

## Supplementary Material for:

# Estimation of rate coefficients for the reactions of O<sub>3</sub> 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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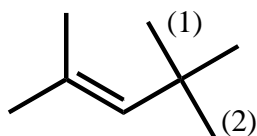
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## A. Acyclic alkenes

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



Reference structure: CHR=CR<sub>2</sub> (Table 1)

Parameter:  $k_{A503}$

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

X<sub>1</sub> = alkyl (acyclic)

X<sub>2</sub> = alkyl (acyclic)

$$F_{\alpha(298)}(X_1) = F_{\alpha(298)}(X_2) = 0.54$$

Rate coefficient calculation:

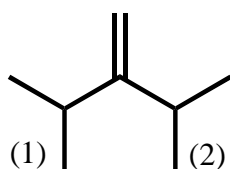
$$k = k_{A03} \prod F_{\alpha}(X) \quad (\text{Equation (1)})$$

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

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

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

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



Reference structure: CH<sub>2</sub>=CR<sub>2</sub> (Table 1)

Parameter:  $k_{A203}$

$$k_{298\text{ K}} = 1.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

X<sub>1</sub> = alkyl (acyclic)

X<sub>2</sub> = alkyl (acyclic)

$$F_{\alpha(298)}(X_1) = F_{\alpha(298)}(X_2) = 0.54$$

Rate coefficient calculation:

$$k = k_{A03} \prod F_{\alpha}(X) \quad (\text{Equation (1)})$$

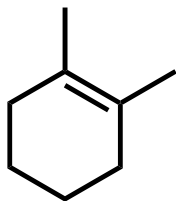
$$= 1.4 \times 10^{-17} \times 0.54 \times 0.54 = 4.08 \times 10^{-18}$$

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

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

## B. Cyclic alkenes

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



Reference structure:  $\text{CR}_2=\text{CR}_2$  (Table 1)

Parameter:  $k_{A603}$

$$k_{298 \text{ K}} = 110 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F_{\text{ring (6)}} = 0.52$$

Rate coefficient calculation:

$$k = k_{A03} \prod F_{\text{ring}} F_{\alpha}(X) \quad (\text{Equation (2)})$$

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

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

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

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



Reference structure: *cis*-CHR=CHR (Table 1)

Parameter:  $k_{A303}$

$$k_{298 \text{ K}} = 12 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F_{\text{ring (5)}} = 3.9$$

$$F_{\text{ring (6)}} = 0.52$$

Rate coefficient calculation:

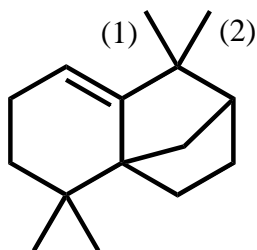
$$k = k_{A03} \prod F_{\text{ring}} F_{\alpha}(X) \quad (\text{Equation (2)})$$

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

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

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

**B3: (1R)-2,2,7,7-tetramethyltricyclo[6.2.1.0<sup>1,6</sup>]undec-5-ene (isolongifolene)**



Reference structure: CHR=CR<sub>2</sub> (Table 1)

Parameter:  $k_{A5O3}$

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

X<sub>1</sub> = alkyl (acyclic)

X<sub>2</sub> = alkyl (acyclic)

$$F_{\text{ring}(6)} = 0.52$$

$$F_{\text{ring}(9)} = 2.1$$

$$F_{\text{ring}(10)} = 0.24$$

$$F_{\alpha}(X_1) = 0.54$$

$$F_{\alpha}(X_2) = 0.54$$

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

Rate coefficient calculation:

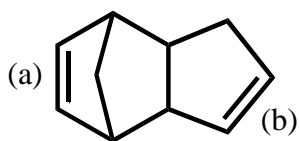
$$k = k_{A03} \prod F_{\text{ring}} F_{\alpha}(X) \quad (\text{Equation (2)})$$

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

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

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

**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)  $k_{A3O3}$

$$k_{a\ 298\text{ K}} = 12 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{b\ 298\text{ K}} = 12 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F_{\text{ring-a}}(6) = 0.52$$

$$F_{\text{ring-a}}(5) = 3.9$$

$$F_{\text{ring-a}}(9) = 2.1$$

$$F_{\text{ring-b}}(5) = 3.9$$

$$F_{\text{ring-b}}(8) = 2.8$$

$$F_{\text{ring-b}}(9) = 2.1$$

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

Partial rate coefficients:

