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DETERMINATION OF RATES OF REACTION

IN THE GAS-PHASE IN THE TROPOSPHERE

THEORY AND PRACTICE

5. Rate of Indirect Photoreaction: Evaluation of the Atmospheric Oxidation Computer Program of Syracuse Research Corporation for Estimating the Second-Order Rate Constant for the Reaction of an Organic Chemical with Hydroxyl Radicals

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Abstract

Atkinson (of the University of California at Riverside), in support of the research programs of the Exposure Assessment Branch, Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, developed structure/reactivity relationships (S/R) for estimating the second-order rate constant for the reaction of hydroxyl radicals with organic chemicals in the gas-phase in the troposphere (k_{OH}). Meylan, of Syracuse Research Corporation, computerized these S/R relationships and, in addition, developed S/R relationships for a few other classes of organic chemicals. This computer program is called the Atmospheric Oxidation Program (AOP)[1]. Furthermore, at the request of Leifer, Meylan incorporated a data base of the experimental values of k_{OH} for a large number of organic chemicals in AOP[2].

This computer program is operated by inserting in it the SMILES notation for a given molecular structure. This SMILES notation is a machine-readable code for the molecular structure of an organic chemical. AOP then estimates k_{OH}, lists an experimental value (if available from the scientific literature),

[1] This computer program also contains S/R relationships of Atkinson for estimating the second-order rate constant for the reaction of organic chemicals with ozone (k_{O_3}) in the gas-phase in the troposphere. This report, however, will only review the hydroxyl radical portion of this computer program.

[2] AOP also lists the experimental values of k_{O_3}, if available; and also lists the experimental values of k_{NO_3} for the reaction of an organic chemical with nitrate radicals (NO_3), if available.

gives a detailed description of the calculations, and estimates the half-life in the troposphere for this chemical. This computer program was thoroughly evaluated by comparing the estimated and experimental values of k_{OH} from AOP with the hand calculated and experimental values of Leifer for 454 organic compounds covering a wide variety of classes of compounds. These k_{OH} data are listed in Tables 14-30.

When comparing the estimated values of k_{OH} by AOP and those by Leifer in a hand calculation (HC), a few comments can be made about the number of significant figures used. In general, the summary table in AOP lists k(i) and k_{OH} (the rate constant corresponding to each individual reaction pathway i and the total hydroxyl radical rate constant k_{OH}, respectively) with up to a maximum of six significant figures. However, the group rate constants (e.g., k_p^o, k_s^o, k_t^o, k_o^{is}, k_o^{co}, k(>N-), k(-SH), etc.) and the substituent factors F(i) and C(i) [e.g., F(-CH_2-), F(-Cl), F(>N-H), F(for strained rings containing n atoms), C(-F), C(=O), C(-C≡N), etc.] are known, at best, to three significant figures and, in general, to two significant figures. Therefore, it is recommended that AOP show the detailed calculations to four significant figures and list k(1a), k(1c), k(>N-), $k_{add,nar}$, $k_{add,ar}$, etc. and k_{OH} in the summary table with three significant figures.

In general, after evaluating all 454 chemicals covering a wide range of chemical classes, it was found that there was excellent agreement between the estimated values of k_{OH} and HC.

Furthermore, the S/R relationships of Meylan for fused ring polyaromatic hydrocarbons are superior to those of Atkinson. In addition, Meylan's S/R relationships have been expanded to cover heterocyclic aromatic compounds such as the thiazoles, oxazoles, pyridines, furans, etc. whereas Atkinson does not have corresponding S/R relationships. However, it must be emphasized that considerably more experimental k_{OH} data are needed for a number of substituted heterocyclic and fused ring polynuclear aromatic hydrocarbons to verify the S/R relationships of Meylan. There are, however, some differences between the estimated values of k_{OH} from AOP and HC for a few classes of compounds which will be described in the following paragraphs.

For the alkyl sulfides (both acyclic and cyclic), a comparison of the estimated values of k_{OH} from AOP and HC indicates that k_{OH} is larger from AOP. The reason for this discrepancy is that k_{OH} was measured in the absence of oxygen and from Atkinson's S/R relationships, k(-S-) = 0 so that only H-atom abstraction is observed. However, AOP estimates k_{OH} by assuming that k(-S-) = 2.0 and not 0. Hence, when estimating k_{OH} for these compounds it is necessary to specify whether the estimation is made under the boundary condition of the presence or absence of oxygen. Therefore, it is recommended that AOP should be modified to take into account this boundary condition.

For the aromatic compounds 3,5-dimethyl phenol, N,N-dimethylaniline, and 2,4-toluenediamine, AOP lists the maximum value for OH addition to an aromatic ring as 200×10^{-12}

$cm^3molecule^{-1}s^{-1}$ [i.e., k(7) = $k_{add,ar}$] where HC lists a maximum value k_{OH} of 200 x $10^{-12}cm^3molecule^{-1}s^{-1}$. Since the maximum allowed collision rate is 200 x $10^{-12}cm^3molecule^{-1}s^{-1}$ [Atkinson (1987)], this boundary condition must be invoked on the estimation of k_{OH} and not on k(7)[=$k_{add,ar}$]. Furthermore, by using this boundary condition, the estimated values of k_{OH} for the above mentioned aromatic compounds are much closer to the experimental values [See Table 28 of this report and Leifer (1992a)]. It should be noted that this comment is only applicable to aromatic compounds and not to all compounds.

For the compounds tetralin, indan, fluorene, and 2,3-dihydrobenzofuran, AOP makes a slight error in estimating the rate constant for the addition of OH radicals to the aromatic ring [i.e., k(7) = $k_{add,ar}$]. For these compounds, AOP uses the incorrect value of $\sigma_m^+(-CH_2-)$ = 0.06 ** instead of the correct value of 0.064 **. Furthermore, the compounds tetralin, indan, and fluorene contain five membered strained rings. In calculating k(1c) for these compounds, AOP makes an error by omitting the ring strain factor F(5) = 0.80. Thus, k(1c) and k_{OH} are erroneous.

Atkinson did not develop S/R relationships for alkyl carboxylic acids, peroxides, sulfoxides, and sulfates because of the very limited availability of experimental k_{OH} data. Meylan did develop S/R relationships for these classes of compounds; however, for a few reasons, these S/R relationships are not valid. For the alkyl carboxylic acids and hydroperoxides,

Meylan made an erroneous assumption about the mechanism of OH reaction for these compounds. For example, for the S/R relationships of the alkyl carboxylic acids, Meylan assumed that OH radicals can react with these compounds by H-atom abstraction from the hydroxyl group in the carboxylic acid group {C(=O)OH, [k(2)]} and from the C-H groups in the alkyl group [k(1a)] and that the dominant reaction pathway was H-atom abstraction from the alkyl group. As a result, Meylan assumed that k(-OH) = 0.036, the same value as assigned to H-atom abstraction from the hydroxyl group in alcohols and glycols. However, based on the analysis of the experimental data of Wine et al. (1986) and Singleton et al. (1986), Atkinson (1989) and Leifer concluded that the major reaction pathway was H-atom abstraction from the hydroxyl group and k(-OH) > k(1a). Therefore, it is recommended that the S/R relationships for the alkyl carboxylic acids and hydroperoxides be deleted from AOP. More experimental k_{OH} data are needed for additional alkyl carboxylic acids and hydroperoxides to develop reliable S/R relationships.

For the alkyl sulfoxides, Meylan developed S/R relationships by assuming that only C-H abstraction from the alkyl groups occurred. However, intuitively, it is expected that the sulfoxide group would undergo further oxidation to the sulfone. Therefore, considerably more experimental k_{OH} data are needed for additional sulfoxides before reliable mechanisms and S/R relations are developed; and these S/R relationships should be deleted from AOP.

Based on the very limited data of the alkyl sulfates (only dimethyl and diethyl sulfate), Meylan developed S/R relationships for this class of compounds. Comparison of the estimated k_{OH} data with the experimental k_{OH} indicated that dimethyl sulfate gave an error of > +250% and diethyl sulfate gave an error of +540%. These results are very poor so that it is recommended that these S/R relationships be deleted from AOP until considerably more experimental k_{OH} data is available for additional sulfates to develop reliable S/R relationships.

Meylan, in AOP, used the S/R relationships of Atkinson for the nitroalkanes based on the available experimental k_{OH} data for these compounds. However, it must be emphasized that some of the experimental data is suspect because nitroalkanes are very labile to direct photolysis and it is not clear whether photolysis occurred under the experimental conditions of the relative rate study of Nielson et al. (1988) or whether photolysis was taken into account. Therefore, it is recommended that AOP delete these S/R relationships. More reliable experimental k_{OH} data are needed for these nitroalkanes under carefully controlled experimental conditions to eliminate, or account for, direct photolysis in order to develop more reliable S/R relationships.

Comparison of the experimental values of k_{OH} from AOP and Leifer for 454 chemicals indicates that, in general, the agreement is excellent. There are, however, a few differences. The primary difference is related to the number of significant

figures used in AOP. For example, for 2-methylpentane, AOP lists an experimental value of 5.60 while Atkinson (1989) and Leifer (1992a) list a recommended value of 5.6; for 2,3-dimethyl-2-butene, AOP lists a value of 110.0 while the recommended value by Atkinson and Leifer is 110; for dimethylhydroxylamine, AOP lists a value of 90.0 while Atkinson and Leifer recommend a value of 90; for p-cresol, AOP lists a value of 47.0 while Atkinson and Leifer recommend a value of 47; for 4-chlorobiphenyl, AOP lists a value of 3.9 while Atkinson and Leifer list a value of 3.86.

For other chemicals with differences, Leifer lists an average value from the literature while AOP selects one set. For example, for trans-1,4-hexadiene, Leifer lists an average value of 90.6 from two sets of experimental data while AOP selects only one value, namely 90.3; for 2,3-dimethyl-2-pentene, AOP selects one value which is 108.0 while Leifer cites an average value of 103 based on both sets of experimental data. Unless there is good reason for discarding specific sets of experimental k_{OH} data, it is better to use an average value from both sets.

For 12 chemicals, AOP does not list experimental values: for example, four ketenes; Δ^3-carene; sec-butyl acetate; and 2-(chloromethyl)-3-chloro-1-propene. Differences were observed for a few compounds: e.g., for methane, AOP lists a value of 0.00841 while Atkinson and Leifer list a recommended value of 0.00836; for 2-octanone, AOP lists a value of 10.0 while

Atkinson and Leifer list a value of 11.0; for 1,1,1-trifluoroethane, AOP lists a value of 0.017 while Atkinson and Leifer list a value of 0.0017.

I. Introduction

Numerous chemicals, both natural and anthropogenic, are emitted to the troposphere from a variety of sources and may be removed by wet or dry deposition or by three important transformation processes. These three transformation processes are:

(1) direct photoreaction which involves the absorption of sunlight followed by transformation;

(2) indirect photoreaction which involves the reaction of a chemical with hydroxyl radicals (OH); and

(3) oxidation which involves the reaction of a chemical with ozone (O_3).

There is another indirect photoreaction process which involves the reaction of a chemical with nitrate radicals (NO_3) during the night. However, this transformation process only occurs for a few types of chemicals (e.g., olefins, phenols, and cresols); hence, it will not be considered when determining the rate of transformation in the troposphere.

A quantitative measure of the three important transformation processes is given by the rate constants k_{dE}, k_{OH}, and k_{O_3}. The rate constant k_{dE} represents the first-order rate constant for direct photoreaction, while k_{OH} and k_{O_3} represent second-order rate constants for indirect photoreaction and oxidation with OH and O_3, respectively.

The first report in a series titled "DETERMINATION OF RATES OF REACTION IN THE GAS-PHASE IN THE TROPOSPHERE. THEORY AND PRACTICE" describes a hierarchal test scheme for determining the rate constants k_{dE}, k_{OH}, and k_{O_3} and the half-lives $[t_{(1/2)E}]$ for each transformation process and the net half-life in the troposphere [Leifer (1989a)]. The second report describes a screening-level test guideline for determining the maximum rate of direct photoreaction $[k_{dE}]_{max}$ and the minimum half-life $[t_{(1/2)E}]_{min}$ by the use of Ultraviolet-Visible Absorption Spectroscopy [Leifer (1989b)].

The third and fourth reports in this series describe structure/reactivity (S/R) relationships for estimating k_{OH} for the reaction of an organic chemical with hydroxyl radicals in the gas-phase in the troposphere. These methods were developed by Atkinson (1986, 1986a, 1987, 1987a, 1988) for the Exposure Assessment Branch of the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency. Report No. 4 [Leifer (1992b)] represents a test guideline [§796.3900] for use in sections 4 and 5 of the Toxic Substances Control Act; report No. 3 [Leifer (1992a)] represents the technical support document for this test guideline.

Since these S/R relationships are excellent [Leifer (1992a)], they have been computerized by Syracuse Research Corporation [Meylan (1990a, 1990b)]. At the suggestion of Leifer, Syracuse incorporated a data base in this computer program which lists the experimental values of k_{OH} as reported

in the literature [Meylan (1990b)]. This document, describes an assessment of this computer program for estimating k_{OH} and represents report No.5 in this series.

II. Mathematical Synopsis of the Structure/Reactivity Relationships of Atkinson and Meylan

Atkinson (1986, 1986a, 1987, 1987b, 1988, 1988a) critically analyzed the hydroxyl radical rate data (k_{OH}) for a large number of organic chemicals and developed a number of S/R relationships based solely on the molecular structure of these chemicals. In developing these S/R relationships, he assumed that a number of OH radical reaction pathways exist and the various OH radical reaction pathways could be separated and treated individually. Therefore, he calculated rate constants for each of these reaction pathways. The reaction pathways and rate constants for each of these pathways were:

$$k(1) = k \left[\begin{array}{l}\text{H-atom abstraction from acyclic} \\ \text{saturated, cyclic saturated, and} \\ \text{unsaturated C-H groups by OH radicals}\end{array}\right] \quad (1)$$

$$k(2) = k \left[\begin{array}{l}\text{H-atom abstraction from O-H groups} \\ \text{by OH radicals}\end{array}\right] \quad (2)$$

$$k(3) = k \left[\begin{array}{l}\text{OH radical addition to >C=C<,} \\ \text{>C=C-C=C<, -C}\equiv\text{C-, and >C=C=C<,} \\ \text{>C=C=O groups}\end{array}\right] \quad (3)$$

$$k(4) = k \left[\begin{array}{l}\text{OH radical interaction with -SH,} \\ \text{-S-, and -S-S- groups}\end{array}\right] \quad (4)$$

$$k(5) = k \left[\begin{array}{l}\text{OH radical interaction with -NH}_2\text{,} \\ \text{>NH, and >N- groups}\end{array}\right] \quad (5)$$

$$k(6) = k \left[\begin{array}{l}\text{OH radical interaction with} \\ \text{phosphorus groups}\end{array}\right] \quad (6)$$

$$k(7) = k \text{ [OH radical addition to aromatic rings]} \quad (7)$$

$$k(8) = k \left[\begin{array}{l}\text{OH radical addition to fused ring} \\ \text{polyaromatic compounds (i.e.,} \\ \text{polyaromatic hydrocarbons)}\end{array}\right] \quad (8)$$

Atkinson postulated that the overall OH radical rate constant k_{OH} is equal to the sum of the rate constants for each of these reaction pathways. Therefore, the OH radical rate constant is given by the equation

$$k_{OH} = \sum_{i=1}^{8} k(i) \quad (9)$$

and the individual rate constants [k(1), k(2), $\cdots\cdots$, k(8)] and k_{OH} are all in the units $cm^3 molecule^{-1} s^{-1}$. Structure/reactivity relationships will be described for each of these reaction pathways.

Pathway 1: H-atom abstraction from acyclic and cyclic saturated and unsaturated C-H groups by OH radicals

The overall rate constant for reaction pathway 1 is given by the equation

$$k(1) = k(1a) + k(1c) + k(1, \text{ UNS CH}) \quad (10)$$

where k(1a) represents the rate constant for H-atom abstraction from all acyclic saturated C-H groups by OH radicals at 298 K;

k(1c) represents the rate constant for H-atom abstraction from all cyclic saturated C-H groups by OH radicals at 298 K; and k(1, UNS CH) represents the rate constant for H-atom abstraction from all unsaturated C-H groups (e.g.,=C-H) by OH radicals at 298 K.

The rate constant k(1a) is given by the mathematical relationship

$$k(1a) = \sum_{i(a)} k_p^o F_i(X) + \sum_{j(a)} k_s^o F_j(X) F_j(Y) + \sum_{m(a)} k_t^o F_m(X) F_m(Y) F_m(Z) \quad (11)$$

$$k(1c) = \left[\sum_{j(c)} k_s^o F_j(X) F_j(Y) + \sum_{m(c)} k_t^o F_m(X) F_m(Y) F_m(Z) \right] F(n) \quad (12)$$

$$k(1, \text{ UNS CH}) = 0 \quad (13)$$

where k_p^o, k_s^o, k_t^o represent the group rate constants for primary (CH_3-), secondary (>CH_2), and tertiary (>CH-) groups, respectively, and the values for these parameters at 298 K are listed in Table 1 of an EPA report by Leifer (1992a), in Table 1 of a report by Meylan (1990b)[3], and in Table 1, Section IV, of this report; $\sum_{i(a)}$, $\sum_{j(a)}$, $\sum_{m(a)}$, $\sum_{j(c)}$, $\sum_{m(c)}$, represent the summation over all primary acyclic, secondary acyclic, tertiary acyclic, secondary and tertiary cyclic groups, respectively, in

[3] Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1, 1990.

the molecule; F(X), F(Y), F(Z) represent the substituent factors for substituents X, Y, and Z and the values for various substituents at 298 K are listed in Table 2 of an EPA report by Leifer (1992a), in Table 6 of a report by Meylan (1990b)[3], and in Table 2, Section IV, of this report; F(n) represents the ring strain factor for saturated and unsaturated rings and heterocyclic rings containing n (3,4,5) atoms at 298 K and the values are listed in Table 2 of an EPA report by Leifer (1992a), in Table 10 of a report by Meylan (1990b)[3], and in Table 3, Section IV, of this report. For rings with n(6,7,8, etc.), with essentially no ring strain, F(n) ≈ 1.0 at 298 K.

Pathway 2: H-Atom abstraction from -O-H groups in alcohols and glycols by OH radicals

The overall rate constant for reaction pathway 2 is given by the equation

$$k(2) = n(\text{-O-H})\ k(\text{-OH}) \qquad (14)$$

where n(-O-H) represents the number of hydroxyl groups (-O-H) in the molecule; k(-OH) represents the group rate constant for H-atom abstraction from the hydroxyl group in alcohols and glycols and is equal to $0.036 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ at 298 K [Table 1 of an EPA report by Leifer (1992a), in Table 1 of a report by Meylan (1990b)[3], and in Table 1, Section IV, of this report].

Pathway 3: OH radical addition to isolated alkene groups (>C=C<), nonaromatic conjugated groups (>C=C-C=C<), and other unsaturated groups (-C≡C-, >C=C=C<, >C=C=O)

The overall rate constant for reaction pathway 3 is given by the equation

$$k(3) = k_{add,nar}$$

$$= \sum_i k_o^{is} C_i(X) C_i(Y) + \sum_j k_o^{co} C_j(X) C_j(Y) + \sum_m k_o^{ou} C_m(X) C_m(Y) \quad (15)$$

where k_o^{is}, k_o^{co}, k_o^{ou} represent the group rate constants for OH radical addition (add) to isolated (is) carbon-carbon double bonds, nonaromatic (nar) conjugated (co) carbon-carbon bond systems, and other unsaturated (ou) carbon-carbon systems, respectively, and the values of these group rate constants at 298 K are given in Tables 9, 11, and 12, respectively, of an EPA report by Leifer (1992a), in Tables 2, 5, (3 and 4), respectively, of a report by Meylan (1990b)[3], and in Tables 4, 5, (6 and 7), respectively, Section IV, of this report; $\sum_i$, $\sum_j$, $\sum_m$, represent the summation over all isolated carbon-carbon double bond systems, nonaromatic conjugated carbon-carbon double bond systems, and other unsaturated carbon-carbon groups, respectively, in the molecule; C(X) and C(Y) represent the substituent factors at 298 K for substituents X and Y and are listed in Table 10 of an EPA report by Leifer (1992a), in Table

7 of a report by Meylan (1990b)[3], and in Table 8, Section IV, of this report.

Pathway 4: OH radical interaction with -SH, -S-, and -S-S- groups

The overall rate constant for reaction pathway 4 is given by the equation

$$k(4) = n(-SH)k(-SH) + n(-S-)k(-S-) + n(-S-S-)k(-S-S-) \quad (16)$$

where n(-SH), n(-S-), and n(-S-S-) represent the number of -SH, -S-, and -S-S- groups, respectively, in the molecule; k(-SH), k(-S-), k(-S-S-) represent the group rate constants for OH radical interaction with the -SH, -S-, and -S-S- groups, respectively, and the values of these group rate constants at 298 K are listed in Table 1 of an EPA report by Leifer (1992a), in Table 1 of a report by Meylan (1990b)[3], and in Table 1, Section IV, of this report.

Pathway 5: OH radical interaction with $-NH_2$, >NH, and >N- groups

The overall rate constant for reaction pathway 5 is given by the equation

$$k(5) = n(-NH_2)k(-NH_2) + n(>NH)k(>NH) + n(>N-)k(>N-) \quad (17)$$

where $n(-NH_2)$, n(>NH), n(>N-) represent the number of $-NH_2$, >NH, and >N- groups, respectively, in the molecule; $k(-NH_2)$, k(>NH), k(>N-) represent the group rate constants for $-NH_2$, >NH, and >N-, respectively, and the values of these group rate constants

at 298 K are listed in Table 1 of an EPA report by Leifer (1992a), in Table 1 of a report by Meylan (1990b)[3], and in Table 1, Section IV, of this report.

Pathway 6: OH radical interaction with phosphorous groups

The overall rate constant for reaction pathway 6 is given by the equation

$$k(6) = n[>P(S)-]k[>P(S)-] + n[>P(O)-]k[>P(O)-] + n[>P(Cl)<]\ k[>P(Cl)<] \quad (18)$$

where n[>P(S)-], n[>P(O)], n[>P(Cl)<] represent the number of >P(S)-, >P(O)-, and >P(Cl)< groups, respectively, in the molecule; k[>P(S)-], k[>P(O)-], k[>P(Cl)<] represent the group rate constants for OH radical interaction with the >P(S)-, >P(O)-, and >P(Cl)< groups, respectively, and the values of these group rate constants at 298 K are listed in Table 1 of an EPA report by Leifer (1992a), in Table 1 of a report by Meylan (1990b)[3], and in Table 1, Section IV, of this report.

