

## ESTIMATION OF GAS-PHASE HYDROXYL RADICAL RATE CONSTANTS FOR ORGANIC CHEMICALS

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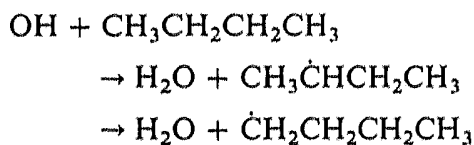
**Abstract**—A structure-activity relationship developed for the estimation of rate constants for the gas-phase reactions of the hydroxyl radical with organic compounds is described and extended to certain organophosphorus compounds. The use of this estimation method is illustrated.

**Keywords**—Hydroxyl radical    Organic compounds    Atmospheric lifetimes  
Gas-phase reactions    Structure-activity relationship

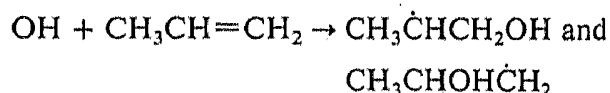
### INTRODUCTION

Organic chemicals emitted into the troposphere are removed by chemical reaction with a number of reactive intermediate species, including OH, HO<sub>2</sub> and NO<sub>3</sub> radicals and O<sub>3</sub>, and by photolysis and wet and dry deposition [1]. For the majority of organic chemicals present in the troposphere, reaction with the OH radical during daylight hours is expected to be the dominant atmospheric removal process [1,2] leading to transformation of the initial chemical to a variety of reaction products.

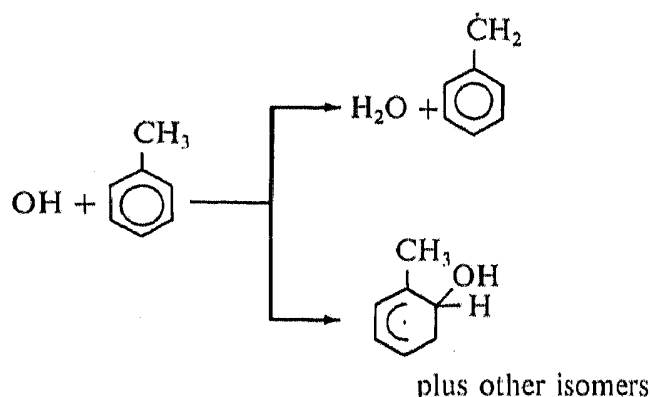
Thus, for example, alkanes and other saturated organic compounds, such as alcohols, esters and ethers, react with the OH radical by abstraction of an H atom from C—H or O—H bonds:



Alkenes, alkynes and other organic compounds containing  $\text{>C=C<}$  and  $\text{—C}\equiv\text{C—}$  bonds react with the OH radical mainly by OH radical addition to the carbon-carbon double or triple bonds:



Compounds containing aromatic rings react with the OH radical by addition to the ring and H-atom abstraction from the substituent group(s):



Subsequent reactions of these initially formed radicals lead to a wide spectrum of product species.

In order to allow the dominant tropospheric removal process(es) of organic compounds to be assessed and their atmospheric lifetimes calculated, it is necessary to know the reaction rate constants (over the temperature range appropriate for the troposphere) and the ambient atmospheric concentrations of the reactive intermediates.

While rate constants for the gas-phase reactions of a large number (400 or more) of organic chemicals with the OH radical have been measured to date [2], the inherent complexity and concurrent low volatility of many industrially and agriculturally used organic chemicals make such measurements difficult and time- and cost-consuming.

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With the increasingly large database available, the development and use of estimation techniques for the reliable calculation of OH radical reaction rate constants for a wide number of classes of organic compounds have become feasible. Such estimation techniques can be classified into two general categories: those that rely solely on the structure of the organic chemical (structure-activity relationships, or SARs) and those that utilize a physical or chemical property, such as the ionization potential or bond dissociation energy or correlations between gas- and solution-phase OH-radical reaction rate constants.