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

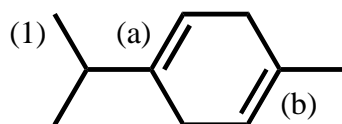
$$k_a = 12 \times 10^{-17} \times 0.52 \times 3.9 \times 2.1 = 5.11 \times 10^{-16}$$

$$k_b = 12 \times 10^{-17} \times 3.9 \times 2.8 \times 2.1 = 2.75 \times 10^{-15}$$

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

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

#### B5: 1-isopropyl-4-methyl-cyclohexa-1,4-diene ( $\gamma$ -terpinene)



Reference structures: (a)  $\text{CHR}=\text{CR}_2$ ; (b)  $\text{CHR}=\text{CR}_2$  (Table 1)

Parameter: (a)  $k_{\text{A4O3}}$ ; (b)  $k_{\text{A4O3}}$

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

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

$$F_{\text{ring}}(6) = 0.52$$

$X_1 = \text{alkyl (acyclic)}$

$$F_{\alpha(298)}(X_1) = 0.54$$

Rate coefficient calculation:

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

$$k_a = 47 \times 10^{-17} \times 0.52 \times 0.54 = 1.32 \times 10^{-16}$$

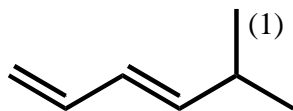
$$k_b = 47 \times 10^{-17} \times 0.52 = 2.44 \times 10^{-16}$$

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

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

### C. Acyclic conjugated dialkenes

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



Reference structure:  $\text{CH}_2=\text{CH}=\text{CH}=\text{CHR}$  (Table 4)

Parameter:  $k_{\text{D}3\text{O}3}$

$$k_{298\text{ K}} = 3.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$X_1$  = alkyl (acyclic)

$$F_{\alpha(298)}(X_1) = 0.54$$

Rate coefficient calculation:

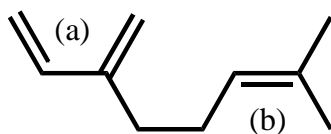
$$k = k_{\text{D}3\text{O}3} \Pi(F_{\alpha}(X))^{\frac{1}{2}} \quad (\text{Equation (3)})$$

$$= 3.6 \times 10^{-17} \times 0.54^{\frac{1}{2}} = 2.65 \times 10^{-17}$$

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

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

#### C2: $\beta$ -myrcene



Reference structures: (a)  $\text{CH}_2=\text{C}(\text{R})\text{CH}=\text{CH}_2$  (Table 4); (b)  $\text{CHR}=\text{CR}_2$  (Table 1)

Parameter: (a)  $k_{\text{D}1\text{O}3}$ ; (b)  $k_{\text{A}4\text{O}3}$

$$k_{a\ 298\text{ K}} = 1.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

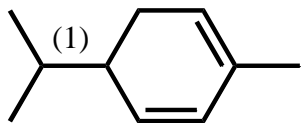
$$k_{b\ 298\text{ K}} = 47 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

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

## D. Cyclic conjugated dialkenes

### D1: $\alpha$ -phellandrene



Reference structure:  $\text{CHR}=\text{C}(\text{R})\text{CH}=\text{CHR}$  (Table 4)

Parameter:  $k_{\text{D803}}$

$$k_{298\text{ K}} = 100 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$\text{X}_1 = \text{alkyl (acyclic)}$

$$F'_{\text{ring}(6)} = 4.5$$

$$F_{\alpha(298)}(\text{X}_1) = 0.54$$

Rate coefficient calculation:

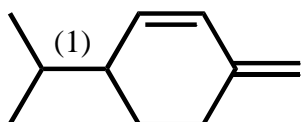
$$k = k_{\text{D03}} \Pi F'_{\text{ring}}(F_{\alpha}(\text{X}))^{1/2} \quad (\text{Equation (4)})$$

$$= 1.0 \times 10^{-15} \times 4.5 \times 0.54^{1/2} = 3.31 \times 10^{-15}$$

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

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

### D2: $\beta$ -phellandrene



Reference structure:  $\text{CH}_2=\text{C}(\text{R})\text{CH}=\text{CHR}$  (Table 4)

Parameter:  $k_{\text{D403}}$

$$k_{298\text{ K}} = 8.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$\text{X}_1 = \text{alkyl (acyclic)}$