Pathway 7: OH radical addition to aromatic rings

The overall rate constant k(7)[=$k_{add,ar}$] for reaction pathway 7 is given by the equation

$$k(7) = k(7A) + k(7B) \quad (19)$$

where k(7A) corresponds to the addition of OH radicals to an aromatic ring (ar) and k(7B) corresponds to OH reaction with an heteroaromatic (monocyclic) ring (ar').

For reaction of OH radicals with an aromatic ring

$$k(7A) = k_{add,ar} \tag{20}$$

$$\log_{10} k'_{add,ar} = \sum_i \left[0.31 - 1.35 \text{ Min } \left(\sum_j \sigma_j^+ \right) \right] \tag{21}$$

$$k_{add,ar} = 10^{-12} \, k'_{add,ar} \tag{22}$$

where $\sum_i$ represents the summation over all aromatic rings in the molecule; $\left(\sum_j \sigma_j^+ \right)$ represents the summation of the electrophilic substituent constants of Brown and Okamoto (1958) with respect to a given ring position (i.e., ortho, meta, para); and Min$\left(\sum_j \sigma_j^+ \right)$ σ_j^+) represents the summation of the electrophilic substituent constants with respect to the ring hydrogen position that gives the most negative summation value (i.e., Min). Electrophilic substituent constants (σ_m^+ and σ_p^+) for a number of substituents are given in Table 22 of an EPA report by Leifer (1992a), in Table 8 of a report by Meylan (1990b)[3], and in Table 9, Section IV, of this report.

Atkinson did not develop S/R relationships for OH radical addition to a heteroaromatic ring (monocyclic) while Meylan (1990b)[4] did develop S/R relationships. For OH radical addition to the heteroaromatic ring (ar'), AOP uses the equation

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[4] User's Guide for the Atmospheric Oxidation Program, Version 1.10, November 1, 1990.

$$k(7B) = k_{add,ar'} \quad (23)$$

$$\log_{10}k_{add,ar'} = \sum_i \left[A_i - 1.35 \text{ Min } (\sum_j \sigma_j^+) \right] \quad (24)$$

where $\sum_i$ represents the summation over all heteroaromatic rings, A_i is a function of the experimental value of $k_{add,ar'}$ of the basic, or parent, heteroaromatic ring in the units 10^{-12} $cm^3molecule^{-1}s^{-1}$ [Table 10, Section IV, of this report and on page 7 of a document by Meylan (1990b)[4]]; and the other parameters have been described previously. The use of equations 23 and 24 will be discussed in more detail in Section IV.B.

Pathway 8: OH radical addition to fused ring polyaromatic compounds

The overall rate constant k(8) for reaction pathway 8 is given by the equation

$$k(8) = k(8A) + k(8B) \quad (25)$$

where k(8A) corresponds to the addition of OH radicals to a polynuclear aromatic hydrocarbon ring (PAH) and k(8B) corresponds to the OH radical addition of OH radicals to a polynuclear heteroaromatic ring (PAH'). For OH addition to the polyaromatic hydrocarbon ring

$$k(8A) = k_{add,PAH} \quad (26)$$

$$\log_{10}k'_{add,PAH} = \sum_i \left[10.11 - 1.08 \ (IP)_i - 1.35 \text{ Min}(\sum_j \sigma_j^+) \right] \quad (27)$$

$$k_{add,PAH} = 10^{-12} k'_{add,PAH} \quad (28)$$

where $\sum_i$ represents the summation of all PAHs, $(IP)_i$ represents the ionization potential of the parent PAH in electron volts (eV) obtained from Weast (1976-1977); ($\sum_j \sigma_j^+$) is derived for the monocyclic substituted portion of the molecule to allow for the effects of substituent groups on the reactivity and represents the summation of the electrophilic substituent constants of Brown and Okamoto (1958) with respect to a given ring position (i.e., ortho, meta, para); and Min ($\sum_j \sigma_j^+$) represents the summation of the electrophilic substituent constants with respect to the ring hydrogen position that gives the most negative summation (i.e., Min). Electrophilic substituent constants (σ_m^+ and σ_p^+) for a number of substituents are given in Table 22 of an EPA report by Leifer (1992a), in Table 8 of a report by Meylan (1990b)[3], and in Table 9, Section IV, of this report.

For OH radical addition to fused polynuclear aromatic hydrocarbon rings, Meylan (1990b)[3], developed a different approach to estimate $k_{add,PAH}$. Meylan, in AOP, uses the equation

$$\log_{10} k_{add,PAH} = \sum_i \left[B_i - 1.35\ de_j^+ \right] \quad (29)$$

where $\sum_i$ represents the summation over all fused polynuclear aromatic hydrocarbon rings, B_i is a function of the experimental value of $k_{add,PAH}$ of the basic, or parent, polynuclear hydrocarbon aromatic ring in the units $10^{-12} cm^3 molecule^{-1} s^{-1}$

[Table 11, Section IV, of this report and from Meylan (1990b)[4] for naphthalene, anthracene, and phenanthrene] or is given an assigned value based primarily on the experimental ionization potential of the basic, or parent, polynuclear aromatic hydrocarbon ring in the units $10^{-12}cm^3molecule^{-1}s^{-1}$ [Table 12, Section IV, of this report and from Meylan (1990b)[4]] for 4, 5, and 6 fused benzene rings. The term de_j^+ is related to the substituent factors σ_m^+ and σ_p^+ for various substituents and is determined in the following way. For monosubstituted PAH compounds, de_j^+ corresponds to the most negative value of σ_m^+ or σ_p^+ for a given substituent on the ring. For polysubstituted PAH compounds, de_j^+ corresponds to the sum of the average values of σ_m^+ and σ_p^+ for each substituent on both rings.

For OH radical addition to polynuclear heteroaromatic rings (PAH'), Meylan (1990b)[4] uses a modified form of equation 29 which is

$$\log_{10}k_{add,PAH'} = \sum_i \left[B_i' - 1.35\ de_j^+ \right] \qquad (30)$$

where B_i' is now related to the experimental ionization potential of the basic, or parent, fused polynuclear heteroaromatic ring in the units $10^{-12}cm^3molecule^{-1}s^{-1}$ [obtained from Table 13, Section IV, of this report for a few fused polynuclear heteroaromatic rings and from Meylan (1990b)[4]]. The term de_j^+ is the same as the one described previously. It should be noted that at present, AOP cannot estimate $k_{add,PAH'}$ for fused ring structures contain-

ing five-membered heterocyclic rings. The use of equations 29 and 30 will be discussed in more detail in Section IV.B.

III. Syracuse Research Corporation Atmospheric Oxidation Computer Program (Developed by Meylan)

III.A. Introduction

The Atmospheric Oxidation Computer Program [designated as AOP] was purchased from Syracuse Research Corporation by the Exposure Assessment Branch of the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency, based on the recommendation of Leifer. The first version, labeled Version 1.00, was received July 10, 1990 [Meylan (1990a)]. The Atmospheric Oxidation Program estimates the second-order rate constant for the reaction of an organic chemical with hydroxyl radicals (k_{OH}) and ozone (k_{O_3}) in the gas-phase. These rate constants are then used to calculate the half-life [$t_{(1/2)E}$] for these two reaction pathways based on average hydroxyl radical and ozone concentrations in the troposphere.

Based on a very preliminary evaluation of the hydroxyl radical portion of this program, a few errors were uncovered. After a discussion by phone with Meylan on August 2, 1990, changes were made in the hydroxyl radical portion of this program. The new AOP computer program, Version 1.30, was received on November 1, 1990 and contained a data base for experimental values for the reaction of organic chemicals with hydroxyl radicals (k_{OH}), ozone (k_{O_3}), and nitrate radicals (k_{NO_3}). This report covers the evaluation of the hydroxyl

radical portion of AOP. Future EPA reports will be devoted to the discussion of the S/R relationships of Atkinson and Carter (1984) for ozone and the evaluation of AOP for estimating k_{O_3} and the corresponding half-life [$t_{(1/2)E}$].

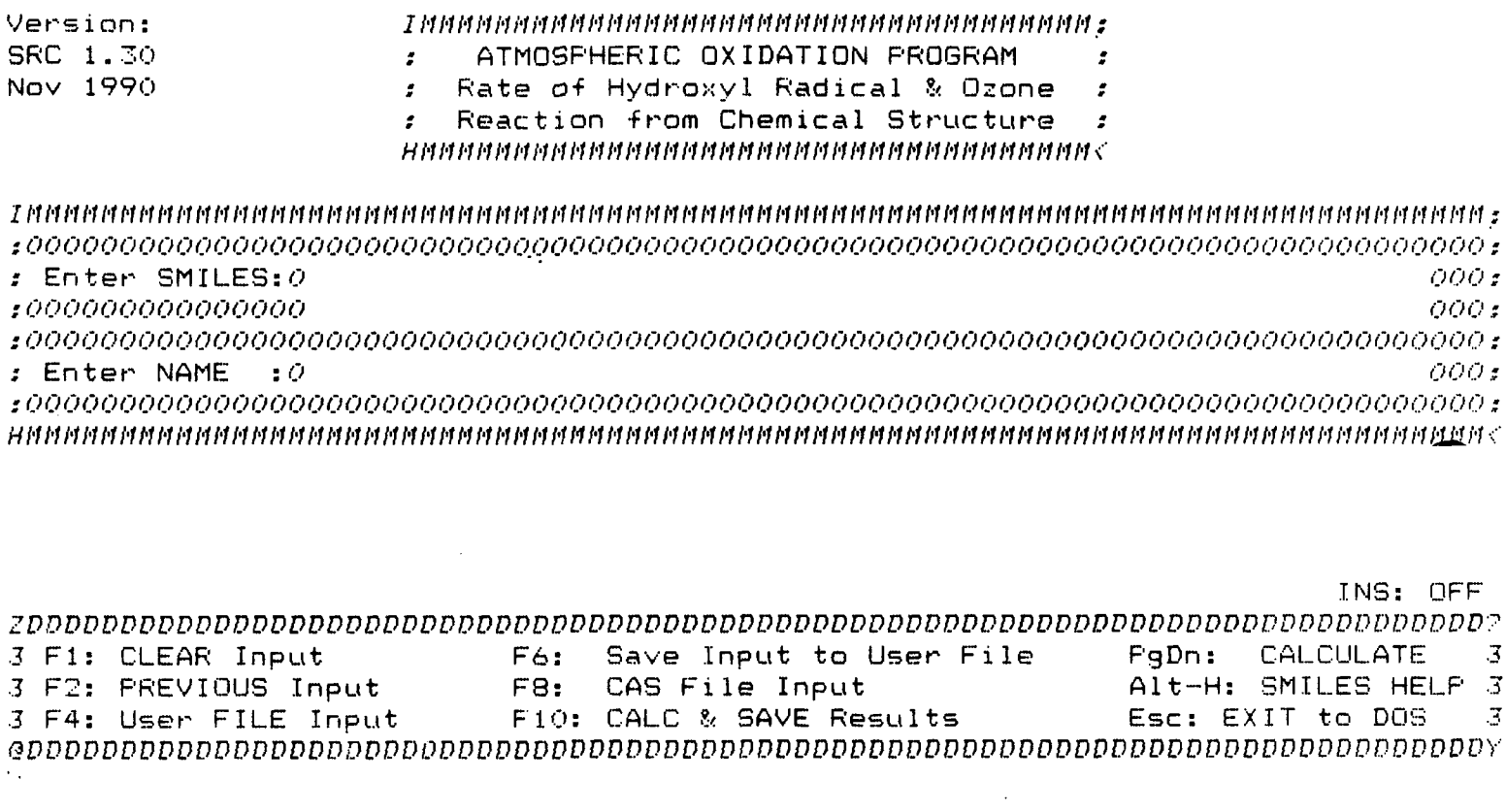
III.B. Atmospheric Oxidation Computer Program (AOP)

The estimation methods used in AOP are based on the structure/reactivity relationships of Atkinson (1986, 1986a, 1987, 1987a, 1988, 1988a) for the gas-phase reaction of hydroxyl radicals with organic chemicals in the troposphere as described in detail in the report by Leifer (1992a) and the structure/ reactivity relationships of Atkinson and Carter (1984) for the gas-phase reaction of ozone with organic chemicals in the troposphere. As stated in Section III.A., only the AOP program for estimating k_{OH} and $t_{(1/2)E}$ will be discussed in this report.

AOP has been designed for use in an IBM or an IBM-compatible series of personal computers running the MS-DOS or PC-DOS operating systems. Approximately 350 K of free memory are required to run AOP. All program outputs occur in the text mode and are run from a floppy disk drive.

The AOP program is started by pressing key F-8 of the Workstation Menu, typing in AOP, and then pressing the Enter key. Program execution begins by displaying the data input screen shown in Figure 1. The program version and date are displayed in the upper left corner of the screen. The present version is specified in three lines:Version:/SRC 1.30/Nov 1990. The large

Figure 1. Atmospheric Oxidation Program Data Entry Display



rectangular box in the upper center of the screen contains the program name and purpose. A large box in the middle portion of the screen is used to enter the SMILES notation corresponding to the chemical to be used in the estimation. The SMILES notation is a computer readable molecular structure system. Currently, a maximum of 120 characters are allotted for the SMILES notation. Directly below the Enter SMILES box, is a box with Enter NAME. This box is used to enter the name of the chemical and a maximum of 60 characters are allotted for this purpose. The blank space in the lower portion of the screen is used to display error messages corresponding to the SMILES entry. Finally, the lower box contains the various edit keys. The reader is referred to the USERS GUIDE for AOP, Version 1.10, prepared by William Meylan of Syracuse Research Corporation, for a detailed discussion of the operation of AOP.

The only data required for AOP to produce estimated and experimental values of k_{OH} and $t_{(1/2)E}$ is the SMILES notation corresponding to the molecular structure of the chemical. The name of the chemical is optional and is not required to run AOP. As an illustration of the operation of AOP and the output data to the monitor screen, consider the chemical α-methyl styrene, (2-phenyl-1-propene) which has a SMILES notation C=C(C)c1ccccc1. This SMILES notation is entered at the point adjacent to the ENTER SMILES notation on the screen and pressing key PgDn. If the SMILES notation is correct, the data entry screen is removed and the k_{OH} data are displayed on the screen, Figure 2.A. The

Figure 2. Atmospheric Oxidation Program Data Display for the Compound α-Methyl Styrene (2-Phenyl-1-Propene): Summary Hydroxyl Radical Data and Experimental Data.

Figure 2A

A. Screen Display when Key PgDn is pressed.

```
SMILES : C=C(C)c1ccccc1
CHEM   :
MOL FOR: C9 H10
MOL WT : 118.18
------------------------- SUMMARY: HYDROXYL RADICALS -------------------------
Hydrogen Abstraction       =     .1440 E-12 cm3/molecule-sec
Reaction with N, S and -OH =     .0000 E-12 cm3/molecule-sec
Addition to Triple Bonds   =     .0000 E-12 cm3/molecule-sec
** Addition to Olefinic Bonds =  51.4000 E-12 cm3/molecule-sec
** Addition to Aromatic Rings =   1.9187 E-12 cm3/molecule-sec
Addition to Fused Rings    =     .0000 E-12 cm3/molecule-sec

   OVERALL yOH Rate Constant =  53.4627 E-12 cm3/molecule-sec
   HALF-LIFE =       .300 Days (at conc 5E5 yOH/cm3)
.......................  ** Designates Estimation(s) Using ASSUMED Value(s)
     ZDDDDDDDDDDDDDDDDDDDDD4 EXPERIMENTAL DATA CDDDDDDDDDDDDDDDDDDDDDDDDD?
-----3                                                                    3--
   OV3 Name:  2-Phenyl-1-propene (α-methyl styrene)                       3
   HA3 CAS Number:  00098-83-9                                            3
     3 Exper OH rate constant    :  52.0  E-12  cm3/molecule-sec          3
     3 Exper Ozone rate constant :  ---  cm3/molecule-sec                 3
     3 Exper NO3 rate constant   :  ---  cm3/molecule-sec                 3
     3                                                                    3
     3                                                                    3
     @DDDDDDDDDDDDDDDDDDD4 Press any key to continue... CDDDDDDDDDDDDDDDDDDDY
```

Figure 2B

B. Screen Display when Key F-10 is pressed.

```
SMILES : C=C(C)c1ccccc1                                  IMMMMMMMMMMMMMMMMMMMMMMM;
CHEM   :                                                 ;  Summary Saved to:   ;
MOL FOR: C9 H10                                          ; file --> AOP1.DAT    ;
MOL WT : 118.18                                          HMMMMMMMMMMMMMMMMMMMMMMM<
------------------------- SUMMARY: HYDROXYL RADICALS -------------------------
Hydrogen Abstraction          =     .1440 E-12 cm3/molecule-sec
Reaction with N, S and -OH =     .0000 E-12 cm3/molecule-sec
Addition to Triple Bonds    =     .0000 E-12 cm3/molecule-sec
** Addition to Olefinic Bonds =   51.4000 E-12 cm3/molecule-sec
** Addition to Aromatic Rings =    1.9187 E-12 cm3/molecule-sec
Addition to Fused Rings      =     .0000 E-12 cm3/molecule-sec

   OVERALL yOH Rate Constant =   53.4627 E-12 cm3/molecule-sec
   HALF-LIFE =       .300 Days (at conc 5E5 yOH/cm3)
 ..........................  ** Designates Estimation(s) Using ASSUMED Value(s)
     ZDDDDDDDDDDDDDDDDDDDDD4 EXPERIMENTAL DATA CDDDDDDDDDDDDDDDDDDDDDDDDDD?
 ----3                                                                    3--
   OV3 Name:  2-Phenyl-1-propene (α-methyl styrene)                       3
   HA3 CAS Number:  00098-83-9                                            3
     3 Exper OH rate constant    :  52.0  E-12  cm3/molecule-sec          3
     3 Exper Ozone rate constant :  ---  cm3/molecule-sec                 3
     3 Exper NO3 rate constant   :  ---  cm3/molecule-sec                 3
     3                                                                    3
     3                                                                    3
     @DDDDDDDDDDDDDDDDDDD4 Press any key to continue... CDDDDDDDDDDDDDDDDDDDY
```

SMILES notation, molecular formula, and molecular weight of α-methyl styrene are displayed at the top left portion of the screen. Directly below these data and in the center of the screen, this figure displays the SUMMARY: HYDROXYL RADICALS data and the EXPERIMENTAL DATA. Directly under SUMMARY: HYDROXYL RADICALS, the estimated rate constants for each of the specific reaction pathways (k_i) for α-methyl styrene are listed. Immediately below the summary data, the overall k_{OH} rate constant {which represents the sum of each of the individual rate constants [k(i)]} and the corresponding half-life are listed. The half-life (in days) corresponds to an average OH radical concentration of 5E5 radicals cm^{-3} and a 24-hour daylight day.

The table in the lower box summarizes the available experimental k_{OH}, k_{O_3}, and k_{NO_3} data for this compound. The experimental value of k_{OH} is listed as 52.0 E-12 $cm^3molecule^{-1}s^{-1}$ as obtained from Atkinson (1989). No experimental rate data are available for the reaction of α-methyl styrene with ozone (k_{O_3}) and with nitrate radicals (k_{NO_3}). If, after the SMILES notation for α-methyl styrene is entered, key F-10 is pressed instead of PgDn, the results are then displayed on the screen as shown in Figure 2.B. In this case, the estimated and experimental data are the same as the data in Figure 2.A. except that the estimated data are now stored in a file as indicated in the top right corner box.

Pressing key PgDn displays the same OH rate data but now the SUMMARY: OZONE REACTION data replaces the available experimental

data, Figure 3A. The ozone data corresponds to the overall estimated ozone rate constant (k_{O_3}) and the associated half-life [$t_{(1/2)E}$] in days corresponding to an average ozone concentration of 7E11 molecules cm^{-3} and a 24-hour day. If, after the SMILES notation for α-methyl styrene is entered, key F-10 is pressed twice, then the results are depicted in Figure 3.B. In this case, the estimated data is the same as the data displayed in Figure 3.A. except that the data is now stored in a file as indicated in the box in the upper right corner.

When pressing key F-9 five times, the screen displays sequentially for α-methyl styrene:

(1) the detailed calculations for hydrogen abstraction [k(1a)], Figure 4.A.;

(2) OH addition to the olefinic group [k(3) = $k_{add,nar}$], Figure 4.B.;

(3) ozone reaction with the olefinic group, Figure 5.A.;

(4) OH addition to the aromatic ring (ar) [k(7A) = $k_{add,ar}$], Figure 5.B; and

(5) Figure 6, which corresponds to the same estimated data for OH addition to the aromatic ring (Figure 5.B.) and the experimental data in the lower box corresponds to the same experimental data displayed in Figure 2.A.

If key F-9 is pressed again five times, the same sequence of data is displayed as described above. Pressing any key but F-9 returns the screen display to Figure 1 for entry of a SMILES notation for another compound. If key F-2 is pressed, Figure 1

Figure 3. Atmospheric Oxidation Program Data Display for the Compound α-Methyl Styrene (2-Phenyl-1-Propene): Summary Hydroxyl Radical and Ozone Data.