The intrinsically simplest of these estimation techniques, which should be applicable to all organics, are those utilizing SARs, and these are of interest to regulatory agencies in preparing risk assessments of organic chemicals emitted into the atmosphere. Recently, two SARs have been developed, one by Davenport et al. [3], based upon an update of the earlier Hendry and Kenley SAR [4], and the other by Atkinson [2,5,6]. In this article, the latter SAR [2,5,6] is described and further extended to deal with organophosphorus compounds. The use of this estimation method is illustrated and several environmentally relevant reaction rate constants are estimated.

### FORMULATION OF THE SAR

The estimation method utilizes the fact that there are several separate OH radical reaction pathways that can be dealt with individually [2]. As presently understood, these processes involve (a) H-atom abstraction from C-H bonds in alkanes, carbonyls and other saturated organics, and from O-H bonds in alcohols and glycols, (b) OH radical addition to  $\text{>C=C<}$  and  $\text{-C}\equiv\text{C-}$  unsaturated bonds, (c) OH radical addition to aromatic rings and (d) OH radical interaction with nitrogen-, sulfur- and phosphorus-containing groups.

The total OH radical reaction rate constant is then given by

$$k_{\text{total}} = k(\text{H-atom abstraction from C-H and O-H bonds}) \\ + k(\text{OH radical addition to } \text{>C=C<} \text{ and } \text{-C}\equiv\text{C-} \text{ bonds}) \\ + k(\text{OH radical addition to aromatic rings}) \\ + k(\text{OH radical interaction with N-, S- and P-containing groups})$$

(All rate constants in this article have units of  $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ .) These separate processes are dealt with below.

### H-atom abstraction from C-H and O-H bonds

As discussed by Atkinson [2,5,6], the calculation of overall H-atom abstraction rate constants is based on the estimation of  $\text{-CH}_3$ ,  $\text{-CH}_2\text{-}$ ,  $\text{>CH-}$  and  $\text{-OH}$  group rate constants. The  $\text{-CH}_3$ ,  $\text{-CH}_2\text{-}$  and  $\text{>CH-}$  group rate constants depend on the identity of the substituents around those groups, with

$$k(\text{CH}_3\text{-X}) = k_{\text{prim}}^{\circ} F(\text{X})$$

$$k(\text{X-CH}_2\text{-Y}) = k_{\text{sec}}^{\circ} F(\text{X})F(\text{Y})$$

and

$$k(\text{X-CH}\langle \begin{smallmatrix} \text{Y} \\ \text{Z} \end{smallmatrix} \rangle) = k_{\text{tert}}^{\circ} F(\text{X})F(\text{Y})F(\text{Z})$$

where  $k_{\text{prim}}^{\circ}$ ,  $k_{\text{sec}}^{\circ}$  and  $k_{\text{tert}}^{\circ}$  are the rate constants per  $\text{-CH}_3$ ,  $\text{-CH}_2\text{-}$  and  $\text{>CH-}$  group for a "standard" substituent; X, Y and Z are the substituent groups; and F(X), F(Y) and F(Z) are the corresponding substituent factors. The standard substituent group is chosen to be  $\text{X}(=\text{Y}=\text{Z})=\text{-CH}_3$ , with  $F(\text{-CH}_3)=1.00$  by definition [2].

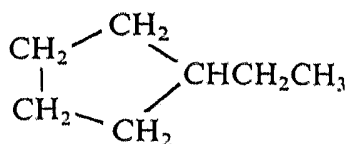
As discussed previously [5,6], the group rate constants  $k_{\text{prim}}^{\circ}$ ,  $k_{\text{sec}}^{\circ}$ ,  $k_{\text{tert}}^{\circ}$  and  $k_{\text{OH}}$  are best expressed in the temperature-dependent form,  $k = AT^2 e^{-E/T}$ , rather than the simple Arrhenius form,  $k = A^1 e^{-E'/T}$ , and the A factors and values of E are given in Table 1. Thus, for *n*-butane,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ , the rate constant is calculated as (starting at the first carbon atom and progressing from carbon atom to carbon atom):

