**Supplementary Material for:**

# Estimation of rate coefficients for the reactions of $O_3$ with unsaturated organic compounds for use in automated mechanism construction

Rate coefficients at 298 K are calculated for selected example alkenes and unsaturated oxygenates, using the SAR methods presented in the main paper.

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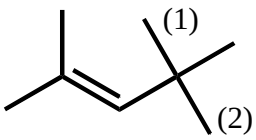
## Contents

# A. Acyclic alkenes

## A1: 2,4,4-trimethyl-pent-2-ene




Reference structure: $CHR=CR_2$ (Table 1)
Parameter: $k_{A5O3}$

$k_{298\,K} = 47 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$X_2$ = alkyl (acyclic)
$F_{\alpha(298)}(X_1) = F_{\alpha(298)}(X_2) = 0.54$

Rate coefficient calculation:

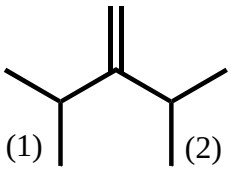
$k = k_{AO3} \Pi F_{\alpha}(X)$ (Equation (1))

$= 4.7 \times 10^{-16} \times 0.54 \times 0.54 = 1.37 \times 10^{-16}$

Calculated rate coefficient: $1.37 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $1.42 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## A2: 3-methyl-2-isopropyl-but-1-ene




Reference structure: $CH_2=CR_2$ (Table 1)
Parameter: $k_{A2O3}$

$k_{298\,K} = 1.4 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$X_2$ = alkyl (acyclic)
$F_{\alpha(298)}(X_1) = F_{\alpha(298)}(X_2) = 0.54$

Rate coefficient calculation:

$k = k_{AO3} \Pi F_{\alpha}(X)$ (Equation (1))

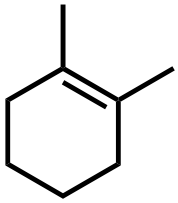
$= 1.4 \times 10^{-17} \times 0.54 \times 0.54 = 4.08 \times 10^{-18}$

Calculated rate coefficient: $4.08 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $3.24 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## B. Cyclic alkenes

### B1: 1,2-dimethyl-cyclohexene



Reference structure: $CR_2=CR_2$ (Table 1)
Parameter: $k_{A6O3}$

$k_{298\,K} = 110 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$F_{ring\,(6)} = 0.52$

Rate coefficient calculation:

$k = k_{AO3} \prod F_{ring}\, F_{\alpha}(X)$ (Equation (2))

$= 110 \times 10^{-17} \times 0.52 = 5.70 \times 10^{-16}$

Calculated rate coefficient: $5.70 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $2.07 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

### B2: bicyclo[2.2.1]-2-heptene (norbornene)

Reference structure: *cis*-CHR=CHR (Table 1)
Parameter: $k_{A3O3}$
$k_{298\,K} = 12 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$F_{ring\,(5)} = 3.9$
$F_{ring\,(6)} = 0.52$

Rate coefficient calculation:

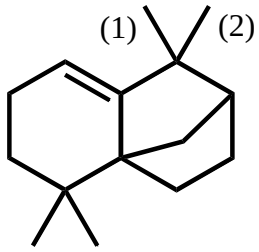
$k = k_{AO3} \prod F_{ring}\, F_{\alpha}(X)$ (Equation (2))

$= 12 \times 10^{-17} \times 0.52 \times 3.9 = 2.43 \times 10^{-16}$

Calculated rate coefficient: $2.43 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $9.0 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

**B3: (1R)-2,2,7,7-tetramethyltricyclo[6.2.1.0$^{1,6}$]undec-5-ene (isolongifolene)**




Reference structure: $CHR=CR_2$ (Table 1)
Parameter: $k_{A5O3}$

$k_{298\ K} = 47 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$X_2$ = alkyl (acyclic)
$F_{ring\ (6)} = 0.52$
$F_{ring\ (9)} = 2.1$
$F_{ring\ (10)} = 0.24$
$F_\alpha(X_1) = F_\alpha(X_2) = 0.54$