Figure 3A

A. Screen Display when Key PgDn is pressed.

```
SMILES : C=C(C)c1ccccc1
CHEM   :
MOL FOR: C9 H10
MOL WT : 118.18
------------------------- SUMMARY: HYDROXYL RADICALS -------------------------
Hydrogen Abstraction       =     .1440 E-12 cm3/molecule-sec
Reaction with N, S and -OH =     .0000 E-12 cm3/molecule-sec
Addition to Triple Bonds   =     .0000 E-12 cm3/molecule-sec
** Addition to Olefinic Bonds =  51.4000 E-12 cm3/molecule-sec
** Addition to Aromatic Rings =   1.9187 E-12 cm3/molecule-sec
Addition to Fused Rings    =     .0000 E-12 cm3/molecule-sec

   OVERALL yOH Rate Constant =  53.4627 E-12 cm3/molecule-sec
   HALF-LIFE =       .300 Days (at conc 5E5 yOH/cm3)
.......................  ** Designates Estimation(s) Using ASSUMED Value(

------------------------- SUMMARY: OZONE REACTION ----------------------------
   OVERALL OZONE Rate Constant =    13.650000 E-17 cm3/molecule-sec
   HALF-LIFE =       .084 Days (at conc 7E11 mol/cm3)



 Press F9 to Show Calc          Press ESC to STOP....anything else to continue
```

Figure 3B

B. Screen Display when Key F-10 is pressed.

```
SMILES : C=C(C)c1ccccc1                                  IHHHHHHHHHHHHHHHHHHHHHHH
CHEM   :                                                 :  Summary Saved to:
MOL FOR: C9 H10                                          : file --> AOP1.DAT
MOL WT : 118.18                                          HHHHHHHHHHHHHHHHHHHHHHHH
------------------------- SUMMARY: HYDROXYL RADICALS --------------------------
Hydrogen Abstraction          =     .1440 E-12 cm3/molecule-sec
Reaction with N, S and -OH =     .0000 E-12 cm3/molecule-sec
Addition to Triple Bonds    =     .0000 E-12 cm3/molecule-sec
** Addition to Olefinic Bonds =  51.4000 E-12 cm3/molecule-sec
** Addition to Aromatic Rings =   1.9187 E-12 cm3/molecule-sec
Addition to Fused Rings     =     .0000 E-12 cm3/molecule-sec

   OVERALL yOH Rate Constant =  53.4627 E-12 cm3/molecule-sec
   HALF-LIFE =       .300 Days (at conc 5E5 yOH/cm3)
.......................  ** Designates Estimation(s) Using ASSUMED Value(s)

------------------------ SUMMARY: OZONE REACTION ----------------------------
   OVERALL OZONE Rate Constant =    13.650000 E-17 cm3/molecule-sec
   HALF-LIFE =       .084 Days (at conc 7E11 mol/cm3)



Press F9 to Show Calc          Press ESC to STOP....anything else to continue
```

Figure 4. Atmospheric Oxidation Program Data Display for the Compound α-Methyl Styrene (2-Phenyl-1-Propene):

Figure 4A

A. Screen Display of the Detailed Calculations for Hydrogen Abstraction.

Hydrogen Abstraction

Kprim = 0.144 F(>C=C<) = 0.144 (1.000) = .144

H Abstraction TOTAL = .144 E-12 cm3/molecule-sec

Press any key to continue

Figure 4B

B. Screen Display of the Detailed Calculations for OH Radical Addition to the Olefinic Bond.

OH Addition to Olefinic Bonds

Kd = K(CH2=C<)C(-Phenyl **)
= 51.400(1.00) = 51.400 E-12 cm3/molecule-sec

..... ASSUMED Value designated by: **

Press any key to continue

Figure 5. Atmospheric Oxidation Program Data Display for the Compound α-Methyl Styrene (2-Phenyl-1-Propene):

Figure 5A

A. Screen Display of the Detailed Calculations with O_3 Reaction with the Olefinic Bond.

Ozone Reaction with Olefins

Ko = K(CH2=C-R2)Ox(-CH3)Ox(-Aromatic)
= .175000(6.500)(12.000) = 13.650000 E-17 cm3/molecule-sec

Press any key to continue

Figure 5B

B. Screen Display of the Detailed Calculations of OH Radical Addition to the Aromatic Ring.

OH Addition to Aromatic Rings

de+ = Most negative value of *ep+* or *em+* (-C=C **) = .020
Log Kar = -11.69 - 1.35 *de+* cm3/molecule-sec
Ring #1 Kar = 1.9187 E-12 cm3/molecule-sec

TOTAL Kar = 1.9187 E-12 cm3/molecule-sec

.....Assumed values designated by **

Press any key to continue

Figure 6. Atmospheric Oxidation Program Data Display for the Compound α-Methyl Styrene (2-Phenyl-1-Propene): Screen Display for OH Addition to the Aromatic Ring and the Experimental Data.

```
                    OH Addition to Aromatic Rings
                    -----------------------------

de+ = Most negative value of ep+ or em+ (-C=C **) =     .020
Log Kar = -11.69 - 1.35 de+ cm3/molecule-sec
Ring #1 Kar =   1.9187 E-12 cm3/molecule-sec

TOTAL Kar =   1.9187 E-12 cm3/molecule-sec

.....................Assumed values designated by **
```

```
ZDDDDDDDDDDDDDDDDDDDDD4 EXPERIMENTAL DATA CDDDDDDDDDDDDDDDDDDDDDDDDDD2
3                                                                      3
3 Name:  2-Phenyl-1-propene (α-methyl styrene)                         3
3 CAS Number:  00098-83-9                                              3
3 Exper OH rate constant    :  52.0  E-12  cm3/molecule-sec             3
3 Exper Ozone rate constant :  ---  cm3/molecule-sec                   3
3 Exper NO3 rate constant   :  ---  cm3/molecule-sec                   3
3                                                                      3
3                                                                      3
@DDDDDDDDDDDDDDDDDDD4 Press any key to continue... CDDDDDDDDDDDDDDDDDDDY
```

is reproduced with the original SMILES notation for α-methyl styrene.

IV. Evaluation of the Atmospheric Oxidation Computer Program for Estimating k_{OH} and the Experimentally Measured k_{OH} Data Listed in the Program

IV.A. Comments on the Group Rate Constants, Substituent Factors, and Other Parameters Used by the Atmospheric Oxidation Program

The group rate constants, substituent factors, and other parameters are listed in Tables 1 through 9 for a large number of classes of compounds as obtained from Meylan (1990b). A few comments will be made in this section on the numerical values of these parameters listed in these tables. More details will be given in Sections IV.C. through IV.F. on specific classes of compounds and specific compounds in each of these classes.

First, consider Table 1 which summarizes the group rate constants for hydrogen abstraction and radical reaction. The value of the group rate constant k(>C<) is listed as zero with one significant figure. However, this value is known much more accurately; conservatively, it is known to three significant figures. Therefore, it is recommended that AOP use k(>C<) = 0.000 which is consistent with the accuracy of the S/R relationships of Atkinson.

Table 1 does not have an entry for H-atom abstraction from unsaturated carbon-carbon functional groups (i.e., =C-H). Even at temperatures up to 500 K, H-atom abstraction from these functional groups is zero [Atkinson (1987)]. Therefore, it is

Table 1. Group Rate Constants for Hydrogen Abstraction and Radical Reaction[1]

Group Rate Constant	k X 10^{12} cm^3/molecule-sec
k(-CH_3)	0.144
k(-CH_2-)	0.838
k(>CH-)	1.83
k(>C<)	0
k(-OH)	0.036[2]
k(-NH_2)	20
k(-NH-)	60
k(>N-)	60
k(-SH)	31[3]
k(-S-)	2.0
k(-S-S-)	200
k(>N-NO)	0
k(>N-NO_2)	0
k[P(=O)]	0
k[P(=S)]	55

[1] Data from Table 1 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

[2] This group rate constant is only applicable to hydroxyl groups in alcohols and glycols.

[3] Used only for aliphatic connections; connection to aromatics not included based upon experimental rate constant for thiophenol.

Table 2. Substituent F(X) Factors for Hydrogen Abstraction[1]

(values marked with "**" are estimated/assumed values)

	Substituent	Factor	
1.	-CH3	1.00	
2.	-CH2-	1.29	
3.	-CH2CL	0.57	
4.	-CH2Br	0.57	
5.	-CH2F	0.85	
6.	-CH2C(=O)-	4.4	
7.	-CH2ONO2	0.30	
8.	-CH2CN	0.5	
9.	-CH2I **	0.57	(given same value as -CH2Br)
10.	>CH-	1.29	
11.	-CHCL2	0.57	
12.	-CHF2	0.10	
13.	-CHBr2 **	0.57	(given same value as -CHCL2)
14.	-CHI2 **	0.57	(given same value as -CHCL2)
15.	>CHC(=O)-	4.4	
16.	>CHONO2	0.30	
17.	>C<	1.29	
18.	-CCL3	0.09	
19.	-CF3	0.075	
20.	-CBr3 **	0.09	(given same values as -CCL3)
21.	-CI3 **	0.09	(given same values as -CCL3)
22.	>CC(=O)-	4.4	
23.	>CONO2	0.30	
24.	-CF2CL	0.025	
25.	-F	0.099	
26.	-CL	0.38	
27.	-Br	0.30	
28.	-I **	0.30	(given same value as -Br)
29.	=O	8.8	
30.	-Aromatic	1.0	
31.	-OH	3.4	
32.	-O-	6.1	
33.	-ONO2	0.18	
34.	-CN	0.14	
35.	-OC(=O)R	1.5	
36.	-C=(O)CL	0.5	
37.	-C(=O)-	0.76	
38.	-CHO	0.76	
39.	-C(=O)OR	0.0	
40.	>C=C<	1.0	
41.	-C≡C-	1.0	
42.	-SH	9.0	

Table 2. Continued

	Substituent	Factor	
43.	-S-	9.0	
44.	-SS-	9.0	
45.	-NH2	10	
46.	-NH-	10	
47.	-N<	10	
48.	-NNO	10	
49.	-NNO2	10	
50.	-NO2	0.18	(new Atkinson value)
51.	-OP-	20	
52.	-SP-	20	
53.	-P- **	1.0	(arbitrarily assigned a value of unity)
54.	=P **	1.0	(arbitrarily assigned a value of unity)
55.	=N **	1.0	(arbitrarily assigned a value of unity)
56.	=S **	9.0	(given same value as sulfur #s 42, 43, 44)
57.	CH-Halogen **	0.57	(estimated by Asa Leifer)
58.	S(+4)=O **	99.0	(based on dimethyl sulfoxide data)
59.	blank	1.0	
60.	Missing	0.0	
61.	-CH-2Halogens **	0.57	(given same value as -CHCL2)
62.	-C-3Halogens **	0.09	(given same value as -CCL3)
63.	-CHF-Halogen **	0.30	(assigned a value between -CHF2 and -CHCL2)
64.	-O-O- **	50	(based on experimental OH rate constants for methyl and t-butyl hydroperoxides)
65.	-O-N= **	2.0	(arbitrarily assigned based on other values for oxygen and nitrogen connections)
66.	>CNO2 **	0.30	(given same value as 68)
67.	>CHNO2 **	0.30	(given same value as 68)
68.	CH2-NO2	0.30	(new nitroalkane data)
69.	CH2-O-	4.50	(new Atkinson value)
70.	2nd -O-	1.00	(new Atkinson value)
71.	Sulfonic acid **	0.20	(arbitrary estimate)
72.	2nd alkyl ketone	1.00	(data for cyclobutanone)
73.	-CH(Halogen)C=O **	3.10	(combination of previous)
74.	-CH(NO2)C=O **	1.3	(combination of previous)
75.	-CH(NO2)Halogen **	0.21	(combination of previous)
76.	>C(NO2)C=O- **	1.3	(combination of previous)
77.	>C(ONO2)C=O- **	1.3	(combination of previous)
78.	-CH(ONO2)C=O **	1.3	(combination of previous)
79.	>C-O- **	4.5	(given same value as CH2-O-)

[1] Data from Table 6 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

Table 3. Factors Used for Aliphatic Ring Strain Effects[1]

	Factor
3-Membered Ring	0.017
4-Membered Ring	0.22
5-Membered Ring	0.80
6-Membered Ring	1.00
7 to 10-Membered Ring	100[2]

[1] Data from Table 10 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

[2] Note: aliphatic rings containing more than 10 members do not have any ring strain effect factor applied to them.

Table 4. Group Rate Constants for OH Radical Addition to Isolated Olefinic Units[1]

Structure		k X 10^{12} cm^3/molecule-sec
CH_2=CH-		26.3
CH_2=CH<		51.4
-CH=CH-	(cis-)	56.1
-CH=CH-	(trans-)	63.7
-CH=C<		86.9
>C=C<		110.0
-CH=CH-	(cyclic)	56.1[2]

[1] Data from Table 2 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

[2] The group rate constant for cyclic alkenes such as cyclopentene and cyclohexene is assumed to be the same as the cis-iosmer value although the trans-isomer value yields slightly better estimates.

Table 5. Group Rate Constants for OH Radical Addition to Conjugated Olefinic Units[1]

No. Alkyl Groups	Structure	k X 10^{12} cm^3/molecule-sec
1	CH_2=CH-CH=CH-	105
1	CH_2=CH-$\overset{|}{C}$=CH_2	105
2	CH_2=CH-CH=C<	135
2	CH_2=CH-$\overset{|}{C}$=CH-	135
2	CH_2=$\overset{|}{C}$-CH=CH-	135
2	-CH=CH-CH=CH-	135
2	CH_2=$\overset{|}{C}$-$\overset{|}{C}$=CH_2	135
3	CH_2=CH-$\overset{|}{C}$=C<	180
3	CH_2=$\overset{|}{C}$-CH=C<	180
3	-CH=CH-CH=C<	180
3	CH_2=$\overset{|}{C}$-$\overset{|}{C}$=CH-	180
3	-CH=CH-$\overset{|}{C}$=CH-	180

Table 5. Continued

No. Alkyl Groups	Structure	k X 10^{12} cm^3/molecule-sec
4	>C=CH-CH=C<	230
4	-CH=C(-)-CH=C<	230
4	-CH=CH-C(-)=C<	230
4	CH_2=C(-)-C(-)=C<	230
4	-CH=C(-)-C(-)-CH-	230
5	>C=C(-)-C(-)=CH-	285[2]
5	>C=CH-C(-)=C<	285[2]
6	>C=C(-)-C(-)=C<	350[2]

[1] Data from Table 5 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

[2] These values have been estimated....estimates are based upon the increasing relationship for the 1 to 4 alkyl group structures.

Table 6. Group Rate Constants for OH Radical Addition to Alkyne Units[1]

Structure	k X 10^{12} cm^3/molecule-sec
CH≡C-	6.4
-C≡C-	29.0

[1] Data from Table 3 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

Table 7. Group Rate Constants for OH Radical Addition to 1,2-Dialkene (Allene) Units[1]

Structure	k X 10^{12} cm^3/molecule-sec
CH_2=C=CH-	31.0
-CH=C=CH-	57.0
CH_2=C=C<	57.0[2]
-CH=C=C<	85.0[2]
>C=C=C<	110.0[2]

[1] Data from Table 4 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

[2] These values have been estimated....the estimates are based upon analogy to the single unit olefin rate constants (see Table 2).

Table 8. Substituent Factors [C(X)] for OH Radical Addition to Olefins and Acetylenes[1]

(values marked with "**" are estimated/assumed values)

	Substituent	Factor	
1.	-F	0.4	
2.	-CL	0.20	
3.	-Br	0.26	
4.	-CH2CL	0.76	
5.	-CN	0.15	
6.	-CHO	0.26	
7.	-C(=O)CH3	0.91	
8.	-OCH3	1.3	
9.	=O	1.0	
10.	-I **	0.26	(given same value as -Br)
11.	-CH2Br **	0.76	(given same value as -CH2CL)
12.	-CH2F **	0.76	(given same value as -CH2CL)
13.	-CH2I **	0.76	(given same value as -CH2CL)
14.	-C=C **	0.85	
15.	not used		
16.	-Phenyl **	1.0	(Atkinson assumption, Int. J. Chem. Kinet. 19:822.)
17.	-C(=O)X **	0.91	(given same value as -C(=O)CH3
18.	-OC **	1.3	(given same value as -OCH3)
19.	-C≡C **	1.10	(based on experimental rate constant for diacetylene)
20.	-S **	1.0	(arbitrarily assigned a value of unity)
21.	-O **	1.0	(arbitrarily assigned a value of unity)
22.	-P **	1.0	(arbitrarily assigned a value of unity)
23.	-NO2 **	0.5	(arbitrary estimate)
24.	-ONO2 **	0.6	(arbitrary estimate)
25.	=S **	1.0	(arbitrarily assigned a value of unity)
26.	-N **	0.6	(arbitrary estimate)
27.	=P **	1.0	(arbitrarily assigned a value of unity)
28.	=N **	1.0	(arbitrarily assigned a value of unity)
29.	cyclic C=O **	0.20	(based on data for naphthaquinone)
30.	Missing	1.0	
31.	R	1.00	(for an alkyl or a cycloalkyl group)

[1] Data from Table 7 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

Table 9. Electrophilic Substituent Factors for OH Radical Addition to Aromatic Rings[1]

(values marked with "**" are estimated/assumed values)

The q_m^+ and q_p^+ values which are <u>not</u> considered "assumed" values are taken directly from the following reference: Brown, H.C. and Okamoto, Y (1958), "Electrophilic Substituent Constants", J. Am. Chem. Soc. 80: 4979-4987. Various "assumed" values are based on similar structures with known σ^+ values.

		q_m^+	q_p^+
1.	Amino (-NH2)	-0.16	-1.3
2.	Dimethylamino (CH3-N-CH3)	-0.16 **	-1.7
3.	Anilino (C6H5-NH-)	-0.16 **	-1.4
4.	Acetylamino (CH3C(=O)-NH-)	0.21 **	-0.6
5.	Benzoylamino (C6H5-C(=O)-NH-)	0.21 **	-0.6
6.	Hydroxy (-OH)	0.121 **	-0.92
7.	Methoxy (-OCH3)	0.047	-0.778
8.	Phenoxy (C6H5-O-)	0.10 **	-0.50
9.	Methylthio (CH3-S-)	0.158	-0.604
10.	Methyl (CH3-)	-0.066	-0.311
11.	Ethyl (CH3-CH2-)	-0.064	-0.295
12.	Isopropyl (CH3-CH-CH3)	-0.060	-0.280
13.	tert-Butyl (-C(CH3)(CH3)(CH3))	-0.059	-0.256
14.	Aromatic (phenyl)	0.109	-0.179
15.	Chloromethyl (-CH2-CL)	0.14	-0.01
16.	Fluoro (-F)	0.352	-0.073
17.	Bromo (-Br)	0.405	0.150
18.	Chloro (-CL)	0.399	0.114
19.	Iodo (-I)	0.359	0.135
20.	Trifluoro (-C-F3)	0.520	0.612
21.	Cyano (-C≡N)	0.562	0.659
22.	Nitro (-NO2)	0.674	0.790
23.	Carboxy (-C(=O)-OH)	0.322	0.421
24.	Carbomethoxy (-C(=O)-O-CH3)	0.368	0.489
25.	Carboethoxy (-C(=O)-O-CH2-CH3)	0.366	0.482
26.	Carbethoxymethyl (-CH2-C(=O)-O-CH2-CH3)	-0.01	-0.164
27.	Bromomethyl (-CH2-Br)	0.14 **	-0.01 **
28.	Iodomethyl (-CH2-I)	0.14 **	-0.01 **
29.	Nitrate (-ONO2)	0.674 **	0.790 **
30.	Olefinic (-C=C)	0.02 **	0.02 **
31.	Acetylenic (-C≡C)	0.21 **	0.23 **
32.	-O-R (assume methoxy)	0.047 **	-0.778 **
33.	Phosporus (-P)	0.0 **	0.0 **
34.	Sulfur (-S) (assume methylthio)	0.158 **	-0.604 **
35.	Carbonyl (-C=O)	0.10 **	0.35 **
36.	Aldehyde (-CHO)	0.36 **	0.22 **
37.	-C-CL3	0.55 **	0.65 **
38.	-C-Br3	0.55 **	0.65 **
39.	-C-I3	0.55 **	0.65 **
40.	-CH2-F	0.10 **	-0.05 **
41.	-CH2- (assume ethyl)	0.06 **	-0.295 **
42.	-CH- (assume isopropyl)	0.06 **	-0.280 **
43.	-CH-Halogen (assume chloromethyl)	0.14 **	-0.01 **
44.	>C< (assume t-butyl)	-0.059 **	-0.256 **

Table 9. Continued

		σ_m^+	σ_p^+
45.	-NH-	-0.16 **	-1.0 **
46.	-N=	-0.03 **	0.15 **
47.	-CH2-CN	0.17 **	0.01 **
48.	-N=N	0.30 **	0.64 **
49.	-O-C(=O)-	0.10 **	-0.10 **
50.	Undefined	0.0 **	0.0 **
51.	-O-P	0.10 **	-0.20 **
52.	-S-CN	0.30 **	0.25 **
53.	-S-CO	0.20 **	0.15 **
54.	-O-Halogen	0.15 **	-0.10 **

For the 55-59, the X refers primarily to halogens, but the program also considers nitro and cyano groups. The estimated values are taken from Atkinson publications pertaining to estimated rate constants for PCBs.

55.	-C6H4-X1	0.25 **	0.02 **
56.	-C6H3-X2	0.39 **	0.22 **
57.	-C6H2-X3	0.53 **	0.42 **
58.	-C6H1-X4	0.67 **	0.62 **
59.	-Phenyl-X5	0.81 **	0.82 **
60.	-SO3	0.50 **	0.50 **
61.	-S=O	-0.16 **	-1.30 **

[1] Data from Table 8 in Group Rate Constants and Substituent Values Used by the Atmospheric Oxidation Program, Version 1.30, November 1990 [Meylan (1990b)].

recommended that AOP adopt the group rate constant k(1, UNS CH) = 0.000, list it in Table 1, and show it in all detailed calculations for H-atom abstraction from various unsaturated functional groups (=C-H).

For the compound O,O-dimethyl chlorophosphorothioate, Atkinson et al. (1988) indicated that the group rate constant k(P-Cl) = 0.00; and this should be added to Table 1 and to the computer program. Furthermore, the group rate constants k(>NNO), k(>N-NO_2), and k[P(=0)] should be listed as 0.00.

Inspection of the data in Table 1 indicates that k(-S-) = 2.0[5]. This value is applicable to OH radical reaction in the presence of air at 1 atmosphere pressure and thus in the presence of oxygen. In the absence of oxygen, k(-S-) = 0.00 [Atkinson et al. (1988)]. These facts are pertinent since AOP incorrectly estimates k_{OH} for acyclic and cyclic sulfides and compares the estimated values with the experimental values[6]. For example, for dimethyl sulfide, the recommended experimental value of k_{OH} from Atkinson (1989) is 4.56, Table 24, which is valid in the absence of oxygen. Therefore, in the data base for these compounds, the experimental value should be qualified to indicate that k_{OH} was

[5] It should be noted that for convenience, the factor $10^{-12}cm^3molecule^{-1}s^{-1}$ has been omitted. In all subsequent discussions on group rate constants, this factor will be omitted. In addition, in all subsequent discussions, all rate constants k(i) for all individual reaction pathways and k_{OH} will be written without the factor $10^{-12}cm^3molecule^{-1}s^{-1}$.

[6] From Meylan (1990b), page 10, "Estimation Accuracy of AOP vs. PCFAP."

obtained from measurements in the absence of oxygen. If one wants to compare the estimated value with the experimental value, then k_{OH} should be estimated under the boundary condition in the absence of oxygen and k_{OH} = 2.59 [since k(-S-) = 0.00]. Thus, a footnote should be added to the numerical value of the group rate constant k(-S-) in Table 1 [i.e., for k(-S-)]. The numerical value should be $(2.0)^3$ and the footnote 3 at the bottom of this table should be --- [3] Applicble at 298 K and a total pressure of 1 atmosphere in air (and thus in the presence of oxygen). In the absence of air, and thus in the absence of oxygen, k(-S-) = 0.00. This is discussed in more detail in Section IV.E.1.b.

From the experimental k_{OH} data of diethylhydroxylamine, it was found that k(>NOH) = 0.00 [Leifer (1991a)] and this group rate constant should be entered into Table 1 and in the AOP Computer program.

In Table 1, it is indicated that k(-SH) = 31 for RSH, where R is an alkyl group. This group rate constant is not valid when R is an aromatic group, based on the experimental rate constant for thiophenol [Meylan (1990b)]. For the present, this assignment can be tentatively used. However, the experimental k_{OH} data from Barnes et al. (1986) may not be valid. Therefore, more experimental data is needed on thiophenol and other alkyl and aromatic thiols to confirm the assignment for k(-SH).