Table 1. Temperature-dependent parameters, in the form,  $k = AT^2 e^{-E/T}$ , for  $\text{CH}_3\text{-}$ ,  $\text{-CH}_2\text{-}$ ,  $\text{>CH-}$  and  $\text{-OH}$  group rate constants [6]

	$10^{12} \times k (298 \text{ K})$ ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )	$10^{18} \times A$	E(K)
$k_{\text{prim}}^{\circ}$	0.144	4.47	303
$k_{\text{sec}}^{\circ}$	0.838	4.32	-233
$k_{\text{tert}}^{\circ}$	1.83	1.89	-711
$k_{\text{OH}}$	0.036	1.89	460

$$\begin{aligned}
 k_{\text{total}} &= k_{\text{prim}}^{\circ} F(-\text{CH}_2-) \\
 &+ k_{\text{sec}}^{\circ} F(-\text{CH}_3) F(-\text{CH}_2-) \\
 &+ k_{\text{sec}}^{\circ} F(-\text{CH}_3) F(-\text{CH}_2-) \\
 &+ k_{\text{prim}}^{\circ} F(-\text{CH}_2-)
 \end{aligned}$$

where  $F(-\text{CH}_3) = 1.00$  and the substituent factors  $F(X)$  are given in Table 2 for 298 K. Thus  $k_{\text{total}} = (0.144 \times 1.29 + 0.838 \times 1.00 \times 1.29 + 0.838 \times 1.00 \times 1.29 + 0.144 \times 1.29) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K. The effects of ring strain are included by factors that account for the ring size; for example, for ethylcyclopentane,



$$\begin{aligned}
 k &= \{ 2k_{\text{sec}}^{\circ} [F(-\text{CH}_2-)]^2 \\
 &+ 2k_{\text{sec}}^{\circ} F(-\text{CH}_2-) F(>\text{CH}-) \\
 &+ k_{\text{tert}}^{\circ} [F(-\text{CH}_2-)]^3 \} F_5 \\
 &+ k_{\text{sec}}^{\circ} F(>\text{CH}-) F(-\text{CH}_3) \\
 &+ k_{\text{prim}}^{\circ} F(-\text{CH}_2-)
 \end{aligned}$$

where  $F_5$  is the factor for a five-membered ring (only the groups involved in the ring are modified by the ring factor [2,6,7]). For polycyclic systems, the ring factors are multiplicative, as shown in the next section.

The substituent factors  $F(X)$ , including factors to take into account the ring strain per ring,  $F_{\text{ring}}$ , are given in Table 2 for 298 K. With the assumption that the effects of a substituent group do not affect the A factor [5], then  $F(X) = e^{E_x/T}$ . Examples of the calculation of OH radical reaction rate constants for organic molecules of varying complexity follow:

For  $\text{CH}_3\text{CHO}$ :

$$\begin{aligned}
 k &= k_{\text{prim}}^{\circ} F(-\text{CHO}) \\
 &+ k_{\text{tert}}^{\circ} F(-\text{CH}_3) F(=\text{O})
 \end{aligned}$$

For  $\text{CH}_3\text{CH}_2\text{COCH}_3$ :

$$\begin{aligned}
 k &= k_{\text{prim}}^{\circ} F(-\text{CH}_2\text{C}(\text{O})-) \\
 &+ k_{\text{sec}}^{\circ} F(-\text{CH}_3) F(-\text{C}(\text{O})-) \\
 &+ k_{\text{prim}}^{\circ} F(-\text{C}(\text{O})-)
 \end{aligned}$$

Table 2. Substituent factors  $F(X)$  at 298 K [6]