$F_{\text{ring}(6)} = 0.52$  (used rather than  $F'_{\text{ring}(6)}$  because only one double bond is within the ring)

$$F_{\alpha(298)}(\text{X}_1) = 0.54$$

Rate coefficient calculation:

$$k = k_{\text{D03}} \Pi F_{\text{ring}}(F_{\alpha}(\text{X}))^{1/2} \quad (\text{Equation (4)})$$

$$= 8.0 \times 10^{-17} \times 0.52 \times 0.54^{1/2} = 3.06 \times 10^{-17}$$

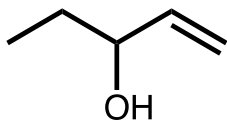
Calculated rate coefficient:  $3.06 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

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



## E. Allylic oxygenates

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



Reference structure: CH<sub>2</sub>=CHR (Table 1)

Parameter:  $k_{A103}$

$$k_{298\text{ K}} = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

X = -OH

$$F_{\alpha(298)}(X) = 1.4$$

Rate coefficient calculation:

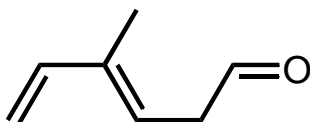
$$k = k_{A03} \Pi F_{\alpha}(X) \quad (\text{Equation (1)})$$

$$= 1.0 \times 10^{-17} \times 1.4 = 1.40 \times 10^{-17}$$

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

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

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



Reference structure: CH<sub>2</sub>=CHCH(R)=CHR (Table 4)

Parameter:  $k_{D403}$

$$k_{298\text{ K}} = 8.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

X = -C(=O)-

$$F_{\alpha(298)}(X) = 0.32$$

Rate coefficient calculation:

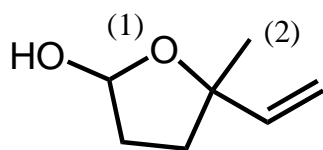
$$k = k_{D03} \Pi (F_{\alpha}(X))^{\frac{1}{2}} \quad (\text{Equation (3)})$$

$$= 8.0 \times 10^{-17} \times 0.32^{\frac{1}{2}} = 4.53 \times 10^{-17}$$

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

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

### E3: 5-methyl-5-vinyl tetrahydrofuranol



Reference structure: CH<sub>2</sub>=CHR (Table 1)

Parameter:  $k_{A103}$

$$k_{298\text{ K}} = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

X<sub>1</sub> = -OR

X<sub>2</sub> = alkyl (acyclic)

$$F_{\alpha(298)}(X_1) = 0.6$$

$$F_{\alpha(298)}(X_2) = 0.54$$

Rate coefficient calculation:

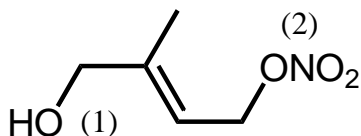
$$k = k_{A03} \prod F_{\alpha}(X) \quad (\text{Equation (1)})$$

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

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

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

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



Reference structure: CHR=CR<sub>2</sub> (Table 1)

Parameter:  $k_{A503}$

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

X<sub>1</sub> = -OH

X<sub>2</sub> = -ONO<sub>2</sub>

$$F_{\alpha(298)}(X_1) = 1.4$$

$$F_{\alpha(298)}(X_2) = 0.044$$

Rate coefficient calculation:

$$k = k_{A03} \prod F_{\alpha}(X) \quad (\text{Equation (1)})$$

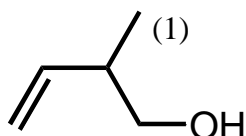
$$= 47 \times 10^{-17} \times 1.4 \times 0.044 = 2.90 \times 10^{-17}$$

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

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

## F. Remotely-substituted oxygenates

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



Reference structure:  $\text{CH}_2=\text{CHR}$  (Table 1)

Parameter:  $k_{A103}$

$$k_{298 \text{ K}} = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$X_1 = \text{alkyl (acyclic)}$

$$F_{\alpha(298)}(X_1) = 0.54$$

Rate coefficient calculation:

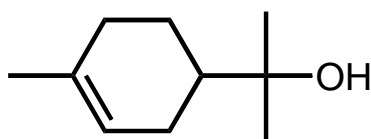
$$k = k_{A03} \prod F_{\alpha}(X) \quad (\text{Equation (1)})$$

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

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

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

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



Reference structure:  $\text{CHR}=\text{CR}_2$  (Table 1)

Parameter:  $k_{A503}$

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

$$F_{\text{ring}(6)} = 0.52$$

Rate coefficient calculation:

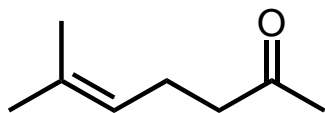
$$k = k_{A03} \prod F_{\text{ring}} F_{\alpha}(X) \quad (\text{Equation (2)})$$

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

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

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

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



Reference structure:  $\text{CHR}=\text{CR}_2$  (Table 1)