(N.B. the value adopted for 9-membered rings, $F_{ring\ (9)} = 2.1$, is a tentative value inferred from the *trans*-cyclononene ring in β-caryophyllene (see text – Section 3.2))

Rate coefficient calculation:

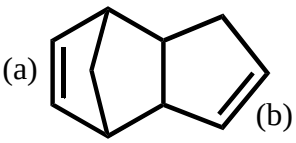
$k = k_{AO3} \Pi F_{ring} F_\alpha(X)$ (Equation (2))

$= 47 \times 10^{-17} \times 0.52 \times 2.1 \times 0.24 \times 0.54 \times 0.54 = 3.59 \times 10^{-17}$

Calculated rate coefficient: $3.59 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $1.0 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

**B4: 3a,4,7,7a-tetrahydro-1H-4,7-methano-indene (dicyclo-pentadiene)**




Reference structures: (a) *cis*-CHR=CHR; (b) *cis*-CHR=CHR (Table 1)
Parameter: (a) $k_{A3O3}$; (b) $k_{A3O3}$

$k_{a\ 298\ K}$ = 12 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$k_{b\ 298\ K}$ = 12 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$F_{ring\text{-}a\ (6)}$ = 0.52
$F_{ring\text{-}a\ (5)}$ = 3.9
$F_{ring\text{-}a\ (9)}$ = 2.1
$F_{ring\text{-}b\ (5)}$ = 3.9
$F_{ring\text{-}b\ (8)}$ = 2.8
$F_{ring\text{-}b\ (9)}$ = 2.1

(N.B. the value adopted for 9-membered rings, $F_{ring\ (9)}$ = 2.1, is a tentative value inferred from the *trans*-cyclononene ring in β-caryophyllene (see text – Section 3.2))

Partial rate coefficients:

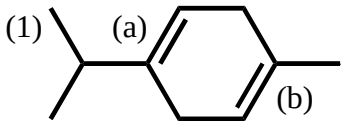
$k$ = $k_{AO3}$ Π $F_{ring}$ $F_{\alpha}(X)$ (Equation (2))

$k_a$ = 12 × $10^{-17}$ × 0.52 × 3.9 × 2.1 = 5.11 × $10^{-16}$
$k_b$ = 12 × $10^{-17}$ × 3.9 × 2.8 × 2.1 = 2.75 × $10^{-15}$

Total calculated rate coefficient ($k_a$ + $k_b$): 3.26 × $10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 1.51 × $10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

## B5: 1-isopropyl-4-methyl-cyclohexa-1,4-diene (γ-terpinene)




Reference structures: (a) $CHR=CR_2$; (b) $CHR=CR_2$ (Table 1)
Parameter: (a) $k_{A4O3}$; (b) $k_{A4O3}$

$k_{a\ 298\ K}$ = 47 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$k_{b\ 298\ K}$ = 47 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$F_{ring\ (6)}$ = 0.52
$X_1$ = alkyl (acyclic)
$F_{\alpha(298)}(X_1)$ = 0.54

Rate coefficient calculation:

$k_a$, $k_b$ = $k_{AO3}$ Π $F_{ring}$ $F_{\alpha}(X)$ (Equation (2))

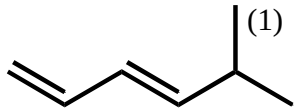
$k_a$ = 47 × $10^{-17}$ × 0.52 × 0.54 = 1.32 × $10^{-16}$
$k_b$ = 47 × $10^{-17}$ × 0.52 = 2.44 × $10^{-16}$

Total calculated rate coefficient ($k_a$ + $k_b$): 3.76 × $10^{-16}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 1.6 × $10^{-16}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

## C. Acyclic conjugated dialkenes

### C1: 5-methylhexa-1,3-diene




Reference structure: $CH_2$=CH=CH=CHR (Table 4)
Parameter: $k_{D3O3}$

$k_{298\,K}$ = 3.6 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$X_1$ = alkyl (acyclic)
$F_{\alpha(298)}(X_1)$ = 0.54

Rate coefficient calculation:

