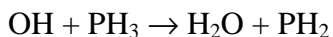
References

1. Atkinson, R., *J. Phys. Chem. Ref. Data*, **1989**, *Monograph 1*, 1.
2. Atkinson, R., *J. Phys. Chem. Ref. Data*, **1994**, *Monograph 2*, 1.
3. Atkinson, R., *J. Phys. Chem. Ref. Data*, **1997**, *26*, 215.

Rate constants and temperature-dependent parameters.

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	n	B (K)	$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference	Temperature Range (K)
27		155	14 ± 3 17 ± 3 13 ± 3 18 ± 3 12 ± 3 13 ± 3 18 ± 3 18 ± 3	249 249 256 296 296 296 370 438	PLP-RF	Fritz <i>et al.</i> , 1982 ^{1,2}	249-438

This is the only study of this reaction to date. The magnitude of the rate constant and the small positive temperature dependence suggest that the reaction proceeds by H-atom abstraction.¹



References

1. Fritz, B.; Lorenz, K.; Steinert, W.; Zellner, R., "Laboratory Kinetic Investigation of the Tropospheric Oxidation of Selected Industrial Emissions", in *Proceedings of the Second European Symposium on the Physico-Chemical Behaviour of Atmospheric Pollutants*, Versino, B.; Ott, H., eds., D. Reidel Publishing Company, Dordrecht, Holland, 1982, pp. 192-202.
2. "Methods of the Ecotoxicological Evaluation of Chemicals. Photochemical Degradation in the Gas Phase, Volume 6: OH Reaction Rate Constants and Tropospheric Lifetimes of Selected Environmental Chemicals", Report 1980-1983, Becker, K. H.; Biehl, H. M.; Bruckmann, P.; Fink, E. H.; Führ, F.; Klöpffer, W.; Zellner, R.; Zetzsch, C., eds., Kernforschungsanlage Jülich GmbH, Germany, November 1984.

Rate constants

$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
38 ± 5	$\sim 295^{\text{a}}$	DF-EPR	Jourdain <i>et al.</i> , 1980 ¹

^aRoom temperature; 295 K assumed by analogy with similar studies from this research group.²

This is the only study of this reaction to date. Cl atoms were observed as a reaction product by EPR spectroscopy.¹

References

1. Jourdain, J.-L.; Laverdet, G.; Le Bras, G.; Combourieu, J., *J. Chim. Phys.*, **1980**, 77, 809.
2. Jourdain, J.-L.; Le Bras, G.; Combourieu, J., *J. Phys. Chem.*, **1982**, 86, 4170.

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
85 ± 5	295	DF-EPR	Jourdain <i>et al.</i> , 1982 ¹

This is the only study of this reaction to date. Br atoms were observed as a reaction product by EPR spectroscopy, with a yield of $[\text{Br}]_{\text{formed}}/[\text{PBr}_3]_{\text{reacted}} = 1.7$.¹

References

1. Jourdain, J.-L.; Le Bras, G.; Combourieu, J., *J. Phys. Chem.*, **1982**, 86, 4170.

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
<0.04	298 ± 2	RR [relative to Si(CH ₃) ₄ = 8.9 × 10 ⁻¹³]	Martin <i>et al.</i> , 2002 ¹

This is the only study of this reaction to date.

References

1. Martin, P.; Tuazon, E. C.; Atkinson, R.; Maughan, A. D., *J. Phys. Chem. A*, **2002**, *106*, 1542.

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
0.067 ± 0.020	298 ± 2	RR [relative to Si(CH ₃) ₄ = 8.9 × 10 ⁻¹³]	Martin <i>et al.</i> , 2002 ¹

This is the only study of this reaction to date.

References

1. Martin, P.; Tuazon, E. C.; Atkinson, R.; Maughan, A. D., *J. Phys. Chem. A*, **2002**, *106*, 1542.

DIMETHYL CHLOROPHOSPHOROTHIOATE, (CH₃O)₂P(S)Cl

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
59.0 ± 3.8	296 ± 2	RR [relative to isoprene = 1.01×10^{-10}]	Atkinson <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Atkinson, R.; Aschmann, S. M.; Goodman, M. A.; Winer, A. M., *Int. J. Chem. Kinet.*, **1988**, *20*, 273.