Parameter:  $k_{A503}$

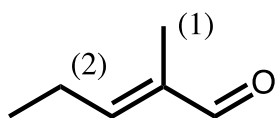
$$k_{298 \text{ K}} = 47 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

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

## G. Vinylic oxygenates

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



Reference structure:  $\text{CHR}=\text{C}(\text{R})\text{C}(=\text{O})\text{H}$  (Table 6)

Parameter:  $k_{VC403}$

$$k_{298 \text{ K}}^{\circ} = 0.57 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\alpha_s = 0.19$$

$$n_1 = 1$$

$$n_2 = 2$$

Rate coefficient calculation:

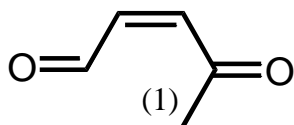
$$k = k_{298 \text{ K}}^{\circ} \times [1 + \sum (\alpha_s (n_i - 1))] \quad (\text{Equation (5)})$$

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

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

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

## 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:  $k_{VC9O3}$

$$k^{\circ}_{298\text{ K}} = 0.5 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\alpha_s = 0.19$$

$$n_1 = 1$$

Rate coefficient calculation:

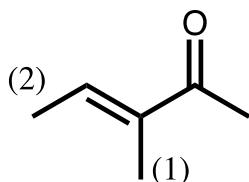
$$k = k^{\circ}_{298\text{ K}} \times [1 + \Sigma(\alpha_s(n_i-1))] \quad (\text{Equation (5)})$$

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

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

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

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



Reference structure: CHR=C(R)C(=O)R (Table 6)

Parameter:  $k_{VC7O3}$

$$k^{\circ}_{298\text{ K}} = 3.9 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\alpha_s = 0.19$$

$$n_1 = 1$$

$$n_2 = 1$$

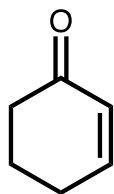
Rate coefficient calculation:

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

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

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

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

**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 in Tables 1 and 4 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:  $k_{A3O3}$

$$k_{298\text{ K}}^{\circ} = 12 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$F_{\text{ring}(6)} = 0.52$$

Rate coefficient calculation:

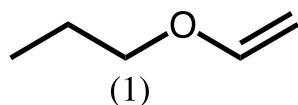
$$k = k_{A3O3} \prod F_{\text{ring}} F_{\alpha}(X) \quad (\text{Equation (2)})$$

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

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

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

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

**G5: *n*-propyl vinyl ether**

Reference structure: ROCH=CH<sub>2</sub> (Table 8)

Parameter:  $k_{V01O3}$

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

$$\alpha_s = 0.19$$

$$n_1 = 3$$

Rate coefficient calculation:

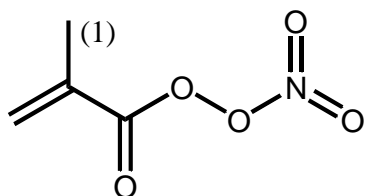
$$k = k_{298\text{ K}}^{\circ} \times [1 + \Sigma(\alpha_s(n_i-1))] \quad (\text{Equation (5)})$$

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

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

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

**G6: peroxy methacryloyl nitrate (MPAN)**



Reference structure:  $\text{ROC(=O)C(R)=CH}_2$  (Table 7). N.B. data for peroxy methacryloyl 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:  $k_{\text{VE2O3}}$

$$k_{298 \text{ K}}^{\circ} = 0.65 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\alpha_s = 0.19$$

$$n_1 = 1$$

Rate coefficient calculation:

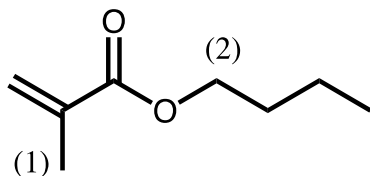
$$k = k_{298 \text{ K}}^{\circ} \times [1 + \Sigma(\alpha_s(n_i-1))] \quad (\text{Equation (5)})$$

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

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

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

**G7: *n*-butyl methacrylate**



Reference structure:  $\text{ROC(=O)C(R)=CH}_2$  (Table 7)

Parameter:  $k_{\text{VE2O3}}$

$$k_{298 \text{ K}}^{\circ} = 0.65 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$\alpha_s = 0.19$$

$$n_1 = 1$$

$$n_2 = 4$$

Rate coefficient calculation:

$$k = k_{298\text{ K}} \times [1 + \sum(\alpha_s(n_i-1))] \quad (\text{Equation (5)})$$

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

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

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