In Table 1, the value of the group rate constant k(-OH) is only applicable to H-atom abstraction from the hydroxyl groups in alcohols and glycols and this fact must be noted in Table 1 for

k(-OH) and in the computer program. This group rate constant is not applicable to H-atom abstraction from the hydroxyl groups in carboxylic acids and alkyl peroxides. See Section IV.C.3.b. for the discussion of the estimation of k_{OH} for carboxylic acids and Section IV.C.4.b. for the discussion of the estimation of k_{OH} for alkyl peroxides.

In Table 2, item, No. 57, should be changed to $F(R_2CHCl)$ = 0.57 [estimated by Leifer from the experimental data of 2,3-dichlorobutane from Mill et al. (1982); and an additional item $F(R_2CH-$ 1 Halogen **) = 0.57 (based on the assignment in No. 57) should be added before item 60.

The substituent factor F(-O-O **) = 50 should be deleted from Table 2 because of the erroneous assumption that k(-OH) = 0.036 for methyl and t-butyl hydroperoxide. For the details, see Section IV.C.4.b. Similarly, the substituent factor dimethyl sulfoxide, No. 58, Table 2, should be deleted since it is expected that the sulfoxide would be readily oxidized to the sulfone. For the details, see Section IV.E.2.b.

Table 4 lists the group rate constant for the functional group >C=C< as 110.0; it should be 110 based on the experimental k_{OH} data for 2,3-dimethyl-2-butene and the recommended value by Atkinson (1986,1989). Therefore, the last significant figure should be deleted. Similarly, the group rate constant for -C≡C- in Table 6 should be 29 and not 29.0 based on the recommendation of Atkinson (1987, page 814).

In Table 8, some of the substituent factors C(X) are marked with the symbol ** to indicate that they are based on estimated/assumed values. However, if a substituent factor is based on experimental k_{OH} data, then the symbol ** should be omitted. For example, consider diacetylene, in Table 8, No. 19; this substituent factor is listed as {C[-C≡C-**]} = 1.10 (based on the experimental data for diacetylene). The entry in this table should be No. 19 C[-C≡C-] = 1.10 (based on the experimental data of diacetylene). Similar comments are applicable to the substituent factors C(X) for numbers 29 and 16, Table 8. Therefore, for the substituent factor C[Cyclic C=O **] (No. 29), the double asterisks should be removed since the value is based on the experimental k_{OH} data of 1,4-naphthoquinone; similarly, for No. 16, C(phenyl **) = 1.0 should be C(phenyl) = 1.00, based on the experimental k_{OH} data of styrene, α- and β-methyl styrene, and β-dimethyl styrene [Atkinson (1987, page 828)]. These comments also apply to the substituent factors F(X) marked with ** in Table 2.

In Table 8, No. 14 is listed as C(C≡C- **) = 0.85 without any notation as to how this value was derived. Since this represents an estimated/assumed value, a qualifying statement should be added to designate how this assignment was made.

Finally, in Table 9, the σ_m^+ value for substituent $-CH_2-$ (No. 41) is listed as 0.06 ** by analogy with the ethyl group. However, σ_m^+ for the ethyl group is -0.064 and this value should be listed in No. 4, Table 9.

IV.B. Some Comments on Hydroxyl Radical Addition to Heteroaromatic and Fused Polyaromatic Ring Systems

Meylan (1990b) developed elegant S/R relationships for estimating the second-order rate constant for OH radical addition to heteroaromatic (mono and fused polycyclic) rings and to fused polynuclear aromatic hydrocarbon (PAH) rings. For monocyclic heteroaromatic compounds (ar′), AOP uses equation 24; for fused ring polynuclear aromatic hydrocarbon compounds (PAH), AOP uses equation 29; and for fused ring polynuclear heterocyclic compounds (PAH′), AOP uses equation 30. The first term in each of these equations [i.e., A_i, B_i, and B_i', respectively] was derived by Meylan from: (1) the experimental values of k_{OH} for the basic, or parent, heterocyclic ring or the fused polynuclear aromatic hydrocarbon ring structure; or from (2) the experimental ionization potentials for the parent fused ring polynuclear aromatic hydrocarbons and fused ring polynuclear heteroaromatic compounds. Tables 10 and 11 list the values of A_i and B_i, respectively, for various heteroaromatic ring structures and polyaromatic hydrocarbons derived from the experimental k_{OH} data for the parent aromatic compounds. Tables 12 and 13 list the values of B_i and B_i', respectively, derived from the experimental ionization potentials of the parent ring compounds.

AOP has a SMILES interpreter which allows it to identify the parent aromatic ring structure and assign it the appropriate value of A_i, B_i, or B_i'. AOP then adjusts this value for any substituent on the ring by utilizing the appropriate substituent

Table 10. Experimental Values of A_i for Some Monocyclic Heteroaromatic Compounds*

Heterocyclic Aromatic Ring Structure	Experimental Value of A_i ($10^{-12}cm^3molecule^{-1}s^{-1}$)
Pyrrole	110.0
Furan	40.5
Thiofuran	9.53
Imidazole	36.0
Oxazole	9.1
Thiazole	1.4
Pyridine	0.37
1,3,5-Triazine	0.15

* Data from page 7 of the User's Guide for the Atmospheric Oxidation Program, Version 1.10, November 1, 1990 [Meylan (1990b)].

Table 11. Experimental Values of B_i for Some Polynuclear Aromatic Compounds*

Polynuclear Aromatic Ring Structure	Experimental Value of B_i ($10^{-12}cm^3molecule^{-1}s^{-1}$)
Naphthalene	21.6
Anthracene	110.0
Phenanthrene	31.0

* Data from page 7 of the User's Guide for the Atmospheric Oxidation Program, Version 1.10, November 1, 1990 [Meylan (1990b)].

Table 12. Values of B_i for Polynuclear Aromatic Hydrocarbon Structures Derived from Experimentally Measured Ionization Potentials*

Polynuclear Aromatic Ring Structure	Assigned Value of B_i Based on the Experimentally Measured Ionization Potential ($10^{-12}cm^3molecule^{-1}s^{-1}$)
4 Fused Benzene Rings	80.0
5 Fused Benzene Rings	150.0
6 Fused Benzene Rings	200.0

* Data from page 7 of the User's Guide for the Atmospheric Oxidation Program, Version 1.10, November 1, 1990 [Meylan (1990b)].

Table 13. Values of B_i' for Polynuclear Heteroaromatic Structures Derived from Experimentally Measured Ionization Potentials*

Polynuclear Heteroaromatic Structure	Assigned Value of B_i' Based on the Experimentally Measured Ionization Potential ($10^{-12}cm^3molecule^{-1}s^{-1}$)
Quinoline	6.5
Isoquinoline	6.5
Quinoxaline	2.0
Quinazoline	2.0
Acridine	27.5

* Data from page 7 of the User's Guide for the Atmospheric Oxidation Program, Version 1.10, November 1, 1990 [Meylan (1990b)].

factors σ_m^+ and σ_p^+ for the substituents on the ring. For example, for 1-chloronaphthalene, the SMILES interpreter in AOP identifies the parent naphthalene ring and selects the value of A_i for this ring. AOP then adjusts this value by considering the effect of the chlorine substituent on the reactivity of the ring.

It should be noted that Meylan did not develop S/R relationships for fused ring aromatic compounds containing five membered heterocyclic rings. For example, AOP cannot estimate k_{OH} for benzothiazole. In principle, however, the basic concepts of Meylan can be used. For example, if k_{OH} is measured for benzothiazole, then B_i' from equation 30 can be determined. Therefore, with this value of B_i', k_{OH} can be estimated for substituted benzothiazoles utilizing the appropriate substituent factors σ_m^+ and σ_p^+ for the substituents on the ring.

More experimental k_{OH} data is needed on a number of additional derivatives of these heteroaromatic (ar'), polynuclear aromatic hydrocarbons (PAH), and polynuclear heteroaromatic ring (PAH') structures to confirm the S/R relationships of Meylan (1990b) [i.e., confirm the validity of equations 24, 29, and 30].

It should be noted that in Tables 10, 11, and 12, AOP lists a few of the values of A_i and B_i to four significant figures. At best, the experimental data used to derive these constants are only valid to three significant figures. Therefore, it is

recommended that the values of A_i and B_i for pyrrole, anthracene, and for 4, 5, and 6 fused benzene rings should be listed to three significant figures.

IV.C. H-Atom Abstraction from C-H and -OH Groups by Hydroxyl Radicals

IV.C.1. Saturated Alkanes

IV.C.1.a. Evaluation of the Experimental k_{OH} Data

Tables 14.A. and 14.B. summarize the pertinent experimental k_{OH} data at 298 K for the reaction of OH radicals with acyclic and cyclic alkanes, respectively, as obtained from AOP and the literature. For this class of compounds, hydroxyl radical reaction only involves the abstraction of H-atoms from the various primary, secondary, or tertiary C-H groups. The first column in these two tables lists the name of each alkane; the second column lists the experimental value of k_{OH} at 298 K in AOP [Meylan (1990b)] and is labeled Experimental/AOP; the third column lists k_{OH} at 298 K as obtained by Leifer from Atkinson (1989) and/or from the literature and is labeled Experimental/(a); the fourth column lists the estimated value of k_{OH} at 298 K as obtained from AOP and is labeled Estimated/AOP; and finally the fifth column lists the estimated, hand calculated (HC), value of k_{OH} at 298 K as obtained by Leifer using the S/R relationships of Atkinson and is labeled Estimated/HC.

Atkinson (1989) critically analyzed the available experimental k_{OH} data and recommended the best values along with the rationale behind each recommendation and the uncertainty for

Table 14.A. Comparison of the Estimated Values of k_{OH} at 298 K for Saturated Acyclic Alkanes from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data Reported in AOP

Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Methane	0.00841	0.00836*	0.00841[b]	(c)
Ethane	0.268	0.268*	0.288	0.288
Propane	1.15	1.15*	1.21	1.21
n-Butane	2.54	2.54*	2.53	2.53
2-Methylpropane	2.34	2.34*	2.39	2.39
n-Pentane	3.94	3.94*	3.93	3.93
2-Methylbutane	3.90	3.9*	4.00	4.00
2,2-Dimethylpropane	0.849	0.849*	0.743	0.743
n-Hexane	5.61	5.61*	5.32	5.32
2-Methylpentane	5.60	5.6*	5.39	5.39
3-Methylpentane	5.70	5.7*	5.77	5.77
2,2-Dimethylbutane	2.32	2.32*	1.82	1.83
2,3-Dimethylbutane	6.20	6.2*	5.46	5.46
n-Heptane	7.15	7.15*	6.72	6.71
2,2-Dimethylpentane	3.37	3.37[d]	3.22	3.22
2,4-Dimethylpentane	5.16	5.16[d']	6.86	6.85
2,2,3-Trimethylbutane	4.23	4.23*	3.29	3.30
n-Octane	8.68	8.68*	8.11	8.11
2,2-Dimethylhexane	4.83	4.83[d]	4.61	4.61
2,2,4-Trimethylpentane	3.68	3.68*	4.68	4.68
2,3,4-Trimethylpentane	7.0	6.97[e]	8.70	8.70

Table 14.A. Continued

Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
2,2,3,3-Tetramethylbutane	1.08	1.08*	1.11	1.11
n-Nonane	10.20	10.2*	9.51	9.50
2-Methyloctane	10.1	10.1[d]	9.58	9.58
4-Methyloctane	9.72	9.72[d]	9.95	9.95
2,3,5-Trimethylhexane	7.88	7.88[d]	10.1	10.1
n-Decane	11.6	11.6*	10.9	10.9
n-Undecane	13.2	13.2*	12.3	12.3
n-Dodecane	14.2	14.2*	13.7	13.7
n-Tridecane	16.0	16*	15.1	15.0
n-Tetradecane	19.2	19.2*	16.5	16.5
n-Pentadecane	22.2	22.2[f]	17.9	17.9
n-Hexadecane	24.9	24.9[f]	19.3	19.3

[a] Experimental values from Atkinson (1989) and the literature.
[b] Estimated value is based on the measured value.
[c] Cannot be estimated by the S/R methods of Atkinson.
[d] Experimental value from Behnke et al. (1988).
[d'] Experimental value from Atkinson et al. (1984).
[e] Experimental value from Harris and Kerr (1988).
[f] Experimental value from Nolting et al. (1988).

Table 14.B. Comparison of the Estimated Values of k_{OH} at 298 K for Saturated Cyclic Alkanes from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data Reported in AOP

Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Cyclopropane	0.07	0.071[b]	0.0711	0.0711
i-Propylcyclopropane	2.84	2.84[c]	2.85	2.85
Cyclobutane	1.20	1.2[d]	1.23	1.23
Cyclopentane	5.16	5.16*	5.58	5.58
Cyclohexane	7.49	7.49*	8.37	8.37
Methylcyclohexane	10.4	10.4[e]	10.2	10.2
1,1,3-Trimethylcyclohexane	8.73	8.73[f]	9.18	9.18
Cycloheptane	12.5	12.5[g]	9.76	9.77
Cyclooctane	13.7	13.7[h]	11.2	11.2
Bicyclo [2.2.1] heptane	5.49	5.49[i]	9.49	9.49
Bicyclo [2.2.2] octane	14.7	14.7[i]	16.2	16.2
Bicyclo [3.3.0] octane	11.0	11.0[i]	10.4	10.4
cis-Bicyclo [4.3.0] nonane	17.2	17.2[i]	14.1	14.1
trans-Bicyclo [4.3.0] nonane	17.6	17.6[i]	14.1	14.1
cis-Bicyclo [4.4.0] decane	19.9	19.9[i]	19.0	19.0
trans-Bicyclo [4.4.0] decane	20.4	20.4[i]	19.0	19.0
Tricyclo [5.2.1.0 ^{2,6}] decane	11.3	11.3[i]	12.3	12.3
Tricyclo [3.3.1.1 ^{3,7}] decane	22.6	22.6[j]	24.1	24.1

[a] Experimental values from Atkinson (1989) and the literature.
[b] Average value from the experimental data of Zetzsch (1980) and Jolly et al. (1983).
[c] Experimental value from Atkinson and Aschmann (1988).
[d] Experimental value from Gorse and Volman (1974).
[e] Experimental value from Atkinson et al. (1984).
[f] Experimental value from Behnke et al. (1988) as reported in Atkinson (1989).
[g] Average value of the experimental data of Zetzsch (1980) and Jolly et al. (1985).
[h] Experimental value from Behnke et al. (1988) as reported in Atkinson (1989).
[i] Experimental value from Atkinson, Aschmann, Carter (1983a).
[j] Average value from the experimental data of Atkinson, Aschmann, and Carter (1983a) and Behnke et al. (1988).
Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

each recommendation. These recommended values have an asterisk after each value.

In general, the experimental values of k_{OH} listed in AOP are the same as those obtained by Leifer; there are, however, a few differences. For methane, the recommended Atkinson value is 0.00836* while AOP lists 0.00841. For 2,3,4-trimethylpentane, the k_{OH} value of 6.97 was obtained by extrapolation of the data and Kerr (1988) and appears to be the best value. The best value of k_{OH} for cyclopropane should be 0.071 as obtained by averaging the data of Zetzsch (1980) and Jolly et al. (1985) rather than the value of 0.07 listed in AOP. For a few compounds, the incorrect number of significant figures was cited by AOP; the recommended values list two significant figures whereas AOP lists three significant figures. For example, for 2-methylbutane, the Atkinson recommended value is 3.9* while AOP lists 3.90. For cyclobutane, the value of k_{OH} reported by Gorse and Volman (1974) and Atkinson (1989) is 1.2 and not 1.20 as listed in AOP. The experimental k_{OH} data of Gorse and Volman is only good to two significant figures.

It should be noted that the names of two tricyclic decanes {tricyclo [5.2.1.0] decane and tricyclo [3.3.1.1] decane} entered in AOP are incorrect. The correct names should be tricyclo [5.2.1.0 ^{2,6}] and tricyclo [3.3.1.1 ^{3,7}] decane since the superscript numbers on the last digit must be specified to identify the bridgehead carbons on the last ring. Finally, the

name of methylcyclohexane is the correct name and not 1-methylcyclohexane as listed in AOP.

IV.C.1.b. Evaluation of the Estimated k_{OH} Data

A preliminary evaluation of the AOP computer program [Meylan (1990a)] in July 1990 indicated that for some bicyclic and tricyclic alkanes, the method of estimating k_{OH} in AOP was incorrect. The AOP computer program did not use the ring strain factors [F(3), F(4), F(5), or in Meylan's notation RS3, RS4, RS5] correctly in the calculations. The discrepancies were discussed with Meylan by phone and a set of the calculations were sent to him for evaluation. As a result, Meylan (1990b) revised the AOP computer program for these types of compounds to accurately reflect the Atkinson S/R relationships for strained ring compounds [Version 1.30, November 1, 1990].

In evaluating the estimated values of k_{OH} by AOP and HC, a few comments can be made about the number of significant figures used. In general, the summary table in AOP lists the estimated k_{OH} with a maximum of six significant figures and the detailed calculations list k(1a) or k(1c) with a maximum of five significant figures. However, the group rate constants k_p^o, k_s^o, and k_e^o, [or k_{prim}, k_{sec}, and k_{tert} in Meylan's notation] and the substituent factors F(CH_3-), F(-CH_2-), and F(>C<) are, at best, known to three significant figures. Therefore, it is recommended that AOP show the detailed calculations with four significant figures and list k(1a) or k(1c), or k(1a) + k(1c), and k_{OH} in the

summary table rounded off to 3 significant figures. These comments on the use of an excessive number of significant figures apply to all classes of chemicals and specific chemicals.

Comparison of the estimated values of k_{OH} from AOP with those from HC (after rounding off all estimated values to three significant figures) in the last two columns in Tables 14.A. and 14.B. indicates that, except for methane, the values are essentially the same. The trivial differences in the last digit are due to the method of rounding off the last digit in HC. For methane, AOP lists a value of 0.00841 which is the experimental value [which really should be 0.00836* as recommended by Atkinson] whereas HC does not list a value; k_{OH} cannot be estimated by the S/R relationships of Atkinson for this compound.

The number of significant figures for RS3, RS4, and RS5 for strained rings is incorrect. For example, for cyclobutane, RS4 = 0.22000 is used in the detailed calculation section. However, for RS4, Atkinson listed it as 0.22.

The detailed calculations for H-atom abstraction are somewhat confusing when the ring strain factor is used. For example, for bicyclo [2.2.1] heptane, AOP gives

$$k_{sec} = 0.838\ F(-CH_2-)F(>CH-)(RS5)(RS5)$$
$$= 0.838(1.29)(1.29)(0.64)$$
$$= 0.892$$

It seems to me that a more consistent notation for RS5 would be $(RS5)^2 = (0.80)^2$ rather than (RS5)(RS5) = 0.64. Therefore, k_{sec}

should read

$$k_{sec} = 0.838\ F(-CH_2-)F(>CH-)(RS5)^2$$
$$= 0.838\ (1.29)(1.29)(0.80)^2$$
$$= 0.892$$

or

$$k_{sec} = 0.838\ F(-CH_2-)F(>CH-)(RS5)(RS5)$$
$$= 0.838(1.29)(1.29)(0.80)(0.80)$$
$$= 0.892$$

IV.C.2. Haloalkanes

IV.C.2.a. Evaluation of the Experimental k_{OH} Data

Table 15 summarizes the pertinent experimental k_{OH} data at 298 K for the reaction of OH radicals with haloalkanes as reported in AOP, in Atkinson (1989), and in the literature. In general, the literature values listed in the column Experimental/(a) are the same as those in the column Experimental/AOP; there are, however, some differences. For 1,1,1-trifluoroethane, AOP lists a value of 0.017, a ten-fold higher value than the correct value of 0.00171 from Martin and Paraskevopoulos (1983) and Atkinson (1989). [Please note that these values are listed in the units $10^{-12}cm^3molecule^{-1}s^{-1}$ rather than $10^{-14}cm^3molecule^{-1}s^{-1}$ as listed in Table 15; see footnote 5, page 42.] For 1,1,2-trichloroethane, the extrapolated value from the data of Jeong and Kaufmann (1979) and Jeong et al. (1984) obtained by Leifer is 0.324 while AOP lists a value of 0.328. For three haloalkanes, AOP does not list an experimental value

Table 15. Comparison of the Estimated Values of k_{OH} at 298 K for Haloalkanes from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in t[illegible] Literature Versus the Experimental k_{OH} Data in AOP

Chemical	$10^{14}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Fluoromethane	1.68	1.68*	1.43	1.43
Chloromethane	4.36	4.36*	5.47	5.47
Bromomethane	4.02	4.02*	4.32	4.32
Difluoromethane	1.09	1.09*	0.82	0.821
Fluorochloromethane	4.41	4.41*	3.15	3.15
Dichloromethane	14.2	14.2*	12.1	12.1
Trifluoromethane	0.024	0.024[b]	0.18	0.178
Difluorochloromethane	0.468	0.468*	0.682	0.682
Fluorodichloromethane	3.03	3.03*	2.62	2.62
Trichloromethane	10.3	10.3*	10.0	10.0
Fluoroethane	23.2	23.2[c]	20.5	20.5
Chloroethane	39	39*	40.1	40.0
1,1-Difluoroethane	3.4	3.4*	3.23	3.23
1,2-Difluoroethane	11.2	11.2[d]	14.1	14.1
1,1-Dichloroethane	26	26.0[e]	34.6	34.6
1,2-Dichloroethane	22	22.0[e]	36.3	36.3
1,2-Dibromoethane	25	25.0[e]	28.7	28.7
1,1,1-Trifluoroethane	1.7	0.171[d]	1.08	1.08
1,1,1-Trichloroethane	1.19	1.19*	1.30	1.30
1,1-Difluoro-1-chloroethane	0.358	0.358*	0.36	0.360
1,1,2-Trifluoroethane	1.8	1.83[d]	2.35	2.35
1,1,2-Trichloroethane	32.8	32.4[f]	33.2	33.3
1,1,1,2-Tetrafluoroethane	0.854	0.854*	0.62	0.622
1-Chloro-2,2,2-Trifluoro-ethane	1.62	1.62*	2.39	2.39
1,1,2,2-Tetrafluoroethane	(j)	0.67[g]	0.36	0.359

Table 15. Continued

Chemical	$10^{14}k_{OH}$($cm^3$$molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Pentafluoroethane	0.25	0.249[d]	0.13	0.135
1-Chloro-1,2,2,2-Tetrafluoroethane	1.02	1.02*	0.52	0.516
1,1-Dichloro-2,2,2-Trifluoroethane	3.35	3.35*	1.98	1.98
1,2-Dibromo-3-chloropropane	44	43.5[k]	50.3	50.3
2-Chlorobutane	(j)	230[i]	164	164
2,3-Dichlorobutane	(j)	96[i]	95.7	95.7

[a] Experimental values from Atkinson (1989) and the literature.
[b] Since the experimental data was obtained at temperatures ≥ 387 K, the value at 298 K should be used with caution [Atkinson (1989)].
[c] Experimental value from Nip et al. (1979).
[d] Experimental value from Martin and Paraskevapoulos (1983).
[e] Experimental value from Howard and Evenson (1976).
[f] Extrapolated from the experimental data of Jeong and Karfmann (1979) and Jeong et al. (1984).
[g] Extrapolated from the experimental data of Clyne and Holt (1979).
[i] Experimental value from Tuazon et al. (1986).
[k] Experimental value from Mill et al. (1982).
[j] No experimental value given in the AOP data base.
* Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

(i.e., for 1,1,2,2- tetrafluoroethane, 2-chlorobutane, and 2,3-dichlorobutane). For six compounds, the literature values have three significant figures while AOP lists two significant figures [e.g., for 1,1-dichloroethane, the literature value of Howard and Evenson (1976) is 0.260 while AOP lists 0.26].