DIMETHYL PHOSPHONATE (DIMETHYL PHOSPHITE), (CH₃O)₂P(O)H

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
4.63 ± 0.18	~298	RR [relative to propane, <i>n</i> -butane and <i>n</i> -hexane] ^a	Kleindienst and Smith, 1996 ¹
5.08 ± 0.18	298 ± 2	RR [relative to dimethyl ether = 2.84×10^{-12}]	Martin <i>et al.</i> , 2002 ²

^aThe data presented¹ cannot be accurately re-evaluated for each reference compound used. Based on the presently recommended rate constants for propane, *n*-butane and *n*-hexane (this evaluation) being 4.4%, 7.1% and 7.3% lower than those used by Kleindienst and Smith,¹ the cited rate constant of Kleindienst and Smith¹ of $(4.94 \pm 0.19) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ has been decreased by 6.3% (the average decrease for the three reference compounds used).

The two independent measurements of the room temperature rate constant for this reaction,^{1,2} both using relative rate methods but with different reference compounds, agree to within 10%. An average of the rate constants of Kleindienst and Smith¹ and Martin *et al.*² leads to the recommendation of

$$k(\text{dimethyl phosphite}) = 4.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K,}$$

with an estimated overall uncertainty of $\pm 15\%$.

Dimethyl phosphate, $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{OH}$, was tentatively identified as a reaction product by Martin *et al.*²

References

1. Kleindienst, T. E.; Smith, D. F., "Chemical Degradation in the Atmosphere", Final report on the "Atmospheric Chemistry of Three Important Volatile Chemical Precursors", Sub-Contract by ManTech Environmental Technology, Inc. to Contract No. F08635-93-C-0020 for the Armstrong Laboratory Environics Directorate, Tyndall AFB, FL, September 1996.
2. Martin, P.; Tuazon, E. C.; Atkinson, R.; Maughan, A. D., *J. Phys. Chem. A*, **2002**, *106*, 1542.

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
711 ± 55	298 ± 2	RR [relative to cyclohexene = 6.77 x 10 ⁻¹¹]	Martin <i>et al.</i> , 2002 ¹

This is the only study of this reaction to date. Formation of HCHO and trimethyl phosphate [(CH₃O)₃PO] were observed by Martin *et al.*¹ with molar formation yields of 0.29 ± 0.03 and 0.48 ± 0.05, respectively, and dimethyl phosphate [(CH₃O)₂P(O)OH] was also observed.¹

References

1. Martin, P.; Tuazon, E. C.; Atkinson, R.; Maughan, A. D., *J. Phys. Chem. A*, **2002**, *106*, 1542.

DIMETHYL METHYL PHOSPHONATE, (CH₃O)₂P(O)CH₃

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
5.95 ± 0.28	~298	RR [relative to propane and <i>n</i> -hexane] ^a	Kleindienst and Smith, 1996 ¹

^aThe data presented¹ cannot be accurately re-evaluated for each reference compound used. Based on the presently recommended rate constants for propane and *n*-hexane (this evaluation) being 4.4% and 7.3% lower than those used by Kleindienst and Smith,¹ the cited rate constant of Kleindienst and Smith¹ of $(6.32 \pm 0.29) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ has been decreased by 5.8% (the average decrease for the two reference compounds used).

This is the only study of this reaction to date

References

1. Kleindienst, T. E.; Smith, D. F., "Chemical Degradation in the Atmosphere", Final report on the "Atmospheric Chemistry of Three Important Volatile Chemical Precursors", Sub-Contract by ManTech Environmental Technology, Inc. to Contract No. F08635-93-C-0020 for the Armstrong Laboratory Environics Directorate, Tyndall AFB, FL, September 1996.

DIETHYL METHYL PHOSPHONATE, (CH₃O)₂P(O)CH₃

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
31.5 ± 1.1	~298	RR [relative to <i>n</i> -hexane, propene and 1,3-butadiene] ^a	Kleindienst and Smith, 1996 ¹

^aThe data presented¹ cannot be accurately re-evaluated for each reference compound used. Based on the presently recommended rate constant for *n*-hexane (this evaluation), which is 7.3% lower than those used by Kleindienst and Smith¹ (the recommended rate constants for propene and 1,3-butadiene are unchanged), the cited rate constant of Kleindienst and Smith¹ of $(3.23 \pm 0.11) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ has been decreased by 2.4% (the average decrease for the three reference compounds used).