X	$F(X)$ at 298 K
$-\text{CH}_3$	1.00
$-\text{CH}_2-$	1.29
$>\text{CH}-$	
$>\text{C}<$	
$-\text{F}$	0.099
$-\text{Cl}$	0.38
$-\text{Br}$	0.30
$-\text{CH}_2\text{Cl}$	0.57
$-\text{CHCl}_2$	
$-\text{CH}_2\text{Br}$	
$-\text{CCl}_3$	0.090
$-\text{CH}_2\text{F}$	-0.85
$-\text{CHF}_2$	-0.10
$-\text{CF}_2\text{Cl}$	-0.025
$-\text{CF}_3$	0.075
$=\text{O}$	8.8
$-\text{CClO}$	-0.5
$-\text{CHO}$	0.76
$-\text{C}(\text{O})-$	
$-\text{CH}_2\text{C}(\text{O})-$	
$>\text{CHC}(\text{O})-$	4.4
$>\text{CC}(\text{O})-$	
$-\text{C}_6\text{H}_5$	
$>\text{C}=\text{C}<$	-1.0
$-\text{C}\equiv\text{C}-$	
$-\text{OH}$	3.4
$-\text{O}-$	6.1
$-\text{C}(\text{O})\text{OR}$	0.0
$-\text{OC}(\text{O})\text{R}$	1.5
$-\text{CH}_2\text{ONO}_2$	0.21
$>\text{CHONO}_2$	
$>\text{CONO}_2$	
$-\text{ONO}_2$	0.10
$-\text{CN}$	0.14
$-\text{CH}_2\text{CN}$	0.5
3-membered ring	0.017
4-membered ring	0.22
5-membered ring	0.80
6-membered ring	1.00
7-membered ring	-1.0

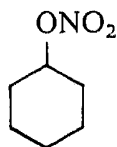
For  $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ :

$$k = k_{\text{prim}}^{\circ} \text{F}(-\text{CH}_2-) + k_{\text{sec}}^{\circ} \text{F}(-\text{CH}_3)\text{F}(-\text{O}-) + k_{\text{sec}}^{\circ} \text{F}(-\text{O}-)\text{F}(-\text{CH}_2-) + k_{\text{sec}}^{\circ} (\text{F}-\text{CH}_2-)\text{F}(-\text{OH}) + k_{\text{OH}}$$

For  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)_2$ :

$$k = k_{\text{prim}}^{\circ} \text{F}(-\text{C}(\text{O})\text{OR}) + k_{\text{tert}}^{\circ} [\text{F}(-\text{CH}_3)]^2 \text{F}(-\text{OC}(\text{O})\text{R}) + 2k_{\text{prim}}^{\circ} \text{F}(\text{>CH}-)$$

For cyclohexyl nitrate:



$$k = \{3k_{\text{sec}}^{\circ} [\text{F}(-\text{CH}_2-)]^2 + 2k_{\text{sec}}^{\circ} \text{F}(-\text{CH}_2-)\text{F}(\text{>CHONO}_2) + k_{\text{tert}}^{\circ} \text{F}(-\text{CH}_2-)^2 \text{F}(-\text{ONO}_2)\} \text{F}_6$$

*OH radical addition to >C=C< and -C≡C- bonds*

The estimation method used to calculate the rate constants for OH radical addition to >C=C< and -C≡C- bond systems is based on the number of unconjugated double or triple bonds or conjugated double bond systems and the degree, identity and configuration of substitution around these double bonds. For example, for  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$  the rate constant is given by

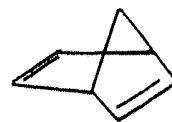
$$k = k(\text{CH}_2=\text{C}<) + k(\text{CH}_2=\text{CH}-) + k_{\text{sec}}^{\circ} \text{F}(\text{>C}=\text{C}<)^2 + k_{\text{prim}}^{\circ} \text{F}(\text{>C}=\text{C}<)$$

where  $k(\text{CH}_2=\text{C}<)$  and  $k(\text{CH}_2=\text{CH}-)$  are the rate constants for OH radical addition to 2-methylpropene and propene, respectively, and  $\text{F}(\text{>C}=\text{C}<) = 1.00$  (Table 2). For conjugated

dialkenes, the >C=C-C=C< structure is considered as a single unit, with the rate constant depending solely on the number of alkyl substituents on this structural unit. The rate constants at 298 K for the various >C=C<, -C≡C- and >C=C-C=C< structural units are given in Table 3.