IV.C.2.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated values of k_{OH} by AOP with HC in Table 15 indicates that they are essentially the same. The only differences being that in a few cases, AOP rounds off the estimated values to two significant figures. The estimated values of k_{OH} are good to three significant figures. For example, for trifluoromethane, the estimated value of k_{OH} by HC is 0.178, while AOP rounds it off to 0.18.

IV.C.3. Carbonyl Compounds

IV.C.3.a. Evaluation of the Experimental k_{OH} Data

Table 16 summarizes the pertinent experimental k_{OH} data at 298 K for the reaction of OH radicals with 57 carbonyl compounds as reported in AOP, in Atkinson (1989), and in the literature. These carbonyl compounds can be divided into several classes of compounds: 11 aldehydes, 19 ketones, 3 α-dicarbonyls, 1 acyl halide, 18 esters, and 5 carboxylic acids. First, consider all the compounds except the carboxylic acids. In these classes of compounds, 12 of them listed by AOP had experimental k_{OH} data with two significant figures. If the original literature sources and Atkinson (1989) are checked, all the k_{OH} data are listed with three significant figures (e.g., formal, 3-hexanone, n-butyl

ble 16. Comparison of the Estimated Values of k_{OH} at 298 K for Carbonyl Compounds from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}(cm^3molecule^{-1}s^{-1})$			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[o]	HC
A. ALDEHYDES				
Formal	9.7	9.77*	7.37	7.37
Ethanal	15.8	15.8*	16.2	16.2
Propanal	19.6	19.6*	22.0	22.0
Butanal	23.5	23.5*	25.5	25.5
2-Methyl Propanal	26.3	26.3*	23.4	23.4
Pentanal	28.5	28.5*	27.6	27.6
3-Methylbutanal	27.4	27.4*	30.0	30.0
2,2-Dimethylpropanal	26.5	26.5*	22.7	22.7
Trichloroacetaldehyde	1.73	1.73[a']	1.45	1.45
Hydroxyethanal (Glycolaldehyde)	9.9	9.9[b]	23.0	23.0
Pentane-1,5-Dial	23.8	23.8[c]	46.9	46.9
B. ACYCLIC KETONES				
Propanone	0.226	0.226*	0.219	0.219
2-Butanone	1.15	1.15*	1.38	1.38
2-Pentanone	4.9	4.9*	4.80	4.81
3-Pentanone	2.0	2.0*	2.54	2.55
2-Hexanone	9.1	9.1*	6.95	6.96
3-Hexanone	6.9	6.90[d]	5.97	5.97
4-Methyl-2-pentanone	14.1	14.1*	9.35	9.35
3,3-Dimethyl-2-butanone	1.21	1.21[e]	2.01	2.01
2-Heptanone	8.67	8.67[e]	8.35	8.35

Table 16. Continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[o]	HC
2,4-Dimethyl-3-pentanone	5.38	5.38[d]	5.32	5.31
2-Octanone	10.0	11.0[e]	9.74	9.74
2-Nonanone	12.2	12.2[e]	11.1	11.1
2,6-Dimethyl-4-heptanone	27.5	27.5*	18.5	18.5
2-Decanone	13.2	13.2[e]	12.5	12.5
2,4-Pentanedione	1.15	1.15[f]	0.703	0.703
2,5-Hexanedione	7.13	7.13[f]	5.82	5.82
C. CYCLIC KETONES				
Cyclobutanone	0.87	0.87[f]	1.17	1.17
Cyclopentanone	2.94	2.94[f]	8.92	8.92
Cyclohexanone	6.39	6.39[f]	12.6	12.6
D. α-DICARBONYLS				
Glyoxal	11.4	11.4*	24.5	24.5
Methylglyoxal	17.2	17.2*	12.3	12.3
Biacetyl	0.238	0.238*	0.219	0.219
E. ACYL CHLORIDES				
Acetyl chloride	0.068	0.068[g]	0.0720	0.0720
F. ESTERS				
Methyl formate	0.23	0.227[h]	0.216	0.216

ble 16. Continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[o]	HC
Ethyl formate	1.0	1.02[h]	1.44	1.44
n-Propyl formate	2.4	2.38[h]	2.89	2.89
n-Butyl formate	3.1	3.12[h]	4.28	4.28
Methyl acetate	0.34	0.341[i]	0.216	0.216
Ethyl acetate	1.6	1.6*	1.44	1.44
n-Propyl acetate	3.4	3.4*	2.89	2.89
i-Propyl acetate	3.4	3.4*	3.12	3.12
n-Butyl acetate	4.2	4.2*	4.28	4.28
s-Butyl acetate	(n)	5.5*	4.99	4.99
Ethyl propionate	2.1	2.14[i]	1.63	1.63
n-Propyl propionate	4.0	4.02[h]	3.08	3.07
Methyl butyrate	3.0	3.04[h]	1.48	1.48
Ethyl butynrate	4.9	4.94[h]	2.71	2.71
n-Propyl butyrate	7.4	7.41[h]	4.16	4.16
n-Butyl butyrate	10.6	10.6[h]	5.55	5.55
Ethoxyethyl acetate	13.0	13[h']	14.0	14.0
Methyl trifluoroacetate	0.05	0.052[h]	0.216	0.0518
G. CARBOXYLIC ACIDS				
Formic acid	0.45	0.45*	0.436[j](-3)	(k)
Acetic acid	0.74	0.74[l]	0.145(-80)	(k)
Propionic acid	1.22	1.22[l]	0.859(-30)	(k)
n-Butyric acid	2.4	2.4[m]	2.12(-12)	(k)
i-Butyric acid	2.00	2.00[l]	1.80(-10)	(k)

[a], Experimental values from Atkinson (1989) and the literature.
[a'] Experimental value from Nelson et al. (1984) as reported by Atkinson (1989).

Table 16. continued

[b] Experimental value from Niki et al. (1987)
[c] Experimental data from Rogers (1989). This value of k_{OH} represents the average value of 25.2 and 22.4x10^{-12}cm^{3}molecule^{-1}s^{-1} as measured with the reference compounds propene and trans-2-butene, respectively.
[d] Experimental value from Atkinson et al. (1982).
[e] Experimental value from Wallington and Kurylo (1987).
[f] Experimental value from Dagaut et al. (1988).
[g] Experimental value from Atkinson (1987).
[h,] Experimental value from Wallington et al. (1988).
[h'] Experimental data from Hartmann et al. (1986, 1987) as reported by Atkinson (1989).
[i] Experimental value from Wallington et al. (1988). The data from Campbell and Parkinson (1978) was not used since the experimental method was probably not valid/Atkinson (1989)].
[j] Estimated by [Meylan (1990b)] assuming that k(HCOOH **) was 0.400.
[k] Atkinson did not develop S/R relationships for carboxylic acids.
[l] Experimental value from Dagaut et al. (1988b). The rate data of Zetzsch and Stuhl (1981) as reported in Atkinson (1989) is subject to significant uncertainties; hence it should not be used [Atkinson (1989)].
[m] Experimental value from Zetzsch and Stuhl (1981) as reported in Atkinson (1989). This value is subject to significant uncertainties and must be used with extreme caution [Atkinson (1989)].
[n] No experimental value is given in the AOP data base. A value of 5.5x10^{-12}cm^{3}molecule^{-1}s^{-1} is given in the document "Estimated Accuracy o[illegible] AOP versus PCFAP.
[o] Based on the experimental values of k_{OH} listed in column Experimental/(a).
[*] Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

formate, methyl butyrate). For ethoxyethyl acetate, AOP lists the experimental value of k_{OH} with three significant figures while Atkinson (1989) and Hartmann et al. (1986, 1987) list it with two significant figures. For 2-octanone, AOP lists a value of k_{OH} of 10.0 while Wallington and Kurylo (1987) and Atkinson (1989) list a value of 11.0. For s-butyl acetate, AOP does not list a value in the data base; from the document "Estimated accuracy of AOP versus PCFAP, AOP does list a value of 5.5 for this compound. The recommended value by Atkinson (1989) is 5.5*.

Experimental k_{OH} data listed in Table 16G. are available for a few alkyl carboxylic acids---formic, acetic, propionic, and n- and i-butyric acids as obtained from Atkinson (1989) and the literature. The k_{OH} data from Zetzsch and Stuhl (1981) for acetic, propionic, and n-butyric acids had very large uncertainties since the vapor pressures of these compounds were unknown. Hence, these data should not be used [Atkinson (1989)]. The experimental k_{OH} data for acetic, propionic, and i-butyric acids were obtained from a single source [Dagaut et al. (1988)]; hence, these data should be used with caution until additional k_{OH} data are obtained from other researchers to corroborate the assignments.

It should be noted that for the aldehydes, the incorrect names are used in the AOP data base. Since, the aldehyde functional group can only be at the end of the alkyl chain, there is no need to specify its position with a number.

IV.C.3.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated values of k_{OH} reported by AOP with those from HC in Table 16 indicate that they are essentially the same except for methyl trifluoroacetate and the carboxylic acids. For most of these compounds, the differences are trivial and are due to the method of rounding off the third significant figure. For methyl trifluoroacetate, the estimated value of k_{OH} in AOP is 0.216 in contrast to the estimated value of 0.0518 in HC from Leifer. The apparent error is due to the effect of the very electrophilic group $-CF_3$ on the substituent factor F[-OC(0)R]. Leifer (1991a) derived a substitutent factor

$$F[-OC(0)CF_3] = 0.36 \qquad (31)$$

which gives an estimated value of 0.0518. Therefore, it is recommended that the substituent factor listed in 31 be used in the AOP computer program and in Table 2.

There are problems with the S/R relationships of Meylan (1990b) for the class of carboxylic acid compounds which will be described in the following paragraphs.

For the alkyl carboxylic acids, Atkinson did not develop S/R relationships while Meylan (1990b), in AOP, did develop S/R relationships. For these compounds, two reaction pathways were postulated by Meylan: H-atom abstraction from an alkyl group and H-atom abstraction from the OH group. Therefore, for these two reaction pathways,

$$R(=O)OH + \cdot OH \xrightarrow{k(1) = k(1a)} \cdot R'C(=O)OH + HOH \qquad (32)$$

$$RC(=O)OH + \cdot OH \xrightarrow{k(2) = k(-OH)} RC(=O)O\cdot + HOH \qquad (33)$$

where R' is an alkyl free radical [i.e., $\cdot R'$ or for formic acid, it is $\cdot C(=O)OH$]. The overall rate of reaction with hydroxyl radicals is then

$$k_{OH} = k(1) + k(2) = k(1a) + k(-OH) \qquad (34)$$

and Meylan assumed that reaction pathway 32 was the dominant pathway [i.e., $k(1a) > k(-OH)$]. Therefore, Meylan used the group rate constant $k(-OH) = 0.036$, derived from the alcohols; and the rate constant $k(1a)$, for H-atom abstraction from the alkyl group, was calculated in the standard manner using the S/R relationship of Atkinson. These results were then used in equation 34 to calculate k_{OH}.

For formic acid, Meylan (1990b) assumed that

$$k(1a) = k[HC(=O)OH\ **\ ] \approx 0.400 \qquad (35)$$

so that

$$k_{OH}\ (\text{formic acid, estimated}) = 0.436 \qquad (36)$$

and this result is listed in the fourth column of Table 16. The values of k_{OH} (estimated) for the other carboxylic acids are calculated in the standard manner in AOP and these results are listed in Table 16. The percent error for these compounds, based

on the experimental values of k_{OH} listed in the column Experimental/(a), are listed in parentheses in the column Estimated/AOP. Inspection of these results indicate that k_{OH} (estimated) for acetic acid was very poor (an error of -80%). On the other hand, the average percent error for the other carboxylic acids was -14 which is excellent.

Atkinson (1989) reviewed the available k_{OH} data for the reaction of OH radicals (or OD radicals) with formic acid (or deuteroformic acids) over the temperature range 297-445 K. Based on the experimental data of Wine et al. (1986) and Singleton et al. (1986) for the reaction of OH radicals with HC(O)OH and DC(O)OH and OD radicals with HC(O)OD and DC(O)OD, Atkinson (1989) concluded that the major reaction pathway was H- or D-atom abstraction from the -OH(or-OD) groups. This contradicts the assumption of Meylan (1990b) in AOP; that is, k(-OH) = 0.036 and reaction 33 is the minor reaction pathway. Furthermore, as stated in Section IV.C.3.a., the experimental k_{OH} data for these carboxylic acids are available from a single source and the k_{OH} data for acetic, propionic, and butyric acids have large uncertainties so that these data must be used with caution. Considerably more experimental k_{OH} data are needed for these carboxylic acids and for additional compounds in this class before reliable S/R relationships can be developed.

It should be noted that for formic acid, the detailed calculation for H-atom abstraction from formic acid is listed in

AOP as k[HCOOH **] = 0.400 (Measured). The molecular structure for formic acid is [HC(=O)OH] and not HCOOH.

IV.C.4. Alcohols, Glycols, Ethers, and Hydroperoxides

IV.C.4.a. Evaluation of the Experimental k_{OH} Data

Table 17 summarizes the pertinent experimental k_{OH} data at 298 K for the reaction of OH radicals with 16 alcohols, 3 glycols, 26 acyclic ethers, 10 cyclic ethers, and 2 hydroperoxides as reported in AOP, in Atkinson (1989), and in the literature. Inspection of the experimental k_{OH} data listed in columns 2 and 3 indicate that five compounds have differences. The differences in four of these compounds are related to the number of significant figures used. Inspection of the original literature references and the data in Atkinson (1989) clearly indicated that the preferred values are listed in the column Experimental/(a). The experimental values for 1-chloro-2,3-epoxypropane are different; the preferred value listed in the third column represents the average value from the experimental k_{OH} data of Zetzsch (1985) and Edney et al. (1986) assuming that k_{OH} = 0.55 of Edney.

IV.C.4.b. Evaluation of the Estimated k_{OH} Data

Comparison of the estimated values of k_{OH} from AOP and HC for the alcohols, glycols, and ethers indicates that they are essentially the same. The trivial differences are due to the method of rounding off the third significant figure in HC.

Table 17. Comparison of the Estimated Values of k_{OH} at 298 K for Alcohols, Glycols, Ethers, and Hydroperoxides from the Atmospheric Oxidatic Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[m]	HC
A. ALCOHOLS				
Methanol	0.932	0.932*	0.526	0.526
Ethanol	3.27	3.27*	3.07	3.08
1-Propanol	5.34	5.34*	4.98	4.99
2-Propanol	5.21	5.21*	6.63	6.63
1-Butanol	8.3	8.31[b]	6.37	6.38
2-Methyl-2-Propanol	1.12	1.12*	0.593	0.593
1-Pentanol	10.8	10.8[c]	7.77	7.77
2-Pentanol	11.8	11.8[d]	10.9	10.9
3-Pentanol	12.2	12.2[d]	12.9	12.9
3-Methyl-2-butanol	12.4	12.4[d]	11.0	11.0
1-Hexanol	12.4	12.4[d]	9.17	9.17
2-Hexanol	12.1	12.1[d]	12.3	12.3
1-Heptanol	13.6	13.6[d]	10.6	10.6
2-Chloroethanol	1.4	1.4	2.07	2.07
1-Hydroxy-2-propanone	3.02	3.02[e]	2.31	2.32
Cyclopentanol	10.7	10.7[d]	12.8	12.7
B. GLYCOLS				
1,2-Ethanediol	7.7	7.7	7.42	7.42
1,2-Propanediol	12.0	12	12.0	11.9

Table 17. Continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[m]	HC
C. ACYCLIC ETHERS				
Dimethyl ether	2.98	2.98*	1.76	1.76
Diethyl ether	13.3	13.3*	11.5	11.5
Di-n-Propyl ether	17.2	17.2*	21.1	21.1
Methyl-t-butyl ether	2.83	2.83*	2.82	2.82
Methyl-n-butyl ether	16.4	16.4[d]	13.6	13.6
Ethyl-n-butyl ether	18.1	18.1[f]	18.5	18.5
Ethyl-t-butyl ether	6.9	6.88[f]	7.70	7.20
Methyl-t-amyl ether	7.91	7.91[d]	6.13	6.13
Di-n-butyl ether	22.4	22.4[f]	25.5	25.5
Di-i-butyl ether	26.0	26.0[g]	30.4	30.4
Di-n-pentyl ether	34.7	34.7[d]	28.2	28.2
1,1-Dimethoxy ethane	8.89	8.89[e]	13.1	13.1
Diethoxymethane	16.8	16.8[e]	16.6	16.6
1,2-Dimethoxypropane	14.3	14.3[e]	22.9	22.9
2,2-Dimethoxypropane	3.92	3.92[e]	3.05	3.05
2,2-Diethoxypropane	11.7	11.7[e]	12.8	12.8
2-Methoxyethyl ether	17.5	17.5[e]	28.1	28.1
1,1,3-Trimethoxypropane	19.2	19.2[e]	28.5	28.5
2-Ethoxyethyl ether	26.8	26.8[e]	37.9	37.8
Methoxy acetone	6.77	6.77[e]	4.87	4.87
2-Methoxy ethanol	12.5	12.5[e]	11.2	11.2
2-Ethoxy ethanol	15.4	15.4[h]	16.1	16.1
3-Ethoxy-1-propanol	22.0	22.0[e]	20.9	20.9
3-Methoxy-1-butanol	23.6	23.6[e]	20.6	20.6
2-Butoxy ethanol	18.6	18.6[h]	23.0	23.0

Table 17. Continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[m]	HC
2-Hydroxyethyl ether (Dihydroxyethyl ether)	30.0	30	20.6	20.6
D. CYCLIC ETHERS				
Ethylene oxide	0.076	0.076*	0.224	0.224
1,2-Epoxypropane (propylene oxide)	0.052	0.52*	0.543	0.543
1-2-Epoxy butane (1,2-Butylene oxide)	2.1	2.1	1.69	1.69
1-Chloro-2,3-epoxypropane	0.44	0.50[i]	0.662	0.662
Trimethylene oxide	10.3	10.3[e]	3.73	3.73
Tetrahydrofuran	16.1	16.1*	18.3	18.3
1,3-Dioxane	9.15	9.15[e]	22.1	22.1
1,4-Dioxane	10.9	10.9[e]	26.4	26.4
1,3,5-Trioxane	6.2	6.2[j]	15.3	15.3
Oxepane (Hexamethylene oxide)	15.4	15.4[e]	25.7	2.57
E. ALKYL HYDROPEROXIDES				
Methyl hydroperoxide	5.54	5.54*	7.24(+31)	(1)
t-Butyl hydroperoxide	3.0	3.0[k]	1.98(-34)	(1)

[a] Experimental values from Atkinson (1989) and the literature.
[b] Experimental value from Wallington and Kurylo (1987a). The data from Campbell et al. (1976) was not used since the validity of the experimental method is questionable [Atkinson (1989)].
[c] Experimental value from Wallington and Kurylo (1987a).
[d] Experimental value from Wallington et al. (1988b).

ble 17. continued

[e] Experimental value from Dagaut et al. (1988a).
[f] Average value from the experimental data of Wallington et al. (1988b) and Bennet and Kerr (1989).
[g] Experimental value from Bennett and Kerr (1989).
[h] Experimental value from the experimental data of Hartmann et al. (1987) and Dagaut et al. (1988a).
[i] Average value from the experimental data of Zetzsch (1980) and Edney et al. (1986) assuming $k_{OH} = 0.55 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ of Edney.
[j] Extropolated from the experimental data of Zabernick et al. (1988).
[k] Experimental value from Anastasi et al. (1978).
[l] Atkinson did not develop S/R relationships for alkyl hydroperoxides.
[m] Based on the experimental values of k_{OH} listed in column Experimental/(a).
[*] Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

There are, however, problems with the S/R relationships for the alkyl hydroperoxides in AOP which will be described below.

For the alkyl peroxides [RCOOH], Atkinson did not develop S/R relationships while Meylan (1990b), based on the experimental k_{OH} data of methyl and t-butyl hydroperoxide, did develop S/R relationships. For alkyl peroxides, two reaction pathways were postulated by Meylan: H-atom abstraction from the alkyl group and H-atom abstraction from the hydroperoxy groups. Therefore,

$$RCOOH + \cdot OH \xrightarrow{k(1) = k(1a)} \cdot R'COOH + HOH \qquad (37)$$

$$RCOOH + \cdot OH \xrightarrow{k(2) = k(-OH)} ROO\cdot + HOH \qquad (38)$$

where R is an alkyl group and $\cdot R'$ is an alkyl free radical group. The overall reaction with OH radicals is then

$$k_{OH} = k(1) + k(2) = k(1a) + k(-OH) \qquad (39)$$

and reaction pathway 37 was considered by Meylan (1990b) to be the dominant reaction pathway. Therefore, Meylan assumed that k(-OH) = 0.036 and

$$F(-O-O- \text{ ** }) = 50 \qquad (40)$$

and k(1a) and k_{OH} were calculated in the standard manner. For methyl and t-butylhydroperoxides, the estimated values from AOP were 7.24 and 1.98, respectively. The percent error for these two compounds, based on the experimental values listed in column Experimental/(a), were +31 and -34, respectively, and these

results were very good. However, these results, and the S/R relationships of Meylan must be evaluated very carefully in the light of the experimental k_{OH} data as described in the following paragraphs.