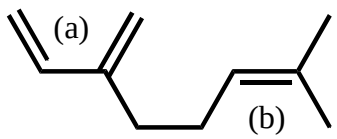
$k = k_{DO3}\,\Pi(F_\alpha(X))^{½}$ (Equation (3))

= 3.6 × $10^{-17}$ × $0.54^{½}$ = 2.65 × $10^{-17}$

Calculated rate coefficient: 2.65 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 2.37 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

### C2: 7-methyl-3-methylene-octa-1,6-diene (β-myrcene)




Reference structures: (a) $CH_2$=C(R)CH=$CH_2$ (Table 4); (b) CHR=$CR_2$ (Table 1)
Parameter: (a) $k_{D1O3}$; (b) $k_{A4O3}$

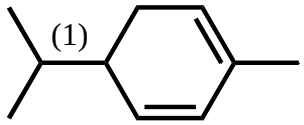
$k_{a\,298\,K}$ = 1.3 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$k_{b\,298\,K}$ = 47 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Total calculated rate coefficient ($k_a$ + $k_b$): 4.83 × $10^{-16}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 4.7 × $10^{-16}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

## D. Cyclic conjugated dialkenes

### D1: 5-isopropyl-2-methyl-cyclohexa-1,3-diene (α-phellandrene)




Reference structure: CHR=C(R)CH=CHR (Table 4)
Parameter: $k_{D8O3}$

$k_{298\,K} = 100 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$F'_{ring\,(6)} = 4.5$
$F_{\alpha(298)}(X_1) = 0.54$

Rate coefficient calculation:

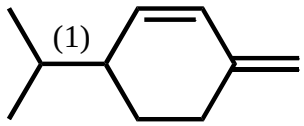
$k = k_{DO3}\,\Pi F'_{ring}(F_\alpha(X))^{½}$ (Equation (4))

$= 1.0 \times 10^{-15} \times 4.5 \times 0.54^{½} = 3.31 \times 10^{-15}$

Calculated rate coefficient: $3.31 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $2.9 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

### D2: 3-isopropyl-6-methylene-cyclohexene (β-phellandrene)




Reference structure: $CH_2$=C(R)CH=CHR (Table 4)
Parameter: $k_{D4O3}$
$k_{298\,K} = 8.0 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$F_{ring\,(6)} = 0.52$ (used rather than $F'_{ring(6)}$ because only one double bond is within the ring)
$F_{\alpha(298)}(X_1) = 0.54$

Rate coefficient calculation:

$k = k_{DO3}\,\Pi F_{ring}(F_\alpha(X))^{½}$ (Equation (4))

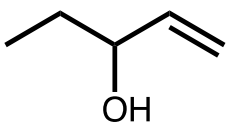
$= 8.0 \times 10^{-17} \times 0.52 \times 0.54^{½} = 3.06 \times 10^{-17}$

Calculated rate coefficient: $3.06 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $5.2 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## E. Allylic oxygenates

### E1: pent-1-ene-3-ol




Reference structure: $CH_2$=CHR (Table 1)
Parameter: $k_{A1O3}$

$k_{298\,K}$ = 1.0 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
X = -OH
$F_{\alpha(298)}$(X) = 1.4

Rate coefficient calculation:

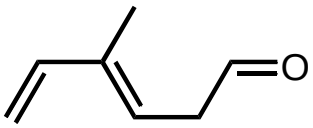
$k = k_{AO3} \Pi F_{\alpha}(X)$ (Equation (1))

= 1.0 × $10^{-17}$ × 1.4 = 1.40 × $10^{-17}$

Calculated rate coefficient: 1.40 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 1.8 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

### E2: 4-methylhex-3,5-dienal (3(*Z*-) or 3(*E*-))




Reference structure: $CH_2$=CHCH(R)=CHR (Table 4)
Parameter: $k_{D4O3}$

$k_{298\,K}$ = 8.0 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
X = -C(=O)-
$F_{\alpha(298)}$(X) = 0.32

Rate coefficient calculation:

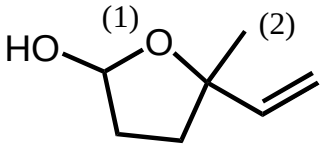
$k = k_{DO3} \Pi(F_{\alpha}(X))^{½}$ (Equation (3))