Hydrogen atom abstraction from vinyl hydrogens is negligible at temperatures of 500 K or below [2]. While the contribution of H-atom abstraction from C-H bonds on substituted alkyl groups to the overall room temperature rate constants is generally minor (being, for example, less than 20% for *n*-heptene [6]), this is taken into account, as shown above for  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$ .

There are no ring strain effects for OH radical addition to >C=C< bonds [2]. As an example, for bicyclo[2.2.1]-2,5-heptadiene,



$$k = 2k(\text{cis-CH}=\text{CH}-) + \{2k_{\text{tert}}^{\circ} [\text{F}(\text{>C}=\text{C}<)]^2 \text{F}(-\text{CH}_2-) + k_{\text{sec}}^{\circ} [\text{F}(\text{>CH}-)]^2\} \text{F}_5^2 \text{F}_6$$

Table 3. Room temperature group rate constants for OH radical addition to >C=C<, -C≡C- and >C=C-C=C< structural units [2,6]

Structure	$10^{11} \times k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )
$\text{CH}_2=\text{CH}-$	2.63
$\text{CH}_2=\text{C}<$	5.14
<i>cis</i> -CH=CH-	5.61
<i>trans</i> -CH=CH-	6.37
-CH=C<	8.69
>C=C<	11.0
$\text{HC}\equiv\text{C}-$	0.64
-C≡C-	2.9
>C=C-C=C< unit	
One-alkyl substituent	10.5
Two-alkyl substituents	13.5
Three-alkyl substituents	18.
Four-alkyl substituents	23.

For alkenes containing substituent groups other than alkyl groups, substituent factors,  $C(X)$ , are used. For example, for  $\text{CH}_2=\text{CXY}$  the rate constant is given by

$$k = k(\text{CH}_2=\text{C}\langle)C(X)C(Y) \\ + k(\text{H}- \text{abstraction from the X} \\ \text{and Y substituent groups})$$

The substituent factors  $C(X)$  at room temperature [6] are given in Table 4. As noted previously [2,6], a negative temperature dependence of the rate constants for these reactions, equivalent to an Arrhenius activation energy of  $-1 \text{ kcal mol}^{-1}$ , is generally applicable for calculating OH radical addition rate constants at temperatures of 500 K or below.

#### OH radical addition to aromatic rings

As discussed elsewhere by Zetzsch [8] and Atkinson [2,6], the linear correlation between the logarithm of the rate constant for OH radical addition to aromatic rings and the sum of the electrophilic substituent constants,  $\sum \sigma^+$ , of Brown and Okamoto [9] provides a means of estimating the rate constants for OH radical addition to aromatic rings.

A least-squares correlation of the room temperature rate constants for OH radical addition to the aromatic ring and the  $\sum \sigma^+$  values for 34 aromatic compounds [6] yields

$$\log_{10} k(\text{OH radical addition to aromatic rings}) \\ = -11.69 - 1.35 \sum \sigma^+ (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$

$\sum \sigma^+$  is calculated by assuming [8] that (a) steric hindrance can be neglected and  $\sigma_{\text{ortho}}^+$  is set equal to  $\sigma_{\text{para}}^+$ ; (b)  $\sum \sigma^+$  is the sum of all substituent constants of the substituents connected to the aromatic ring; (c) the OH radical adds to the position yielding the most negative value of  $\sum \sigma^+$  (preferably to a free position); and (d) if all positions are occupied, the ipso position is treated as a meta position.