Atkinson (1989) analyzed the experimental rate data of Vaghjiani and Ravishankara (1989) and Niki et al. (1983) for methyl hydroperoxide. The most comprehensive study is that of Vaghjiani and Ravishankara (1989) who studied the rates of reaction of ^{16}OH, ^{18}OH, and ^{16}OD radicals with CH_3OOH and ^{16}OD radicals with CH_3OOD. Based on an analysis of all the experimental data, the mechanism involves two reaction pathways; H-atom abstraction from the CH_3 group and from the OH group. Therefore,

$$CH_3OOH + \cdot OH \xrightarrow{k(2) = k(-OH)} CH_3OO\cdot + HOH \qquad (41)$$

$$CH_3OOH + \cdot OH \xrightarrow{k(1) = k(1a)} \cdot CH_2OOH + HOH \qquad (42)$$

with the $\cdot CH_2OOH$ radical rapidly decomposing to give hydroxyl radicals and formaldehyde

$$\cdot CH_2\text{-}O\text{-}O\text{-}H \xrightarrow{\text{Rapid}} CH_2{=}O + \cdot OH \qquad (43)$$

The overall rate, from reactions 41 and 42, is

$$k_{OH} = k(1) + k(2) = k(1a) + k(-OH) \qquad (44)$$

Relative rate studies gives k_{OH} [= k(1a) + k(-OH)] while flash photolysis or laser photolysis experiments, which measure the disappearance of OH radicals, gives only the rate constant k(-OH) assuming that OH radical regenerated contains the same oxygen isotope as the reactant OH radical. Therefore, the reaction of the ^{16}OH radical with $CH_3O^{16}OH$ (or ^{16}OD radical with $CH_3O^{16}OD$) gives the rate constant k(-OH). Furthermore, reaction of OD radicals with CH_3OOH yields the overall rate constant k_{OH} [= k(1a) + k(-OH)] for the OD radical reaction.

Atkinson (1989) carried out a unit-weighted least-squares analysis of the experimental data of Vaghjiani and Ravishankara (1989) for the reaction of ^{18}OH and OD radical with CH_3OOH over the temperature range 203-348K. Based on these data, Atkinson recommended the value of

$$k(-OH) = 3.73 \qquad (45)$$

at 298 K (in the units $10^{-12}cm^3molecule^{-1}s^{-1}$); from the experimental data involving ^{18}OH and OD radicals over the temperature range 223-423 K, Atkinson recommended a value of

$$k_{OH} = 5.54 \qquad (46)$$

at 298 K (in the units $10^{-12}cm^3molecule^{-1}s^{-1}$). Hence,

$$k(1a) = 1.81 \qquad (47)$$

and H-atom abstraction from the OH radical in methyl hydroperoxide is the major reaction pathway.

For t-butyl hydroperoxide, Atkinson (1989) indicated that because the C-H bonds in the CH_3 group are stronger than the O-H bond, the reaction is expected to proceed principally via H-atom abstraction from the weaker OH bond (reaction pathway 41) and this result is consistent with the magnitude of k_{OH} determined experimentally by Anastasi et al. (1978).

Therefore, all the data presented by Atkinson (1989) contradicts the S/R relationships of Meylan (1990b) for the alkyl hydroperoxides. Considerably more experimental rate data is needed for additional alkyl hydroperoxides to develop S/R relationships for this class of compounds.

IV.C.5. Alkyl Nitrates and Nitriles

IV.C.5.a. Evaluation of the Experimental k_{OH} Data

Table 18 summarizes the pertinent experimental k_{OH} data at 298 K for acyclic and cyclic alkyl nitrates and acyclic alkyl nitriles as reported in AOP, in Atkinson (1989), and in the literature. Inspection of the k_{OH} data in columns 2 and 3 indicate that the experimental values for all acyclic and cyclic nitrates are identical. However, for the nitriles, there are differences. For acetonitrile, the correct value of k_{OH} is 0.0214* as recommended by Atkinson (1989) and the correct value for propionitrile is 0.194 as given by Harris et al. (1981) and Atkinson (1989).

Table 18. Comparison of the Estimated Values of k_{OH} at 298 K for Alkyl Nitrates and Alkyl Nitriles from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$ ($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. ACYCLIC NITRATES				
Methyl nitrate	0.034	0.034[b]	0.0259	0.0259
Ethyl nitrate	0.49[c]	0.49[c]	0.194	0.194
1-Propyl nitrate	0.67	0.67[d]	0.632	0.632
2-Propyl nitrate	0.41	0.41[e]	0.416	0.416
1-Butyl nitrate	1.78	1.78[e]	1.79	1.79
2-Butyl nitrate	0.92	0.92[e]	0.905	0.905
2-Pentyl nitrate	1.85	1.85[f]	2.06	2.06
3-Pentyl nitrate	1.12	1.12[f]	1.42	1.42
2-Methyl-3-butyl nitrate	1.72	1.72[g]	1.39	1.39
2,2-Dimethyl-1-propyl nitrate	0.85	0.85[g]	0.752	0.752
2-Hexyl nitrate	3.17	3.17[f]	3.45	3.45
3-Hexyl nitrate	2.70	2.70[f]	2.58	2.58
2-Methyl-2-pentyl nitrate	1.72	1.72[g]	1.68	1.68
3-Methyl-2-pentyl nitrate	3.02	3.02[g]	2.63	2.63
3-Heptyl nitrate	3.69	3.69[g]	3.97	3.97
3-Octyl nitrate	3.88	3.88[f]	5.37	5.37
B. CYCLIC NITRATES				
Cyclohexyl nitrate	3.30	3.30[g]	5.38	5.38
C. ALKYL NITRILES				
Acetonitrile	0.021	0.0214*	0.0202	0.0202
Propionitrile	0.19	0.194[h]	0.189	0.189

Table 18. continued

[a] Experimental values from Atkinson (1989) and the literature.
[b] Atkinson (1987, 1989) reported a value of 0.034×10^{-12} and 0.38×10^{-12} $cm^3 molecule^{-1} s^{-1}$ from Gaffney et al. (1986) and Kerr and Stocker (1986), respectively. Atkinson (1987) used the value of 0.034×10^{-12} since it was more consistent with the entire set of k_{OH} data used to develop the S/R relationships and the value from Kerr and Stocker was systematically too high. Atkinson (1989) also tentatively preferred the value of Gaffney et al. (1986) since the value of Kerr and Stocker was too high.
[c] The experimental data of Kerr and Stocker (1986) was considered too high and was not considered to be valid [Atkinson (1987, 1989)].
[d] This value of k_{OH} represents the average value from the experimental data of Kerr and Stocker (1986) and Atkinson and Aschmann (1989a).
[e] Experimental value from Atkinson and Aschmann (1989a).
[f] Experimental value from Atkinson et al. (1982a).
[g] Experimental value from Atkinson et al. (1984b).
[h] Experimental value from Harris et al. (1981).
* Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

IV.C.5.b. Evaluation of the Estimated k_{OH} Data

Inspection of the estimated values for the nitrates and nitriles in columns 4 and 5 indicate that both AOP and HC have exactly the same k_{OH} data.

IV.C.6. Nitroalkanes

IV.C.6.a. Evaluation of the Experimental k_{OH} Data

Table 19.A. summarizes the pertinent experimental k_{OH} data at 298 K for nitroalkanes as reported in Atkinson (1989), in AOP, and in the literature. For nitromethane, AOP lists a range of experimental values for k_{OH}. Atkinson (1989) evaluated the existing experimental k_{OH} data for nitromethane and indicated that the data of Zabarnick et al. (1988) is preferred. Atkinson carried out a unit-weighted least squares analysis of the Zabarnick data using the equation

$$k_{OH} = CT^2\exp(-D/T) \qquad (48)$$

where C and D are constants and T is the absolute temperature in K and found that

$$k_{OH} = 5.6 \times 10^{-19} T^2 \exp(-360/T) \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1} \qquad (49)$$

over the temperature range 299-671 K. At 298 K, equation 49 gives

$$k_{OH} = 0.0149 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \qquad (50)$$

ble 19. Comparison of the Estimated Values of k_{OH} at 298 K for Nitroalkanes and Alkyl Nitrites from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experiment k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[j]	HC
A. NITROALKANES				
Nitromethane	(0.016-0.16)	0.0149[b]	0.0259(+74)	(c)
Nitroethane	0.15	0.15[d]	0.194(+29)	(c)
1-Nitropropane	0.24	0.34[d]	0.632(+86)	(c)
1-Nitrobutane	1.45	1.45[e]	1.79(+23)	(c)
1-Nitropentane	3.30	3.30[d]	3.18(-4)	(c)
B. ALKYL NITRITES				
Methyl nitrite	(0.12-1.08)?	(0.12-1.09)[f]	0.288 (---)	(c)
Ethyl nitrite	1.75?	1.77[g]	2.32(+31)	(c)
1-Propyl nitrite	2.38?	2.36[h]	6.12(+160)	(c)
1-Butyl nitrite	(2.31-5.2)?	5.02[h]	8.29(+65)	(c)
2-Butyl nitrite	5.93?	5.97[i]	6.17(+3)	(c)
2-Methyl-1-propyl nitrite	5.31?	5.35[i]	10.8(+101)	(c)
2-Methyl-2-propyl nitrite	1.40?	1.41[i]	1.94(+38)	(c)

[a] Experimental values from Atkinson (1989) and the literature.
[b] Experimental value from Zabarnick et al. (1988) which represents the preferred value by Atkinson (1989).
[c] Could not be calculated by Leifer since the S/R relationships and substituent factors were unknown.

Table 19A. continued

[d] Experimental value from Nielsen et al. (1988). Atkinson (1989) tentatively accepted this data since "The nitroalkanes are expected to photolyze [Taylor et al. (1990)] and it is not clear whether photolysis occurred under the experimental conditions of the relative rate study of Nielsen et al. (1988) or whether or not photolysis (if it occurred) was taken into account". More experimental k_{OH} data are needed under controlled laboratory conditions to eliminate photolysis.

[e] The average value from the data of Atkinson (1989) and Nielsen et al. (1988). See footnote (d) above relative to the experimental value from Nielsen et al. (1988).

[f] Range in experimental k_{OH} data as obtained from Atkinson (1989) and the literature in the units $10^{-12}cm^3molecule^{-1}s^{-1}$: 0.12 relative to dimethyl ether and 0.21 relative to n-hexane [Tuazon et al. (1983)]; 1.00 [Baulch et al. (1985); 1.09 [Audley et al. (1982)]; and the data of Campbell and Goodman (1975) was omitted since there were fundamental problems associated with the relative method used [Atkinson (1989)].

[g] Experimental value from Audley et al. (1982) and Atkinson (1989).

[h] Average value from the experimental data of Audley et al. (1982) and Baulch et al. (1985) is obtained from Atkinson (1989).

[i] Experimental value from Audley et al. (1982).

[j] Percent error relative to the experimental values listed in column Experimental/(a).

and this is the value listed in column three of Table 19.A. and is the preferred (or recommended) value by Atkinson. For the remaining nitroalkanes, only for 1-nitropropane is there a discrepancy in the k_{OH} data in columns 2 and 3. The correct experimental value for 1-nitropropane is tentatively 0.34 as obtained from Nielsen et al. (1988) and Atkinson (1989).

Some comments must be made about the validity of the experimental k_{OH} data for nitroethane, 1-nitropropane, 1-nitrobutane and 1-nitropentane. For nitroethane, 1-nitropropane, and 1-nitropentane, the experimental data were obtained from Nielsen et al. (1988) and Atkinson (1989) while the experimental data for 1-nitrobutane was obtained from Atkinson and Aschmann (1989) and Nielsen et al. (1988). Atkinson (1989) critically evaluated the experimental k_{OH} data of Nielsen and stated that "The nitroalkanes are expected to photolyze [Taylor et al. (1980)] and it is not clear whether photolysis occurred under the experimental conditions of the relative rate study of Nielsen et al. (1988) or whether or not photolysis (if it occurred) was taken into account." As a result, Atkinson (1989) indicated that the data listed in the column Experimental/(a) for nitroethane, 1-nitropropane, and 1-nitropentane from Nielsen are only <u>tentatively</u> preferred and, therefore, must be used with extreme caution.

IV.C.6.b. Evaluation of the Estimated k_{OH} Data

Leifer did not have available S/R relationships for the nitroalkanes from Atkinson; hence, no entries appear in Table

19.A., column Estimated/HC. Meylan (1990b) did have S/R relationships available for these compounds from Atkinson (unpublished results). For this class of compounds (RNO_2), Atkinson must have postulated that hydroxyl radicals can only react by abstracting a hydrogen from the C-H groups in R and the substituent factors were

$$F(-NO_2) = 0.18 \quad (51)$$

$$F(-CH_2NO_2) = 0.30 \quad (52)$$

In addition, Meylan (1990b) gave the substituents $>CHNO_2$ and $>CNO_2$ the same F values as for the substituent $-CH_2NO_2$ listed in equation 52. Thus, the assumed values for these two substitutes (designated **) are then

$$F(>CHNO_2\ **\ ) = F(>CNO_2\ **\ ) = 0.30 \quad (53)$$

Using the above substituent factors, AOP estimated k_{OH} for the five nitroalkanes listed in Table 19.A. and these results are listed in the column Estimated/AOP. The percent error, relative to the experimental k_{OH} data in column 3, are listed in parentheses adjacent to the estimated value from AOP. Inspection of these data clearly indicate that the results for nitromethane and 1-nitropropane are very poor. In addition, the average percent error ranged from +53 to -4. Therefore, in order to develop better substituent factors for the nitroalkanes, more experimental k_{OH} data are needed for these five compounds and additional nitro compounds under carefully controlled laboratory

conditions to eliminate direct photolysis. Until this work is completed, the substituent factors and estimated values of k_{OH} for the nitroalkanes must be used with extreme caution, or, better, delete them from AOP.

IV.C.7. Alkyl Nitrites

IV.C.7.a. Evaluation of the Experimental k_{OH} Data

Table 19.B. summarizes the pertinent experimental k_{OH} data at 298 K for the alkyl nitrites (RONO) as obtained from AOP, from Atkinson (1989), and from the literature. For these compounds, the experimental k_{OH} data from AOP have question marks immediately after the numbers to indicate that the data are questionable. For the experimental data for methyl nitrite, several values are available from the literature. Thus, the experimental k_{OH} data in columns 2 and 3 list essentially the same range of values. For 1-butyl nitrite, AOP lists a range of values while the column Experimental/(a) lists the average value from the experimental data of Baulch et al. (1985) and Audley et al. (1982). For the other alkyl nitrates there are minor differences listed in columns 2 and 3. The values listed in the third column, as obtained from the literature and Atkinson (1989), appear to be the correct values.

It should noted that for the compound $CH_3CH(CH_3)CH_2ONO$, AOP lists the name 3-methyl-1-propyl nitrite which is incorrect. The correct name is 2-methyl-1-propyl nitrite.

IV.C.7.b. Evaluation of the Estimated k_{OH} Data

Leifer did not have available S/R relationships from Atkinson for the alkyl nitrites; hence, no entries appear in the column Estimated/HC. However, Meylan (1990b) did develop S/R relationships for this class of compounds (RONO) by assuming that the only reaction pathway is H-atom abstraction from the C-H groups in R. Based on the available experimental k_{OH} data, Meylan assumed that for the nitrites

$$F(-O-N = **) = 2.00 \qquad (54)$$

Furthermore, for these compounds, where appropriate, Meylan used the substituent factor $F(-CH_2-O-)$ from Table 2.

Using the above substituent factors, AOP calculated k_{OH}; and these values are listed in Table 19.B. along with the percent error (in brackets adjacent to the estimated values). From an inspection of the percent error data, it is clear that the results are generally very poor; 1-propyl nitrite and 2-methyl-1-propyl nitrite had percent errors greater than +100 while 1-butylnitrite had a percent error of +65. These results are not surprising since Atkinson (1989) Stated "Until the kinetics of OH radicals with alkyl nitrites are fully understood and product studies carried out, the reaction mechanisms remain uncertain. These may proceed via H-atom abstraction from the C-H bonds ---- and this is expected to be the major, if not the only, reaction pathway ---". Therefore, it is apparent that more reliable k_{OH} data and product data are needed for the alkyl nitrites listed in

Table 19.B. and for other alkyl nitrites in order to develop more reliable S/R relationships.

IV.D. Addition of Hydroxyl Radicals to Alkenes, Conjugated Dialkenes, Alkynes, and 1,2-Dialkenes

IV.D.1. Unsubstituted Alkenes

IV.D.1.a. Evaluation of the Experimental k_{OH} Data

Table 20 summarizes the pertinent experimental k_{OH} data at 298 K for the reaction of OH radicals with unsubstituted alkenes as reported in AOP, in Atkinson (1989), and in the literature. A careful inspection of the experimental k_{OH} data reported in the columns Experimental/AOP and Experimental/(a) indicates that, in general, they are the same; there are, however, some differences. For a few chemicals, AOP lists k_{OH} to 4 significant figures while Experimental/(a) reports k_{OH} to 3 significant figures. At best, the experimental k_{OH} data is good to 3 significant figures. For example, for 2,3-dimethyl-2-butene, the experimental k_{OH} data reported in the literature is only given to 3 significant and Atkinson (1989) recommended a value of 110* while AOP lists a value of 110.0. For the other chemicals with differences, Experimental/(a) lists an average value from the literature while AOP selects one set. Unless there is good reason to disregard specific sets of data, it is best to list an average value from all the data sets rather than the value from only one set.

It should be noted that AOP does not list an experimental value for Δ^3- carene in column 2; however, a value is listed in the document "Estimation Accuracy of AOP versus PCFAP" [Meylan

Table 20. Comparison of the Estimated Values of k_{OH} at 298 K for Unsubstituted Alkenes from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. ACYCLIC ALKENES				
Ethene (Ethylene)	8.52	8.52*	8.5200[q]	(r)
Propene (Propylene)	26.3	26.3*	26.4	26.4
1-Butene	31.4	31.4*	27.3	27.3
cis-2-Butene	56.4	56.4*	56.4	56.4
trans-2-Butene	64.0	64.0*	64.0	64.0
2-Methylpropene	51.4	51.4*	51.7	51.7
1-Pentene	31.4	31.4*	28.6	28.6
cis-2-Pentene	65.4	65.7[b]	57.3	57.3
trans-2-Pentene	66.9	66.9[c]	64.9	64.9
2-Methyl-2-butene	86.9	86.9*	87.3	87.3
2-Methyl-1-butene	60.7	60.6[d]	52.6	52.6
3-Methyl-1-butene	31.8	31.8*	28.5	28.5
1-Hexene	37.5	35.2[e]	30.0	30.0
2-Methyl-1-pentene	62.6	62.6[f]	53.9	53.9
2-Methyl-2-pentene	88.8	89.1[g]	88.2	88.2
trans-4-Methyl-2-pentene	60.8	60.5[f]	66.0	66.0
2,3-Dimethyl-2-butene	110.0	110*	111	111
3,3-Dimethyl-1-butene	28.4	28.5[h]	26.9	26.9
1-Heptene	40.5	38.3[i]	31.4	31.4
2,3-Dimethyl-2-pentene	108.0	103[j]	111	111
trans-4,4-Dimethyl-2-pentene	54.5	54.5[f]	64.4	64.4
1,4-Pentadiene	53.3	53.3[c]	53.4	53.4
trans-1,4-Hexadiene	90.3	90.6[c]	91.0	91.0
1,5-Hexadiene	62.1	62.0[c]	54.8	54.8

Table 20. Continued

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
2-Methyl-1,4-pentadiene	78.8	78.8[c]	78.7	78.7
2-Methyl-1,5-hexadiene	96.1	96.1[c]	80.0	80.0
2,5-Dimethyl-1,5-hexadiene	120.0	120[c]	105	105
B. CYCLIC ALKENES				
Cyclopentene	67.3	65.5[k]	58.9	58.9
Cyclohexene	67.7	67.7*	61.1	61.1
1,4-Cyclohexadiene	99.4	99.5[l]	114	114
Cycloheptene	74.4	74.4[m]	62.4	62.5
1-Methylcyclohexene	94.4	94.4[n]	92.0	92.0
Bicyclo [2.2.1]-2-heptene	49.3	49.3[m]	62.7	62.7
Bicyclo[2.2.1]-2,5-heptadiene	120.0	120[m]	116	116
Bicyclo[2.2.2]-2-octene	40.8	40.8[m]	67.8	67.8
α-Pinene	53.7	53.7*	89.5	89.5
β-Pinene	78.9	78.9*	54.2	54.1
d-Limonene	171.0	160[n]	145	145
Δ^3-Carene	(p)	87.8[o]	87.6	87.6
γ-Terpinene	177.0	177[o]	178	178

[a] Experimental values from Atkinson (1989) and the literature.
[b] Average value from the data of Ohta (1984) and Wu et al. (1976).
[c] Experimental value from Ohta (1983) and Atkinson (1989).
[d] Average value from the data of Ohta (1984) and Wu et al. (1976). The experimental value of k_{OH} of Morris and Niki (1971) was considered to be too high and was discounted when making recommendations for other alkenes (e.g., for 1-pentene) by Atkinson (1989).
[e] Average value from the experimental data of Wu et al. (1976) and Atkinson and Aschmann (1984).
[f] Experimental value from Ohta (1984) and Atkinson (1989).
[g] Average value of the relative rate data of Ohta (1984) using 2-methyl-2-butene and cis-2-pentene as reference compounds.

[h] Experimental value from Wu et al. (1976) and Atkinson (1989).
[i] Average value of the experimental data of Darnall et al. (1976) and Atkinson and Aschmann (1984).
[j] Average value of the relative rate data of Ohta (1984) using 2-methyl-2-butene and 2,3-dimethyl-2-butene as reference compounds.
[k] Average value from the experimental data of Atkinson, Aschmann, and Carter (1983) and the relative rate data of Rogers (1989) with cyclohexene as the reference compound.
[l] Average value from the experimental data of Atkinson, Aschmann, and Carter (1983) and Ohta (1983).
[m] Experimental value from Atkinson Aschmann, Carter (1983).
[n] Experimental value from Darnall et al. (1976).
[o] Experimental value from Atkinson, Aschmann, Pitts (1986).
[p] No experimental value is given in the AOP database. An experimental value of $87.8 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ is given in the document estimation accuracy of AOP versus PCFAP.
[q] Estimated value is the experimental value.
[r] Cannot be estimated by the S/R relationships of Atkinson.
[*] Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

(1990b)]. The value of 87.8 should be listed in the AOP database.

IV.D.1.b. Evaluation of the Estimated k_{OH} Data

Comparison of the estimated k_{OH} data in columns 4 and 5 indicates that, in general, they are the same; there are, however, a few differences. For ethene, AOP lists a estimated value of 8.5200 in the summary table which corresponds to the experimental value while HC does not list a value; k_{OH} cannot be estimated by the S/R relationships of Atkinson. Furthermore, AOP lists the estimated value to five significant figures which is incorrect since the recommended experimental value by Atkinson (1989) is 8.52* which only has three significant figures.