This is the only study of this reaction to date

References

1. Kleindienst, T. E.; Smith, D. F., "Chemical Degradation in the Atmosphere", Final report on the "Atmospheric Chemistry of Three Important Volatile Chemical Precursors", Sub-Contract by ManTech Environmental Technology, Inc. to Contract No. F08635-93-C-0020 for the Armstrong Laboratory Environics Directorate, Tyndall AFB, FL, September 1996.

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
7.02 ± 0.71	296 ± 2	RR [relative to dimethyl ether = 2.82 $\times 10^{-12}$]	Tuazon <i>et al.</i> , 1986 ¹

This is the only study of this reaction to date.

References

1. Tuazon, E. C.; Atkinson, R.; Aschmann, S. M.; Arey, J.; Winer, A. M.; Pitts, J. N., Jr.,
Environ. Sci. Technol., **1986**, *20*, 1043.

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
55.3 ± 3.5	296 ± 2	RR [relative to propene = 2.66×10^{-11}]	Atkinson <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Atkinson, R.; Aschmann, S. M.; Goodman, M. A.; Winer, A. M., *Int. J. Chem. Kinet.*, **1988**, *20*, 273.

***O,O,S*-TRIMETHYL PHOSPHOROTHIOATE, (CH₃O)₂P(O)SCH₃**

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
8.64 ± 0.63	298 ± 2	RR [relative to cyclohexane = 6.97 x 10 ⁻¹²]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Arch. Environ. Contam. Toxicol.*, **1988**, *17*, 281.

***O,S,S*-TRIMETHYL PHOSPHORODITHIOATE, (CH₃S)₂P(O)OCH₃**

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at <i>T</i> (K)	Technique	Reference
8.92 ± 0.70	298 ± 2	RR [relative to cyclohexane = 6.97 x 10 ⁻¹²]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Arch. Environ. Contam. Toxicol.*, **1988**, *17*, 281.

O,O,O-TRIMETHYL PHOSPHOROTHIOATE, (CH₃O)₃PS

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
69.7 ± 3.9	298 ± 2	RR [relative to isoprene = 1.01 × 10 ⁻¹⁰]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Arch. Environ. Contam. Toxicol.*, **1988**, *17*, 281.

***O,O,S*-TRIMETHYL PHOSPHORODITHIOATE, (CH₃O)₂P(S)SCH₃**

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
56.0 ± 1.8	298 ± 2	RR [relative to isoprene = 1.01 × 10 ⁻¹⁰]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Arch. Environ. Contam. Toxicol.*, **1988**, *17*, 281.

DIMETHYL PHOSPHOROAMIDATE, (CH₃O)₂P(O)N(CH₃)₂

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
31.9 ± 2.4	296 ± 2	RR [relative to propene = 2.66×10^{-11}]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Environ. Sci. Technol.*, **1988**, 22, 578.

DIMETHYL PHOSPHOROTHIOAMIDATE, (CH₃O)₂P(S)NH₂

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
242 ± 9	296 ± 2	RR [relative to 2,3-dimethyl-2-butene = 1.10 × 10 ⁻¹⁰]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Environ. Sci. Technol.*, **1988**, 22, 578.

DIMETHYL PHOSPHOROTHIOAMIDATE, (CH₃O)₂P(S)NHCH₃

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
233 ± 15	296 ± 2	RR [relative to propene = 2.66 × 10 ⁻¹¹]	Goodman <i>et al.</i> , 1988 ¹
230 ± 13	296 ± 2	RR [relative to 2,3- dimethyl-2-butene = 1.10 × 10 ⁻¹⁰]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date. The two measurements of the rate constant using different reference compounds are in excellent agreement.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Environ. Sci. Technol.*, **1988**, 22, 578.

DIMETHYL PHOSPHOROTHIOAMIDATE, (CH₃O)₂P(S)N(CH₃)₂

February 2002

Rate constants

$10^{12} \times k$ (cm ³ molecule ⁻¹ s ⁻¹)	at T (K)	Technique	Reference
46.8 ± 1.4	296 ± 2	RR [relative to propene = 2.66 × 10 ⁻¹¹]	Goodman <i>et al.</i> , 1988 ¹

This is the only study of this reaction to date.

References

1. Goodman, M. A.; Aschmann, S. M.; Atkinson, R.; Winer, A. M., *Environ. Sci. Technol.*, **1988**, 22, 578.