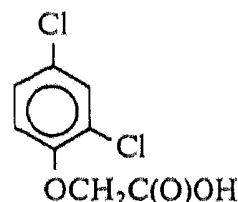
Of course, the contributions of H-atom abstraction from C—H and O—H bonds on alkyl, —OH and —CHO substituent groups and OH radical interaction with —NH<sub>2</sub> and —N(CH<sub>3</sub>)<sub>2</sub> substituent groups (see below) must be taken into account, using  $F(\text{aromatic ring}) = 1.0$  (Table 2). For example, for ethylbenzene, for which  $\sum \sigma^+ = -0.295$  [2],

Table 4. Substituent factors  $C(X)$  at 298 K [6]

Substituent X	$C(X)$
—F	~0.4
—Cl	0.20
—Br	0.26
—CH <sub>2</sub> Cl	0.76
—CN	0.15
—CHO	0.26
—COCH <sub>3</sub>	0.91
—OCH <sub>3</sub>	1.3
=O	1.0

$$k(\text{ethylbenzene}) = 10^{[-11.69 - 1.35(-0.295)]} \\ + k_{\text{sec}}^{\circ} F(-\text{C}_6\text{H}_5) F(-\text{CH}_3) \\ + k_{\text{prim}}^{\circ} F(-\text{CH}_2-)$$

As a further example, for 2,4-D



the values of  $\sigma_p^+$  (Cl) and  $\sigma_m^+$  (Cl) are 0.114 and 0.399, respectively. For the —OCH<sub>2</sub>C(O)OH group, the (perhaps gross) assumption is made that its effect is similar to that of an —OCH<sub>3</sub> group, with values of  $\sigma_p^+$  and  $\sigma_m^+$  of —0.778 and 0.047, respectively. The most negative value of  $\sum \sigma^+ = +0.020$  occurs for OH radical addition at the position ortho to the —OCH<sub>2</sub>C(O)OH group and meta to the two chlorines. This then yields  $k = 1.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.

This estimation method has recently been extended to the polychlorobiphenyls, polychlorodibenzo-*p*-dioxins and polychlorodibenzofurans and related compounds [6,10]. Although the methods used are analogous to that discussed above for the monocyclic aromatics, references 6 and 10 should be consulted for further details.

A plot of the calculated versus experimental room temperature rate constants for about 270 organic compounds that react with the OH radical via H-atom abstraction from C—H and O—H bonds, OH radical addition to  $\text{>C=C<}$  and —C≡C— bonds and OH radical addition to non-fused aromatic rings (including aniline and *N,N*-dimethylaniline) is shown in Figure 1. Only for 18 of those compounds do the calculated and exper-

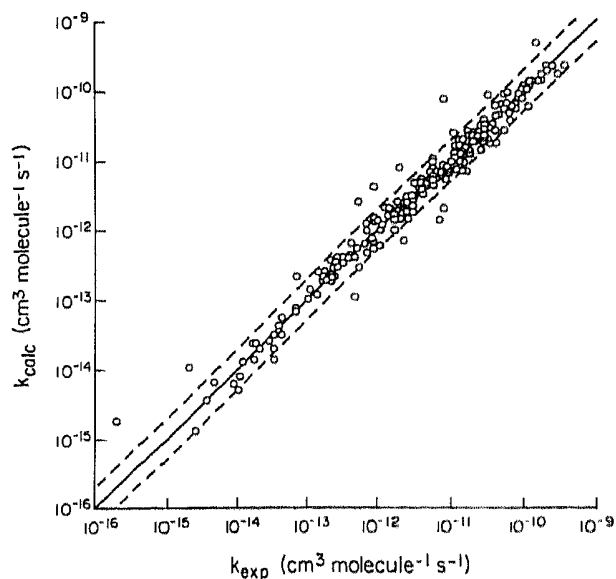


Fig. 1. Plot of calculated versus experimentally measured room temperature rate constants for gas-phase reaction of the OH radical with alkanes, haloalkanes, alkenes, alkynes, haloalkenes, oxygen-containing organics and aromatic compounds (total of about 270 compounds). The solid line indicates perfect agreement; the dashed lines indicate disagreement by a factor of 2.

imental room temperature rate constants disagree by more than a factor of 2.