For OH addition to olefinic bonds, the detailed calculations show an inconsistency. From the mathematical synopsis of the S/R relationships of Atkinson (equation 15), substituent factors attached to the olefinic group can influence $k_{add,nar}$ (or k_d in Meylan's notation), Table 8; therefore, for consistency in calculating the rate constant for this reaction pathway, the term C(R) should be used, even though C(R) = 1.00. For example, for 1-pentene, OH addition to the olefinic group should be

$$k_{add,nar} = k_o^{is}(CH_2{=}CHR)[C(R)] = 26.3(1.00)$$

$$k_{add,nar} = 26.3 \qquad (55)$$

For 2-methyl-2-pentene,

$$k_{add,nar} = k_o^{is}(R_1R_2C{=}CHR_3)[C(R_1)C(R_2)C(R_3)]$$

$$k_{add,nar} = k_O^{is}(R_1R_2C{=}CHR_3)(1.00)(1.00)(1.00)$$

$$k_{add,nar} = 86.9 \qquad (56)$$

This comment is also applicable to the compounds listed in Table 22 for the conjugated dienes, and in Table 23 for the allenes and alkynes.

For C-H abstraction from the olefinic group (e.g., =C-H), the detailed calculations should include this pathway, even though it is zero [i.e., k(1, UNS CH) = 0]. This comment, as well as the above comment, also applies to the other classes of compounds discussed in Section IV.D.

IV.D.2. Substituted Alkenes

IV.D.2.a. Evaluation of the Experimental k_{OH} Data

Table 21 summarizes the pertinent experimental k_{OH} data for the reaction of OH radicals with substituted alkenes as reported in Atkinson (1989), in AOP, and in the literature. A comparison of the experimental k_{OH} data listed in columns 2 and 3 indicate that, in general, they are the same; there are, however, some differences. For six compounds [i.e., 2-(chloromethyl)-3-chloro-1-propene, trans-2-butenal, and the four ketenes, no experimental k_{OH} values are listed in AOP; however, values are reported in the document "Estimation Accuracy of AOP versus PCFAP "[Meylan (1990b)]. The appropriate values should be listed in AOP. For acrylonitrile, AOP lists an experimental value of 4.0 while the correct value should be 4.1, the average value of the

ble 21. Comparison of the Estimated Values of k_{OH} at 298 K for Substituted Alkenes from the Atmospheric Oxidation Computer Program (AOP) and From a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. Haloalkenes				
Vinyl fluoride	5.56	5.56[b]	10.5	10.5
Vinyl chloride	6.60	6.60[b]	5.26	5.26
Vinyl bromide	6.81	6.81[b]	6.84	6.84
1,1-Difluoroethene	2.1	2.1[c]	8.22	8.22
cis-1,2-Dichloroethene	2.38	2.38[d]	2.24	2.24
trans-1,2-Dichloroethene	1.80	1.80[d]	2.55	2.55
Trichloroethene (Trichloroethylene)	2.36	2.36*	0.695	0.695
Tetrachloroethene (Tetrachloroethylene)	0.167	0.167*	0.176	0.176
3-Chloro-1-propene (3-Chloropropylene)	17.0	17*	20.3	20.3
cis-1,3-Dichloro-1-propene	8.41	8.41[d]	8.85	8.85
trans-1,3-Dichloro-1-propene	14.3	14.3[d]	10.0	10.0
2-(Chloromethyl)-3-chloro-1-propene	(e)	33.5[d]		30.3
B. α,B-UNSATURATED CARBONYLS				
Acrolein (2-Propenal)	19.9	19.9*	22.9	22.9
trans-Crotonaldehyde(trans-2-Butenal)	(e)	36*	32.8	32.8
Methacrolein(2-Methyl-2-propenal)	33.5	33.5*	29.6	29.6

Table 21. Continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Methyl vinyl ketone	18.8	18.8*	24.0	24.0
Ketene	(e)	173[f]	51.4	51.4
Methyl ketene	(e)	70[g]	87.0	87.0
Ethyl ketene	(e)	118[f]	87.9	87.9
Dimethyl ketene	(e)	107[f]	110	110
cis-3-Hexene-2,5-dione	63.1	63.1[h]	46.7	46.7
trans-3-Hexene-2,5-dione	53.1	53.1[h]	53.0	53.0
C. NITRILOALKENES				
Acrylonitrile (Cyanoethene)	4.0	4.1[i]	3.95	3.95
D. ALKOXY ALKENES				
Methyl vinyl ether	33.5	33.5[b]	35.1	35.1

[a] Experimental values from Atkinson (1989) and the literature.
[b] Experimental value from Perry, Atkinson, Pitts (1977a).
[c] Experimental data not reliable [Atkinson (1989)].
[d] Experimental value from Tuazon et al. (1988). This data is preferred since these experiments avoided or have taken into account the side reactions of chlorine atoms with the reference compounds [Atkinson (1989)].
[e] No experimental value is given in the AOP data base. However, experimental values are given in the document Estimation Accuracy of AOP versus PCFAP [Meylan (1990b)].
[f] Experimental value from Hatakeyama et al. (1985).
[g] Average value from the data of Hatakeyama et al. (1985).
[h] Experimental value from Tuazon et al. (1985).
[i] Average value from the experimental data of Harris et al. (1988) and Zetzsch (1983) as reported in Atkinson (1989).
* Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

experimental data of Harris et al. (1981) and Zetzsch (1983) as reported in Atkinson (1989). For 3-chloro-1-propene, the recommended value from Atkinson (1989) is 17*, which only has two significant figures, compared to a value of 17.0 listed in AOP.

IV.D.2.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated values of k_{OH} listed in AOP and HC for the compounds listed in Table 21 give the same results.

The use of four significant figures in the detailed calculations and three significant figures in the summary table are applicable in the same manner as described in previous sections.

IV.D.3. Conjugated Dienes

IV.D.3.a Evaluation of the Experimental k_{OH} Data

Table 22 compares the pertinent experimental k_{OH} data at 298 K for the reaction of OH radicals with conjugated dienes as reported in Atkinson (1989), in AOP, and in the literature. A comparison of the experimental k_{OH} data in columns 2 and 3 indicate that they are all different. The difference involves the number of significant figures used. For 2-methyl-1,3-butadiene, Atkinson (1989) lists a recommended value of 101* and not 101.0 as listed in AOP. In all the other cases, AOP incorrectly lists k_{OH} to four significant figures whereas the literature values listed in Atkinson (1989) and the literature contain only three significant figures.

Table 22. Comparison of the Estimated Values of k_{OH} at 298 K for Conjugated Acyclic and Cyclic Dialkenes from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3$$molecule^{-1}$$s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. ACYCLIC DIALKENES				
1,3-Butadiene	66.6	66.6*	66.6000[g]	(h)
cis-1,3-Pentadiene	101.0	101[b]	105	105
2-Methyl-1,3-butadiene	101.0	101*	105	105
trans-1,4-Hexadiene	112.0	112[b]	106	106
3-Methyl-1,3-pentadiene	136.0	136[b]	135	135
4-Methyl-1,3-pentadiene	131.0	131[b]	135	135
2,3-Dimethyl-1,3-butadiene	122.0	122[b]	135	135
2,5-Dimethyl-2,4-hexadiene	210.0	210[b]	231	231
3-Methylene-7-methyl-1,6-octadiene (Myrcene)	215.0	215[c]	194	194
3,7-Dimethyl-1,3,6-octatriene	252.0	252[c]	223	223
B. GYCLIC DIALKENES				
1,3-Cyclohexadiene	164.0	164[d]	137	137
1,3-Cycloheptadiene	139.0	139[e]	139	139
α-Phellandrene	313.0	313[f]	187	187
α-Terpinene	363.0	363[f]	235	235

[a] Experimental values from Atkinson (1989) and the literature.
[b] Experimental value from Ohta (1983).
[c] Experimental value from Atkinson, Aschmann, Pitts (1986).
[d] Experimental value from Atkinson, Aschmann, Carter (1983).
[e] Experimental value from Atkinson, Aschmann, Carter (1984a).
[f] Experimental value from Atkinson et al. (1986).
[g] Estimated value is the experimental value.
[h] Cannot be estimated by the S/R relationship of Atkinson.
* Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

IV.D.3.b. Evaluation of the Estimated k_{OH} Data.

A comparison of the estimated data in columns 4 and 5 of Table 22 indicates that they are identical except for the entree for 1,3-butadiene. For this compound, the value of 66.6000 corresponds to the experimental value [which should be 66.6* as recommended by Atkinson (1989)] and is not an estimated value. There is no entry under the column HC since there is no S/R relationship for this compound.

IV.D.4. Alkynes and 1,2-Dienes (Allenes)

IV.D.4.a. Evaluation of the Experimental k_{OH} Data

Table 23 summarizes the pertinent experimental k_{OH} at 298 K for the reaction of OH radicals with alkynes and 1,2-dienes (allenes) as reported in Atkinson (1989), in AOP, and in the literature. A comparison of the experimental k_{OH} data reported in columns 2 and 3 are the same except for three differences; for propyne and 1-butyne, the correct values with two significant figures, as recommended in Atkinson (1989), should be used in AOP; the value for 1-hexyne reported by Boodegheans et al. (1987) and Atkinson (1989) is 12.6 and not 11.9 as reported by AOP; and finally for propadiene, Atkinson (1989) recommended a value of 9.84* and not 9.82 as reported by AOP.

IV.D.4.b. Evaluation of the Estimated k_{OH} Data

Except for ethyne, butadiyne, and propadiene, the estimated values of k_{OH} at 298 K in columns 4 and 5 are identical. For these three compounds, no estimated values appear under the

Table 23. Comparison of the Estimated Values of k_{OH} at 298 K for Alkynes and 1,2-Dialkenes (Allenes) from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}(cm^3molecule^{-1}s^{-1})$			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. ALKYNES				
Ethyne (Acetylene)	0.815	0.815	0.8150[b]	(c)
Propyne	5.90	5.9*	6.54	6.54
1-Butyne	8.00	8.0*	7.42	7.42
2-Butyne	27.4	27.4*	29.3	29.3
1-Pentyne	11.2	11.2[d]	8.75	8.25
1-Hexyne	11.9	12.6[d]	10.1	10.1
Butadiyne (Diacetylene)	18.9	18.9*	14.08	(c)
B. 1,2 DIENES (ALLENES)				
Propadiene	9.82	9.84*	9.820[b]	(c)
1,2-Butadiene	26.1	26.1[e]	31.1	31.1
1,2-Pentadiene	35.5	35.5[e]	32.0	32.0
3-Methyl-1,2-butadiene	56.9	56.9[e]	57.3	57.3

[a] Experimental values from Atkinson et al. (1989) and the literature.
[b] Estimated value is the experimental value.
[c] Cannot be estimated by the S/R relationships of Atkinson.
[d] Experimental value from Boodaghians et al. (1987).
[e] Experimental value from Ohta (1983).
* Recommended by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

column Estimated/HC since Atkinson never developed S/R relationships for these compounds. It should be noted that the values listed under the column Estimated/AOP for these three compounds are not estimated values but are experimental values and there are too many significant figures; they should only have 3 significant figures.

IV.E. Reaction of Hydroxyl Radicals with Organic Compounds Containing Sulfur, Nitrogen, and Phosphorous Functional Groups

IV.E.1. Reaction with Thiols, Sulfides, and Disulfides

IV.E.1.a. Evaluation of the Experimental k_{OH} Data

Table 24 summarizes the pertinent experimental k_{OH} data for the reaction of OH radicals with alkyl thiols, sulfides, and disulfides as reported in Atkinson (1989), in AOP, and in the literature. A careful inspection of the experimental k_{OH} data in columns 2 and 3 indicate that they are the same except for a few differences. For a few of the compounds, the experimental values in Experimental/(a) are listed with only two significant figures whereas the data listed in Experimental/AOP have three significant figures. A check on the original literature sources indicate that the k_{OH} values with two significant figures are the correct ones. For example, for 1-butanethiol, the recommended value of k_{OH} from Atkinson (1989) is 51* while AOP lists 51.0. For methyl ethyl sulfide, the experimental value from Hynes et al. (1986) and Atkinson (1989) is 8.50 and not 8.5 as listed in AOP. For dimethyl disulfide, AOP does not have an entry in column 2 whereas Atkinson (1989) recommends a value of 211*.

Table 24. Comparison of the Estimated Values of k_{OH} at 298 K for Alkyl Thiols, Sulfides, and Disulfides from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3$$molecule^{-1}$$s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. THIOLS				
Methanethiol	32.9	32.9*	32.3	32.3
Ethanethiol	46.8	46.8*	38.7	38.7
1-Propanethiol	48.3	48.3*	42.0	42.0
2-Propanethiol	42.0	42.0*	47.8	47.8
1-Butanethiol	51.0	51*	43.4	43.4
2-Methyl-1-propanethiol	45.0	45*	43.5	43.5
2-Butanethiol	40.0	40*	53.7	53.7
2-Methyl-2-propanethiol	33.1	33.1*	31.6	31.6
2-Methyl-1-butanethiol	54.0	54.3[b]	44.9	44.9
B.1. ACYCLIC SULFIDES[e]				
Dimethyl sulfide	4.56	4.56*	4.59	2.59
Methyl ethyl sulfide	8.5	8.50[c]	11.0	9.02
Diethyl sulfide	15.0	15*	17.5	15.5
Di-n-Propyl Sulfide	20.0	20.0[d]	24.0	22.0
B.2. CYCLIC SULFIDES[e]				
Tetrahydrothiophene	19.7	19.7*	19.8	17.8
C. DISULFIDES				
Dimethyl disulfide	(f)	211*	203	203

[a] Experimental values from Atkinson (1989) and the literature.
[b] Experimental value from Barnes et al. (1986).
[c] Experimental value from Hynes et al. (1986).
[d] Experimental value from Barnes et al. (1986). The experimental value of Nielsen et al. (1987) appear to be erroneous [Atkinson (1989)].
[e] For these compounds, k_{OH} was measured in the absence of oxygen.

[redacted]ble 24. continued

[f] No experimental value is given in the AOP database. An experimental value of $211 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ is given in the document "Estimation Accuracy of AOP versus PCFAP" [Meylan (1990b)].

* Recommended value by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

Finally, for 2-methyl-1-butanethiol, the correct experimental value of k_{OH} in column 3 is 54.3 obtained from Barnes et al. (1986) and Atkinson (1989), and not 54.0 as reported by AOP.

IV.E.1.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated k_{OH} data from AOP and HC indicates that they are the same except for the alkyl sulfides (acyclic and cyclic). For all these sulfides, k_{OH} is larger from AOP than from HC. The reason for the differences will be described in the following paragraphs.

In estimating k_{OH}, there are two reaction pathways for the reaction of OH radicals with alkyl (acyclic and cyclic) sulfides: (1) H-atom abstraction from the C-H groups in the alkyl groups; and (2) OH radical interaction with the sulfide group to form the adduct [>S$\cdots$OH] which then decomposes rapidly in the presence of oxygen to form the products. The total rate of reaction is then given by the equation

$$k_{OH} = k(1) + k(4) = k(1) + k(-S-) \qquad (57)$$

In the absence of oxygen, k(-S-) is zero [Atkinson (1987) and Leifer (1992a)] so that equation 57 becomes

$$k_{OH} = k(1) \qquad (58)$$

and only C-H abstraction from the alkyl groups takes place.

In estimating k_{OH}, AOP uses equation 57 while HC uses equation 58 and this is the reason why k_{OH} (AOP) > k_{OH}(HC). Since the experimental values listed in the column

Experimental/(a) were obtained in rate measurements without oxygen, k_{OH} must be evaluated using equation 58. Therefore, AOP must qualify the experimental k_{OH} value for the alkyl sulfides to indicate that the data were obtained in the absence of oxygen; and thus, only H-atom abstraction occurs. Then, in the detailed calculation section, AOP must indicate that k(-S-) = 0 in the absence of oxygen.

IV.E.2. Reaction with Sulfoxides and Sulfates

IV.E.2.a. Evaluation of the Experimental k_{OH} Data

Table 25 summarizes the pertinent experimental k_{OH} data at 298 K for alkyl sulfoxides and sulfates as reported in Atkinson (1989), in AOP, and in the literature. A comparison of the experimental data in columns 2 and 3 indicate that only for dimethyl sulfoxide is there a difference. The experimental value from Barnes et al. (1986) and Atkinson (1989) is 62 and not 62.0 as listed in AOP.

IV.E.2.b. Evaluation of the Estimated k_{OH} Data

Atkinson did not develop S/R relationships for alkyl sulfoxides and sulfates; hence, there are no estimated values listed under the column Estimated/HC. Meylan (1990b) did develop S/R relationships for these classes of compounds as described in the following paragraphs.

In developing S/R relationships for the alkyl sulfoxides, Meylan (1990b) assumed that only C-H abstraction occurred from the alkyl group. Therefore,

Table 25. Comparison of Estimated Values of k_{OH} at 298 K for Alkyl Sulfoxides and Sulfates from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP(%Error)[f]	HC
A. SULFOXIDES				
Dimethyl sulfoxide	62.0	62[b]	28.5(-54)	(e)
B. SULFATES				
Dimethyl sulfate	<0.5	<0.5[c]	1.76(>+250)	(e)
Diethyl sulfate	1.8	1.8[d]	11.5(+540)	(e)

[a] Experimental values from Atkinson (1989) and the literature.
[b] Experimental value from Barnes et al. (1986).
[c] Experimental value from Japar et al. (1990).
[d] Experimental value from Japar et al. (1990a).
[e] Atkinson did not develop S/R relationships for alkyl sulfoxides and sulfates.
[f] Calculated using the experimental value listed in Experimental/(a).

$$k_{OH} = k(1) \quad (59)$$

$$F[S(+4)\ **\ ] = 99.000 \text{ (Table 2)} \quad (60)$$

Using equations 59, 60, and 11, AOP estimated that k_{OH} was 28.5 and the percent error, relative to the experimental value listed in the column Experimental/(a), was -54 (listed in parentheses adjacent to the estimated value in column 4). However, intuitively, it is expected that the sulfoxide group would undergo further oxidation to the sulfone in the presence of oxygen

$$R\text{-}S(=O) + \cdot OH \longrightarrow \left[R\text{—}S(=O)\cdots OH\right] \xrightarrow[O_2]{\text{Rapid}} \text{Products} \quad (61)$$

and this reaction pathway should be considered in the S/R relationships. Therefore, considerably more experimental k_{OH} data are needed on OH radical reaction with a member of alkyl sulfoxides (both acyclic and cyclic) and aromatic sulfoxides to determine the reaction mechanism and to develop S/R relationships for this class of compounds. As a result, it is recommended that Meylan drop the S/R relationships for this class of compounds from AOP.

For the alkyl sulfates, Meylan (1990b) assumed that

$$k_{OH} = k(1) \quad (62)$$

and the substituent factors F(-O-) and F($-CH_2-O-$) were valid. Using equations 62 and 11 along with the appropriate substituent

factors, AOP calculated k_{OH} for dimethyl and diethyl sulfate. The percent error for each of these compounds were greater than +250 and +540, respectively. Hence, these results are very poor and more experimental k_{OH} data are needed for a number of additional sulfates to derive better S/R relationships for this class of compounds. Therefore, it is recommended that Meylan delete the S/R relationships for the sulfates from AOP.

IV.E.3. Reaction with Alkyl Amines, Alkyl Hydrazines, and N-Substituted Amines

IV.E.3.a. Evaluation of the Experimental k_{OH} Data

Table 26 summarizes the pertinent experimental k_{OH} data at 298 K for alkyl amines, alkyl hydrazines, and N-substituted amines as obtained from Atkinson (1989), AOP, and the literature. A comparison of the experimental k_{OH} data for these compounds in columns 2 and 3 indicates that they are the same except for two differences. One difference is related to the number of significant figures used. Thus, for diethylhydroxylamine, the reported literature value is 101 which was obtained from Gorse et al. (1977) and Atkinson (1989) while AOP lists a value of 101.0. Similar comments apply to 2-methyl-2-amino-1-propanol, diethylhydroxylamine, and methyl hydrazine. For the other difference, AOP does not report an experimental value for hydrazine.

IV.E.3.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated values of k_{OH} reported by AOP and HC (columns 4 and 5, respectively) indicate that they are the

Table 26. Comparison of the Estimated Values of k_{OH} at 298 K for Alkyl Amines, Hydrazines, and N-Substituted Amines from the Atmospheric Oxidation Computer Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. ALKYL AMINES				
Methylamine	22.0	22.0[b]	21.4	21.4
Ethylamine	27.7	27.7[c]	28.6	28.6
Dimethylamine	65.4	65.4[c]	62.9	62.9
Trimethylamine	60.9	60.9[c]	64.3	64.3
Dimethylhydroxyethylamine (2-Dimethylaminoethanol)	90.0	90[d]	77.4	77.4
2-Methyl-2-Amino-1-propanol	28.0	28[e]	24.1	24.1
B. N-HYDROXYLAMINES				
Diethylhydroxylamine	101.0	101[f]	77.2	77.2
C. N-NITROSAMINES				
Dimethyl-N-nitrosamine	2.53	2.53[g]	2.88	2.88
D. N-NITRAMINES				
Dimethyl-N-nitramine	3.84	3.84[g]	2.88	2.88
E. ALKYL HYDRAZINES				
Hydrazine	(h)	61[i]	(j)	40.0
Methylhydrazine	65.0	65[i]	81.4	81.4

[a] Experimental data from Atkinson (1989) and the literature.
[b] Experimental value from Atkinson, Perry, Pitts (1977).
[c] Experimental value from Atkinson, Perry, Pitts (1978).
[d] Original experimental data is from Anderson and Stephens (1988) which represents the most reliable data [Atkinson (1989)].
[e] Experimental value from Harris and Pitts (1983).
[f] Experimental value from Gorse et al. (1977).
[g] Experimental value from Tuazon et al. (1984).
[h] AOP does not list an experimental value.
[i] Experimental value from Harris et al. (1979) as reported by Atkinson (1987).
[j] AOP cannot estimate k_{OH} for this compound since it does not contain carbon.

same except for hydrazine. AOP cannot estimate k_{OH} for hydrazine since it does not contain carbon while HC lists an estimated value of 40.0. In order for AOP to estimate k_{OH}, the chemical must contain carbon. As stated previously in AOP, the experimental value should be entered in column 4 and qualify it to state that this is the experimental value.

IV.E.4. Reaction with Compounds Containing Phosphorous Functional Groups

IV.E.4.a. Evaluation of the Experimental k_{OH} Data

Table 27 summarizes the pertinent experimental k_{OH} data at 298 K for several classes of organophosphorous compounds as reported in Atkinson (1989), in AOP, and in the literature. A comparison of the experimental k_{OH} data in columns 2 and 3 indicate that there are differences. For trimethylphosphate, triethyl phosphate, O,O,S-trimethyl phosphorothioate, and O,S,S-trimethyl phosphorodithioate, there are slight differences. The correct values, as obtained from Atkinson (1989) and the literature, are 7.37, 55.3, 9.29, and 9.59, respectively. For the compounds O,O-dimethyl phosphoroamidothioate and O,O,N-trimethyl phosphoroamidothioate, the values from Atkinson (1989) and the literature are only good to three significant figures rather than the 4 significant figures listed in AOP.