= 8.0 × $10^{-17}$ × $0.32^{½}$ = 4.53 × $10^{-17}$

Calculated rate coefficient: 4.53 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 4.4 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (3(*Z*-))
5.7 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ (3(*E*-))

**E3: 5-methyl-5-vinyl tetrahydrofuranol**




Reference structure: $CH_2$=CHR (Table 1)
Parameter: $k_{A1O3}$

$k_{298\,K}$ = 1.0 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$X_1$ = -OR
$X_2$ = alkyl (acyclic)
$F_{\alpha(298)}(X_1)$ = 0.6
$F_{\alpha(298)}(X_2)$ = 0.54

Rate coefficient calculation:

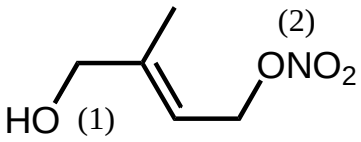
$k$ = $k_{AO3}$ $\Pi F_{\alpha}(X)$ (Equation (1))

= 1.0 × $10^{-17}$ × 0.6 × 0.54 = 3.24 × $10^{-18}$

Calculated rate coefficient: 3.24 × $10^{-18}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

Preferred (observed) rate coefficient: 3.5 × $10^{-18}$ $cm^3$ $molecule^{-1}$ $s^{-1}$

**E4: 2-methyl-4-nitrooxy-but-2-en-1-ol (*Z*- and *E*-)**




Reference structure: $CHR=CR_2$ (Table 1)
Parameter: $k_{A5O3}$

$k_{298\,K}$ = 47 × $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$
$X_1$ = -OH
$X_2$ = $-ONO_2$
$F_{\alpha(298)}(X_1)$ = 1.4
$F_{\alpha(298)}(X_2)$ = 0.044

Rate coefficient calculation:

$k$ = $k_{AO3}$ $\Pi F_{\alpha}(X)$ (Equation (1))

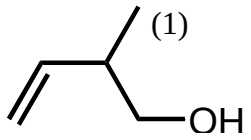
= 47 × $10^{-17}$ × 1.4 × 0.044 = 2.90 × $10^{-17}$

Calculated rate coefficient: $2.90 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $2.9 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## F. Remotely-substituted oxygenates

### F1: 2-methyl-but-3-en-1-ol




Reference structure: $CH_2$=CHR (Table 1)
Parameter: $k_{A1O3}$

$k_{298\ K} = 1.0 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$F_{\alpha(298)}(X_1) = 0.54$

Rate coefficient calculation:

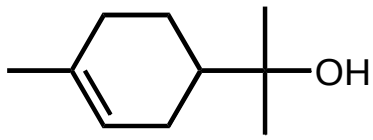
$k = k_{AO3} \Pi F_{\alpha}(X)$ (Equation (1))

$= 1.0 \times 10^{-17} \times 0.54 = 5.4 \times 10^{-18}$

Calculated rate coefficient: $5.4 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $3.74 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

### F2: 2-(4-methylcyclohex-3-en-1-yl)propan-2-ol




Reference structure: CHR=$CR_2$ (Table 1)
Parameter: $k_{A5O3}$

$k_{298\ K} = 47 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$F_{ring\ (6)} = 0.52$

Rate coefficient calculation:

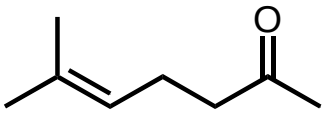
$k = k_{AO3} \Pi F_{ring} F_{\alpha}(X)$ (Equation (2))

$= 47 \times 10^{-17} \times 0.52 = 2.44 \times 10^{-16}$

Calculated rate coefficient: $2.44 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $3.0 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

### F3: 6-methyl-hept-5-en-2-one




Reference structure: CHR=CR$_2$ (Table 1)
Parameter: $k_{A5O3}$

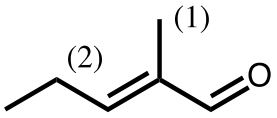
$k_{298\ K} = 47 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Calculated rate coefficient: $4.70 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $3.9 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## G. Vinylic oxygenates