*OH radical reaction with  $-NH_2$ ,  $>NH$ ,  $>N-$ ,  $-SH$  and  $-S-$  containing compounds*

Under atmospheric conditions, the gas-phase reactions of the OH radical with thiols (RSH), sulfides (RSR'), disulfides (RSSR') and amines (RNH<sub>2</sub>, RR'NH and RR'R''N) proceed, at least in part, via initial OH radical addition to the S- and N-atoms [2]. The values of  $F(-S-)$ ,  $F(-SH)$ ,  $F(-NH_2)$ ,  $F(-NH-)$ ,  $F(-N<)$ ,  $F(-NNO)$ ,  $F(-NNO_2)$ ,  $k_{-SH}$ ,  $k_{-S-}$ ,  $k_{-SS-}$ ,  $k_{-NH_2}$ ,  $k_{>NH}$ ,  $k_{>N-}$ ,  $k_{>NNO}$  and  $k_{>NNO_2}$  estimated [6] from the available data are given in Table 5. It should be noted that the substituent factors,  $F(X)$ , given in Table 5 are applicable to H-atom abstraction from C-H bonds only, i.e., for CH<sub>x</sub>NH<sub>y</sub> compounds. A comparison of the calculated and experimental room temperature rate constants for the amines and related compounds and for S- containing compounds is given in Figure 2, and again the calculated and experimental data agree to within a factor of 2 (which may not be surprising, since essentially the entire data set was used to derive the necessary parameters).

Table 5. Substituent factors  $F(X)$  for H-atom abstraction from C-H bonds and group rate constants at 298 K for OH radical reaction with thiols, sulfides, disulfides, amines and related organics [6]

Substituent group X	$F(X)$
$-SH$	9.0
$-S-$	
$-SS-$	
$-NH_2$	10
$-NH-$	
$-N<$	
$-NNO$	
$-NNO_2$	
	$10^{12} \times k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
$-SH$	31
$-S-$	2.0 <sup>a</sup>
$-SS-$	~200
$-NH_2$	20
$>NH$	60
$>N-$	60
$>NNO$	0
$>NNO_2$	

<sup>a</sup>Applicable only for 760 torr total pressure of air and 298 K [6].

#### Phosphorus-containing organics

A large number of phosphorus-containing organic compounds are used in industrial and agricultural operations. However, for these compounds, kinetic data currently are available for only six compounds of the general structure:



where X = O and/or S and R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> [11-13]. The experimental data show that  $k(\text{P}=\text{O}) \sim$  zero;  $k(\text{P}=\text{S}) = 5.5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; and  $F(-\text{OP}-) = F(-\text{SP}-) = 20$  (which can be compared to  $F(-\text{O}-) = 6.1$ , indicating that the  $-\text{OCH}_3$  and  $-\text{SCH}_3$  groups bonded to a P-atom

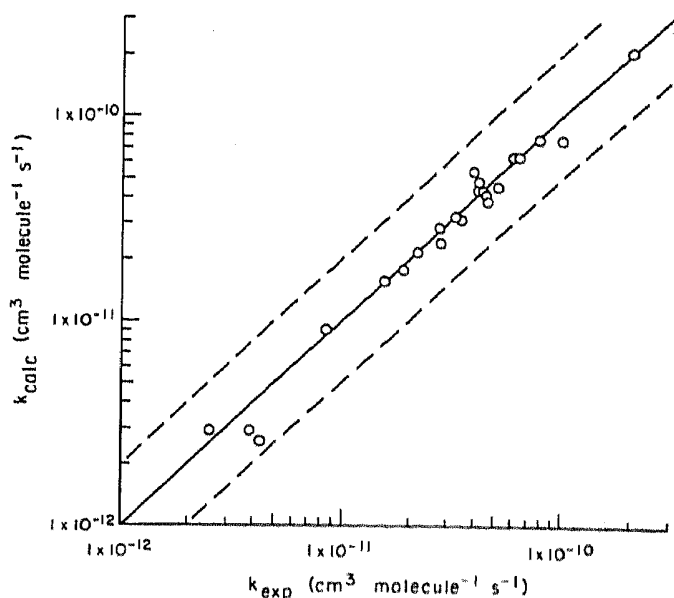


Fig. 2. Plot of calculated versus experimentally measured room temperature rate constants for the gas-phase reaction of the OH radical with sulfur- and nitrogen-containing aliphatic compounds. The solid line indicates perfect agreement; the dashed lines indicate disagreement by a factor of 2.

are more reactive than the  $-OCH_3$  groups in the aliphatic ethers).