IV.E.4.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated k_{OH} data from AOP and HC indicates that they are the same. It should be noted that the summary table and detailed calculations in AOP should include reaction with phosphorous functional groups. For example, for

Table 27. Comparison of the Estimated Values of k_{OH} at 298 K for Aliphatic Compounds Containing Phosphorous Functional Groups from the Atmospheric Oxidation Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. ALKYL PHOSPHATES/ THIOPHOSPHATES				
Trimethyl phosphate $(CH_3O)_3P=O$	7.4	7.37[b]	8.64	8.64
Triethyl phosphate $(CH_3CH_2O)_3P=O$	55.0	55.3[c]	52.2	52.2
O,O,O-Trimethyl phosphorothioate $(CH_3O)_3P=S$	69.7	69.7[d]	63.6	63.6
O,O,S-Trimethyl phosphorodithioate $(CH_3O)_2P(S)CH_3$	56.0	56.0[d]	65.6	65.6
O,O,S-Trimethyl phosphorothioate $(CH_3O)_2P(O)SCH_3$	9.3	9.29[d]	10.6	10.6
O,S,S-Trimethyl phosphorodithioate $(CH_3S)_2P(O)OCH_3$	9.6	9.59[d]	12.6	12.6

Table 27. continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
B. DIALKYL CHLORO-PHOSPHOROTHIOATES				
O,O-Dimethyl chloro-phosphorothioate $(CH_3O)_2P(S)Cl$	59.0	59.0[c]	60.8	60.8
C. ALKYL PHOSPHOROAMIDATES AND ALKYL PHOSPHORO-THIOAMIDATES				
O,O-Dimethyl phosphoroamidothioate $(CH_3O)_2P(S)NH_2$	244.0	244[e]	80.8	80.8
O,O,N-Trimethyl phosphoroamidothioate $(CH_3O)_2P(S)NHCH_3$	232.0	232[e]	122	122
O,O,N,N-Tetramethyl phosphoroamidothioate $(CH_3O)_2P(S)N(CH_3)_2$	46.8	46.8[e]	124	124
O,O,N,N-Tetramethyl phosphoroamidate $(CH_3O)_2P(O)N(CH_3)_2$	31.9	31.9[e]	68.6	68.6

[a] Experimental data from the literature.
[b] Experimental data from Atkinson (1989) and Tuazon et al. (1986).
[c] Experimental data from Atkinson (1989) and Atkinson et al. (1988).
[d] Experimental data from Atkinson (1989) and Goodman et al. (1988).
[e] Experimental data from Atkinson (1989) and Goodman et al. (1988a).

trimethyl phosphate, the summary table should be Reaction with N,P,S, and OH and the detailed calculation should be

Reaction with Nitrogen, Phosphorous, Sulfur, and -OH

$$k[P(=O)] = 0.000 \quad (63)$$

and for $(CH_3O)_2P(=S)NH_2$, the summary table should be Reaction with N,P,S, and OH and the detailed calculation should be

Reaction with Nitrogen, Phosphorous, Sulfur, and -OH

$$k[P(=S)] = 55.0 \quad (64)$$

$$k(NH_2) = 20.0 \quad (65)$$

IV.F. Reaction of Hydroxyl Radicals with Aromatic Compounds, Heterocyclic Aromatic Compounds, and Fused Ring Polyaromatic Compounds

IV.F.1. Aromatic Compounds

IV.F.1.a. Evaluation of the Experimental k_{OH} Data

Table 28 summarizes the pertinent k_{OH} data for the reaction of hydroxyl radicals with a number of chemicals in a variety of classes of aromatic compounds as reported in Atkinson (1989), in AOP, and in the literature. A careful inspection of the experimental k_{OH} data in columns 2 and 3 indicate that they are the same except for some differences. In a few cases, AOP lists the experimental values with more significant figures than the values reported on the literature. For example, for styrene, AOP lists a value of 58.0 while the recommended value by Atkinson (1989) is 58*. For aniline, AOP lists a value of 111.0 while

Table 28. Comparison of Estimated Values of k_{OH} at 298 K for Aromatic Compounds from the Atmospheric Oxidation Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical Class/Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
A. UNSUBSTITUTED AROMATIC COMPOUNDS				
Benzene	1.23	1.23*	2.04	2.04
Biphenyl	7.2	7.2*	7.12	7.12
B. ALKYLBENZENES				
Methylbenzene (Toluene)	5.96	5.96*	5.51	5.51
Ethylbenzene	7.1	7.1*	6.13	6.13
n-Propylbenzene	6.0	6.0*	7.46	7.46
i-Propylbenzene	6.5	6.5*	7.08	7.08
t-Butylbenzene	4.60	4.60[b]	5.08	5.08
o-Xylene	13.7	13.7*	6.88	6.88
m-Xylene	23.6	23.6*	14.4	14.4
p-Xylene	14.3	14.3*	6.88	6.88
o-Ethyltoluene	12.3	12.3*	7.72	7.72
m-Ethyltoluene	19.2	19.2*	14.6	14.6
p-Ethyltoluene	12.1	12.1*	7.72	7.72
1,2,3-Trimethylbenzene	32.7	32.7*	17.8	17.8
1,2,4-Trimethylbenzene	32.5	32.5*	17.8	17.8
1,3,5-Trimethylbenzene	57.5	57.5*	37.5	37.5

Table 28. continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
C. ALKENYLBENZENES				
Phenylethene (Styrene)	58.0	58*	28.2	28.2
2-Phenyl-1-propene (α-Methylstyrene)		52[c]	53.5	53.5
1-Phenyl-1-propene (β-Methylstyrene)		59[c]	65.8	65.7
1-Phenyl-2-methyl-1-propene (β-Dimethylstyrene)	33.0	33[d]	89.1	89.1
D. HALOBENZENES				
Fluorobenzene	0.69	0.69*	2.56	2.56
Chlorobenzene	0.77	0.77*	1.43	1.42
Bromobenzene	0.77	0.77*	1.28	1.28
Iodobenzene	1.1	1.1*	1.34	1.34
o-Dichlorobenzene	0.42	0.42[e]	0.414	0.414
m-Dichlorobenzene	0.72	0.72[e]	1.01	1.01
p-Dichlorobenzene	0.32	0.32[e]	0.414	0.414
1,2,4-Trichlorobenzene	0.532	0.532[f]	0.291	0.291
Hexafluorobenzene	0.172	0.172*	0.151	0.151
n-Propylpentafluoro-benzene	3.06	3.06[g]	2.89	2.90
E. HALOALKYLBENZENES				
Benzotrifluoride	0.46	0.46[h]	0.406	0.406
4-Chlorobenzotrifluoride	0.24	0.24[h]	0.285	0.285
Benzyl chloride	2.9	2.9*	2.42	2.43

Table 28. continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
F. MONOCHLOROBIPHENYLS				
2-Chlorobiphenyl	2.8	2.82[i]	2.95	2.95
3-Chlorobiphenyl	5.3	5.28[i]	4.42	4.42
4-Chlorobiphenyl	3.9	3.86[i]	2.95	2.95
G. HYDROXYBENZENES				
Phenol	26.3	26.3*	35.7	35.6
o-Cresol	42.0	42*	43.9	43.9
m-Cresol	64.0	64*	93.9	93.9
p-Cresol	47.0	47*	43.9	43.9
2,3-Dimethylphenol	80.2	80.2[j]	115	115
2,4-Dimethylphenol	71.5	71.5[j]	54.1	54.1
2,5-Dimethylphenol	80.0	80.0[j]	115	115
2,6-Dimethylphenol	65.9	65.9[j]	54.1	54.1
3,4-Dimethylphenol	81.4	81.4[j]	115	115
3,5-Dimethylphenol	113.0	113[j]	200.3	200
2,3-Dichlorophenol	1.66	1.66[k]	7.27	7.27
2,4-Dichlorophenol	1.06	1.06[k]	3.02	3.02
H. NITROBENZENES				
Nitrobenzene	0.14	0.149[l]	0.251	0.251
o-Nitrophenol	0.90	0.90	4.42	4.42
o-Nitrotoluene	0.70	0.70	0.805	0.805
m-Nitrotoluene	0.95	0.95	0.605	0.605

Table 28. continued

Chemical Class/Chemical	$10^{12}k_{OH}$(cm^3molecule$^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
I. AMINOBENZENES				
Aniline	111.0	111*	136	136
N,N-Dimethylaniline	148.0	148[m]	263	200
p-Chloroaniline	83.0	83.0[n]	53.6	53.6
2,4-Toluenediamine	192.0	192[o]	240	200
J. ADDITIONAL SUBSTITUTED BENZENES				
Methoxybenzene	17.3	17.3*	23.8	23.8
Benzonitrile	0.33	0.33	0.356	0.356
Benzaldehyde	12.9	12.9*	17.1	17.1
Acetophenone	2.74	2.74[p]	1.61	1.61
Thiophenol (Mercaptobenzene)	11.2	11.2[q]	13.3[r]	13.3[r]
Benzyl alcohol	22.9	22.9	7.99	7.99
Tetralin (1,2,3,4-Tetrahydronaphthalene)	34.3	34.3[s]	11.1	11.2
Indan (2,3-Dihydro-1H-indene)	9.2	9.2[t]	9.71	9.09
Fluorene (9H-Fluorene)	13.0	13.0[u]	9.42	9.37
1,4-Benzodioxin	25.2	25.2	33.0	33.0
2,3-Dihydrobenzofuran	36.6	36.6	38.0	36.3
1,4-Naphthoquinone	3.1	3.1	2.75	2.75

Table 28. continued

[a] Experimental data from Atkinson (1989) and the literature.
[b] Experimental data from Ohta and Ohyama (1985).
[c] Experimental data from Bignozzi et al. (1981).
[d] Experimental data from Chiorboli et al. (1983).
[e] Experimental data from Wahner and Zetzsch (1983).
[f] Experimental data from Rinke and Zetzsch (1984).
[g] Experimental data from Ravishankara et al. (1978a).
[h] Experimental data from Atkinson et al. (1985a).
[i] Experimental data from Atkinson and Aschmann (1985).
[j] Experimental data from Atkinson and Aschmann (1989).
[k] Experimental data from Nolting et al. (1987).
[l] Average of the experimental data of Witle et al. (1986) and Zetzsch (1982) as reported in Atkinson (1989).
[m] Experimental data from Atkinson et al. (1987).
[n] Experimental data from Wahner and Zetzsch (1983).
[o] Experimental data from Becker et al. (1988).
[p] Experimental data from Nolting et al. (1987) and Atkinson (1989).
[q] Experimental data from Barnes et al. (1986).
[r] For the thiol group on an aromatic ring, it was assumed that k(4)=k(-SH)=0 [Meylan (1990)].
[s] Experimental data from Atkinson and Aschmann (1988a).
[t] Experimental data from Baulch et al. (1986) as reported by Atkinson (1989).
[u] Experimental data from Klöpffer et al. (1986) and Becker et al. (1984) as reported in Atkinson (1989).
* Recommended value by Atkinson (1989) with the rationale for the recommendation and the uncertainty for the recommendation.

Atkinson (1989) recommends a value of 111*. In a few cases, AOP lists fewer significant figures than the values reported in the literature. For example, for 4-chlorobiphenyl, AOP reports a value of 3.9 while Atkinson and Aschmann (1985) and Atkinson report a value of 3.86.

It should be noted that for 1,4-benzodioxin, AOP lists the erroneous name 1,4-dibenzodioxin; and finally, for aniline, AOP first lists the experimental value for iodobenzene and when a key is pressed, the correct experimental value for aniline is displayed.

IV.F.1.b. Evaluation of the Estimated Data

A comparison of the estimated values of k_{OH} by AOP and HC in Table 28 indicates that they are the same except for some differences. First, consider the compounds 3,5-dimethylphenol, N,N-dimethylaniline, and 2,4-toluenediamine. In all three cases, AOP lists a maximum value of the rate constant for OH addition to an aromatic ring [i.e., $k(7) = k_{add,ar}$, equation 20] as $200 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$ whereas HC lists a maximum value of k_{OH} [equation 9] as $200 \times 10^{-12} cm^3 molecule^{-1} s^{-1}$. Since the maximum allowed collision rate is $200 \times 10^{-12} cm^3 molecules^{-1}$ [Atkinson (1987)], this boundary condition must be invoked on the estimation of k_{OH} and not on the estimation of $k(7) = k_{add,ar}$. It should be noted that this is only applicable to aromatic compounds and not to other compounds (e.g., dimethyl disulfide, α-terpinene, α-phellandrene, etc.)

For the compounds tetralin, indan, and fluorene, AOP makes an error in calculating $k(7) = k_{add,ar}$. For these three

compounds, AOP uses the incorrect value of σ_m^+ ($-CH_2-$) = 0.06** instead of the correct value of -0.064** [see Section IV.A., page 40, Table 9, No. 41 and Leifer (1992a), Table 22, page 109]. Furthermore, for the compounds tetralin, indan, fluorene, and 2,3-dihydrobenzofuran, which contain five membered rings, AOP calculates k(1c) erroneously. That is, for these compounds, AOP *makes an error by omitting the ring strain factor F(5) for the* five membered ring. As a result, the values of k_{OH} for these compounds are erroneous.

Finally, for the compounds β-methylstyrene, chlorobenzene, n-propylpentafluorobenzene, benzylchloride, and phenol, the small differences between the estimated k_{OH} from AOP and HC are a result of the method of rounding off the last digit.

IV.F.2. Heterocyclic Aromatic Compounds

IV.F.2.a. Evaluation of the Experimental k_{OH} Data

Table 29 summarizes the pertinent k_{OH} data for the reaction of hydroxyl radicals with heterocyclic aromatic compounds as reported in Atkinson (1989), in AOP, and in the literature. Inspection of the experimental k_{OH} data in columns 2 and 3 indicate that there are a few differences. For pyrrole, the recommended value by Atkinson (1989) is 110* whereas AOP reports a value of 110.0 which contains one more significant figure than is warranted from the experimental data; and for 1,3,5-triazine, the value from Atkinson et al. (1987) and Atkinson (1989) is 0.145 whereas AOP rounds off the data to 0.15. For imidazole and

ble 29. Comparison of the Estimated Values of k_{OH} at 298 K for Heterocyclic Aromatic Compounds from the Atmospheric Oxidation Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical	$10^{12}k_{OH}(cm^3molecule^{-1}s^{-1})$			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Furan	40.5	40.5*	40.5[b]	(c)
3-Methylfuran	93.5	93.5[d]	106.7(+14)[h]	(c)
Thiophene	9.53	9.53*	9.53[b]	(c)
Pyrrole	110.0	110*	110.0[b]	(c)
Imidazole	36.0	35.9[e]	36.0[b]	(c)
Oxazole	9.1	9.1[e]	9.10[b]	(c)
Thiazole	1.40	1.41[e]	1.40[b]	(c)
Pyridine	0.37	0.37[f]	0.370[b]	(c)
1,3,5-Triazine	0.15	0.145[g]	0.150[b]	(c)

[a] Experimental data from Atkinson (1989) and the literature.
[b] Experimental data for this compound.
[c] Cannot be calculated by HC since Atkinson did not develop S/R relationships for these types of compounds.
[d] Experimental data from Atkinson et al. (1989b).
[e] Experimental data from Witte and Zetzsch (1986) and Atkinson (1989).
[f] Average value from the data of Atkinson et al. (1987) and Witle and Zetzsch (1986) as reported by Atkinson (1989).
[g] Experimental value from Atkinson et al. (1987) as reported by Atkinson (1989).
[h] Percent Error from the value of k_{OH} in column Experimental/(a).

thiazole, the correct values of k_{OH} obtained from Witte and Zetzsch (1986) and Atkinson (1989) are 35.9 and 1.41, respectively, and not 36.0 and 1.40 as listed in AOP.

IV.F.2.b. Evaluation of the Estimated k_{OH} Data

Atkinson did not develop S/R relationships for heterocyclic aromatic compounds whereas Meylan (1990b) did develop S/R relationships for this class of compounds. Meylan used an approach similar to the one used by Atkinson for aromatic compounds (equations 20, 21, and 22). Thus, Meylan postulated that equations 23 and 24 are applicable to heterocyclic aromatic compounds where: (1) A_i is a constant which is equal to the experimental value of k_{OH} for the parent heterocyclic aromatic ring; and (2) the second term is identical to the one used by Atkinson for substituents on the aromatic ring [i.e., -1.35 Min ($\sum_j \sigma_j^+$) in equation 21]. The values of A_i are given in Table 10 for a number of parent heterocyclic aromatic rings.

The only available experimental k_{OH} data for this class of compounds is for 3-methylfuran, a substituted furan. Atkinson (1989b) reported a value of 93.5 for this compound. The estimated value of k_{OH} obtained from equations 23 and 24 is 106.7 which gives a percent error of +14 which is excellent. However, more experimental k_{OH} data are needed for a number of substituted heterocyclic aromatic compounds listed in Table 29 to confirm the validity of equations 23 and 24.

IV.F.3. Fused Ring Polyaromatic Compounds

IV.F.3.a. Evaluation of the Experimental k_{OH} Data

Table 30 summarizes the pertinent experimental k_{OH} data for the reaction of hydroxyl radicals with fused ring polyaromatic compounds [i.e., fused ring polyaromatic hydrocarbons (PAH)]. Inspection of the data in columns 2 and 3 indicate that they are the same except for a few differences. For anthracene, the correct value is 112 as reported by Biermann et al. (1985) and Atkinson (1989) and not 110.0 as reported by AOP. For phenanthrene, the recommended value by Atkinson (1989) is 31* and not 31.0 as reported by AOP.

Unfortunately, there are no available experimental k_{OH} data for fused ring polyheteroaromatic compounds published in the literature. Hence, there are no entries in Table 30 for this class of compounds.

IV.F.3.b. Evaluation of the Estimated k_{OH} Data

A comparison of the estimated values of k_{OH} in columns 4 and 5 of Table 30 indicate that they are the same except for a few differences. The differences are related directly to the dissimilarity between the S/R relationships of Atkinson [equations 26, 27 and 28] and Meylan [equation 29]. First of all, AOP uses the experimental value of k_{OH} for the parent PAH (which is B_i in equation 29) while Atkinson uses the ionization potential of the parent PAH. For naphthalene, both methods give essentially the same results; however, for anthracene and

Table 30. Comparison of the Estimated Values of k_{OH} at 298 K for Fused Ring Polyaromatic Compounds (PAH) from the Atmospheric Oxidation Program (AOP) and from a Hand Calculation (HC) and the Experimental k_{OH} Data Reported in the Literature Versus the Experimental k_{OH} Data in AOP

Chemical	$10^{12}k_{OH}$($cm^3molecule^{-1}s^{-1}$)			
	Experimental		Estimated	
	AOP	(a)	AOP	HC
Naphthalene	21.6	21.6*	21.6[b]	21.4
1-Methylnaphthalene	53.0	53.0[c]	56.9	56.3
2-Methylnaphthalene	52.3	52.3[d]	56.9	56.3
2,3-Dimethylnaphthalene	76.8	76.8[d]	70.0	69.5
1-Nitronaphthalene	5.4	5.4[e]	2.66	2.63
2-Nitronaphthalene	5.6	5.6[e]	2.66	2.63
1,4-Dichloronaphthalene	5.8	5.8[f]	4.38	4.37
Anthracene	110.0	112[g]	110.0[b]	91.2
Phenanthrene	31.0	31*	31.0[b]	22.9

[a] Experimental data from Atkinson (1989) and the literature.
[b] Experimental data for this compound.
[c] Experimental data from Atkinson and Aschmann (1987).
[d] Experimental data from Atkinson and Aschmann (1986).
[e] Experimental data from Atkinson et al. (1989d).
[f] Experimental data from Klöpffer et al. (1986) and Becker et al. (1984) as reported in Atkinson (1989).
[g] Experimental data from Biermann et al. (1985).
* Recommended values by Atkinson (1989) with the rationale for the recommendation, and the uncertainty for the recommendation.

phenanthrene, AOP gives the most reliable results. For the substituted naphthalenes, AOP and Atkinson (HC) give essentially the same results. However, more experimental k_{OH} data are needed for considerably more substituted polyaromatic hydrocarbons to see how reliable both methods are.

Since there are no experimental k_{OH} data for fused ring heterocyclic polyaromatic compounds (i.e., quinoline, isoquinoline, quinoxaline, quinazoline, and acridine), Meylan's S/R method cannot be evaluated. Thus, experimental k_{OH} data is needed on a number of compounds in this class of compounds to confirm and refine the AOP method (i.e., equation 30).

IV.G. Evaluation of the Estimated Half-Life for the Reaction of Hydroxyl Radicals with Organic Chemicals in the Troposphere

Meylan (1990b), in AOP, estimated the half-life [$t_{(1/2)E}$] for the reaction of hydroxyl radicals with organic chemicals in the troposphere by assuming that the average OH radical concentration was 5×10^5 radicals cm^{-3} and a 24-hour daylight day. The assumption of a 24-hour daylight day is incorrect. On the average, a 12-hour daylight day is more reasonable. [Leifer (1992a)]. In addition, based on the literature data [Leifer (1992a)], the average OH radical concentration is closer to 1.5×10^6 radicals cm^{-3}. Therefore, it was recommended that the AOP computer program be changed to the atmospheric conditions described above. This has been done by Meylan in a later version of AOP.

For olefins and acetylenes, which can react with hydroxyl radicals and ozone, it is desirable to have knowledge of the overall oxidative half-life in the troposphere. Therefore,

$$k_{OX} = k'_{OH} + k'_{O_3} \tag{66}$$

where k'_{OH} and k'_{O_3} are the first-order rate constants for reaction of an organic chemical in the troposphere with respect to hydroxyl radicals and ozone, respectively, as calculated under the atmospheric conditions (OH) = 1.5×10^6 radicals cm^{-3} and a 12-hour daylight day and (O_3) = 7×10^{11} molecules cm^{-3}; and the overall oxidative half-life is given by the equation

$$\left[t_{(1/2)} \right]_{OX} = 0.693/k_{OX} \tag{67}$$

Thus, AOP should add

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$$k_{OX} = \tag{68}$$

$$t(1/2)_{OX} = \tag{69}$$

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Abstract (Limit: 200 words)

This document contains a critical review of the Atmospheric Oxidation Computer Program (AOP) for estimating the second-order rate constant (k_{OH}) for the reaction of an organic chemical with hydroxyl radicals in the gas-phase in the troposphere. AOP is being used to regulate industrial chemicals under Sections 4 and 5 of the Toxic Substances Control Act. It describes the computerization of the structure/reactivity relationships of Atkinson of the University of California/Riverside by Syracuse Research Corporation. The only input needed to operate AOP is the SMILES notation, a computerized notation of the molecular structure of the chemical. The computer program will estimate k_{OH} and the associated half-life for the reaction of organic chemicals in the atmosphere. AOP will also list an experimental value of k_{OH} if it is available in the scientific literature.

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