### G1: 2-methyl-pent-2-enal




Reference structure: CHR=C(R)C(=O)H (Table 6)
Parameter: $k_{VC4O3}$

$k°_{298\ K} = 0.57 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$\alpha_s = 0.19$
$n_1 = 1$
$n_2 = 2$

Rate coefficient calculation:

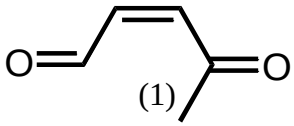
$k = k°_{298\ K} \times [1 + \Sigma(\alpha_s(n_i\text{-}1))]$ (Equation (5))

$= 0.57 \times 10^{-17} \times [1 + (0.19*(2\text{-}1)) + (0.19*(1\text{-}1))] = 6.78 \times 10^{-18}$

Calculated rate coefficient: $6.78 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $7.1 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

**G2: 4-oxo-pent-2-enal**




Reference structure: HC(=O)CH=CHC(=O)R (within the generic "-C(=O)C(-)=C(-)C(=O)-" category in Table 6).
Parameter: $k_{VC9O3}$

$k°_{298\,K} = 0.5 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$\alpha_s = 0.19$
$n_1 = 1$

Rate coefficient calculation:

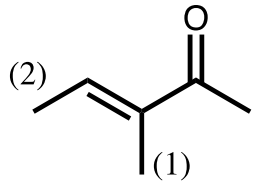
$k = k°_{298\,K} \times [1 + \Sigma(\alpha_s(n_i-1))]$ (Equation (5))

$= 0.5 \times 10^{-17} \times [1 + (0.19*(1-1))] = 5.0 \times 10^{-18}$

Calculated rate coefficient: $5.00 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $4.8 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

**G3: 3-methyl-pent-3-ene-2-one**




Reference structure: CHR=C(R)C(=O)R (Table 6)
Parameter: $k_{VC7O3}$

$k°_{298\,K} = 3.9 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$\alpha_s = 0.19$
$n_1 = 1$
$n_2 = 1$

Rate coefficient calculation:

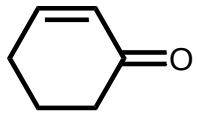
$k = k°_{298\,K} \times [1 + \Sigma(\alpha_s(n_i-1))]$ (Equation (5))

$= 3.9 \times 10^{-17} \times [1 + (0.19*(1-1)) + (0.19*(1-1))] = 3.9 \times 10^{-17}$

Calculated rate coefficient: $3.90 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $4.07 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## G4: cyclohex-2-en-1-one




N.B. Cyclic vinyl ketones and conjugated dienals/dienones are special cases with very limited data, for which a provisional method is applied (see Sect. 4.3). The appropriate alkene or conjugated diene rate coefficient, calculated by the methods in Sect. 3, is reduced by a factor of 50 for each alkyl group replaced by a -C(=O)H or -C(=O)- group.

Reference structure: CHR=CHR (Table 1)
Parameter: $k_{A3O3}$

$k°_{298\ K} = 12 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$F_{ring\ (6)} = 0.52$

Rate coefficient calculation:

$k = k_{AO3} \Pi F_{ring} F_{\alpha}(X)$ (Equation (2))

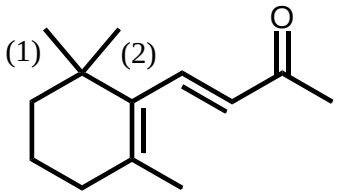
$= 12 \times 10^{-17} \times 0.52 = 6.24 \times 10^{-16}$

Above $k$ reduced by a factor of 50 to account for -R replacement by -C(=O)-

Calculated rate coefficient: $1.25 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $1.2 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## G5: 4-(2,6,6-trimethyl-cyclohex-1-enyl)-but-3-en-2-one (β-ionone)




N.B. Cyclic vinyl ketones and conjugated dienals/dienones are special cases with very limited data, for which a provisional method is applied (see Sect. 4.3). The appropriate alkene or conjugated diene rate coefficient, calculated by the methods in Sect. 3, is reduced by a factor of 50 for each alkyl group replaced by a -C(=O)H or -C(=O)- group.