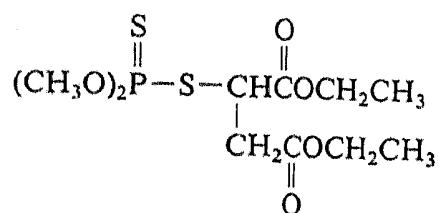
A comparison of the calculated and measured room temperature rate constants for these six phosphorus-containing compounds is given in Table 6. The agreement is excellent, and the data show that the inclusion of a  $P=S$  system leads to a high reactivity, with a calculated atmospheric lifetime of about 4 h for a daytime OH radical concentration of  $1 \times 10^6$  molecule  $cm^{-3}$  [14].

Table 6. Comparison of experimental and calculated room temperature rate constants for reactions of OH radicals with phosphorus-containing organics

Compound	$10^{12} \times k$ ( $cm^3$ molecule $^{-1}$ s $^{-1}$ )	
	Calculated	Observed <sup>a</sup>
$(CH_3O)_3PO$	8.6	7.4
$(CH_3O)_2P(O)SCH_3$	8.6	9.2
$(CH_3S)_2P(O)OCH_3$	8.6	9.5
$(CH_3O)_3P(S)$	64	70
$(CH_3O)_2P(S)SCH_3$	64	56
$(C_2H_5O)_3PO$	51	55

<sup>a</sup>From references 11, 12 and 13.

As an example, the rate constant for malathion,



is calculated as

$$\begin{aligned}
 k &= 2k_{\text{prim}}^{\circ} F(-\text{CH}_2-) \\
 &+ 2k_{\text{sec}}^{\circ} F(-\text{CH}_3)F(-\text{OC(O)R}) \\
 &+ k_{\text{sec}}^{\circ} F(>\text{CH-})F(-\text{C(O)OR}) \\
 &+ k_{\text{tert}}^{\circ} F(-\text{SP-})F(-\text{CH}_2-)F(-\text{C(O)OR}) \\
 &+ k_{\text{P-S}} \\
 &+ 2k_{\text{prim}}^{\circ} F(-\text{OP-}) \\
 &= 6.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K}
 \end{aligned}$$

## CONCLUSIONS

A technique for calculating rate constants for the reaction of OH radicals with organic compounds under atmospheric conditions has been developed and tested against the available database [2,5,6]. Only for 18 out of a total of about 300 organic compounds do the calculated and experimental room temperature OH radical reaction rate constants disagree by more than a factor of 2 [6]. While essentially the entire kinetic database available has been used in developing this estimation procedure, it is expected that OH radical reaction rate constants can be calculated with similar accuracy for organic chemicals for which experimental data do not exist.

While the rate constants for the reactions of organic compounds with the OH radical can be measured to an accuracy of often 25% or better, and often can be estimated to within a factor of 2, the calculated atmospheric lifetimes are much more uncertain because of the large uncertainties in our understanding of the ambient atmospheric concentrations of the OH radical. Thus, the ambient atmospheric OH radical concentrations at any given time and/or place must be judged to be uncertain to a factor of at least 5, and more likely 10 [15]. The diurnally and annually averaged tropospheric OH radical concentrations appear to

be better known, to within possibly a factor of less than 2 [14], being calculated to be about  $5 \times 10^5$  and  $6 \times 10^5$  molecule  $\text{cm}^{-3}$  in the northern and southern hemispheres, respectively.

It is evident that further experimental work is necessary to provide kinetic and mechanistic information for several classes of organic compounds, especially those containing N, S and P heteroatoms and for compounds containing multiple nonalkyl substituent groups.

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