Reference structure: CHR=CHCH(R)=CR$_2$ (Table 4)
Parameter: $k_{D9O3}$

$k_{298\ K} = 3.0 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$X_1$ = alkyl (acyclic)
$X_2$ = alkyl (acyclic)
$F_{ring\ (6)} = 0.52$ (used rather than $F'_{ring(6)}$ because only one double bond is within the ring)
$F_{\alpha(298)}(X_1) = F_{\alpha(298)}(X_2) = 0.54$

Rate coefficient calculation:

$k$ = $k_{DO3}$ $\Pi F_{ring}(F_{\alpha}(X))^{½}$ (Equation (4))

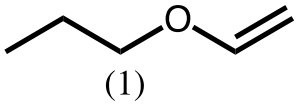
= $3.0 \times 10^{-15} \times 0.52 \times 0.54^{½} \times 0.54^{½} = 8.42 \times 10^{-16}$

Above $k$ reduced by a factor of 50 to account for -R replacement by -C(=O)-

Calculated rate coefficient: $1.68 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $2.2 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## G6: propoxyethene (*n*-propyl vinyl ether)




Reference structure: ROCH=CH$_2$ (Table 8)
Parameter: $k_{VO1O3}$

$k°_{298\,K}$ = $17 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$\alpha_s$ = 0.19
$n_1$ = 3

Rate coefficient calculation:

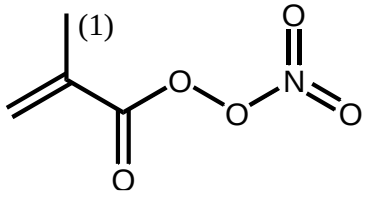
$k$ = $k°_{298\,K} \times [1 + \Sigma(\alpha_s(n_i\text{-}1))]$ (Equation (5))

= $17 \times 10^{-17} \times [1 + (0.19*(3\text{-}1))] = 2.35 \times 10^{-16}$

Calculated rate coefficient: $2.35 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $2.3 \times 10^{-16}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## G7: peroxymethacryloyl nitrate (MPAN)




Reference structure: ROC(=O)C(R)=CH$_2$ (Table 7). N.B. data for peroxymethacryloyl nitrate (MPAN) suggest that parameters for alk-1-enoic alkyl esters can reasonably be applied to corresponding unsaturated PANs, and by inference peracids (see Table 7, comment (a))

Parameter: $k_{VE2O3}$

$k°_{298\,K} = 0.65 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$\alpha_s = 0.19$
$n_1 = 1$

Rate coefficient calculation:

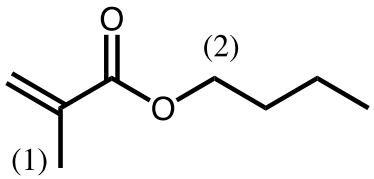
$k = k°_{298\,K} \times [1 + \Sigma(\alpha_s(n_i\text{-}1))]$ (Equation (5))

$= 0.65 \times 10^{-17} \times [1 + (0.19*(1\text{-}1))] = 6.5 \times 10^{-18}$

Calculated rate coefficient: $6.50 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $8.2 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

## G8: 2-methylpropenoic acid butyl ester (*n*-butyl methacrylate)




Reference structure: ROC(=O)C(R)=CH$_2$ (Table 7)
Parameter: $k_{VE2O3}$

$k°_{298\,K} = 0.65 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$
$\alpha_s = 0.19$
$n_1 = 1$
$n_2 = 4$

Rate coefficient calculation:

$k = k°_{298\,K} \times [1 + \Sigma(\alpha_s(n_i\text{-}1))]$ (Equation (5))

$= 0.65 \times 10^{-17} \times [1 + (0.19*(1\text{-}1)) + (0.19*(4\text{-}1)] = 1.02 \times 10^{-17}$

Calculated rate coefficient: $1.02 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$

Preferred (observed) rate coefficient: $1.0 \times 10^{-17}$ cm$^3$ molecule$^{-1}$ s$^{-1}$