Supplement of

Opinion: The germicidal effect of ambient air (open-air factor) revisited

R. Anthony Cox et al.

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S1. Kinetics of ozone + alkene reactions inferred from data presented by Dark and Nash

Rate coefficients for the gas-phase reaction of ozone with alkenes used in the experiments by Dark and Nash (1970) can be estimated from the quantity of alkene needed to produce the ozone half-life of 5 minutes. The alkenes were in excess and dividing the pseudo first order loss rate of ozone ($2.31 \times 10^{-3} \text{ s}^{-1}$) by the alkene concentration used in the experiments gives the bimolecular rate coefficients shown on the y-axis in Fig. S1 below. Plotted on the x-axis are the rate coefficients taken from the 2020 recommendations by IUPAC (Cox et al., 2020) and McGillen et al. (2020). As seen from Fig. S1 the rate coefficients inferred from the experimental conditions reported by Dark and Nash in 1970 are consistent with our current understanding of the kinetics of ozone + alkene reactions, within about a factor of two. This consistency lends credibility to the experiments of Dark and Nash (1970).

Figure S1. Rate coefficients for ozone + alkene reactions inferred from data presented by Dark and Nash (1970) plotted versus current recommendations for these reactions. The solid line represents 1:1 correspondence, the dotted lines show variation by a factor of two. The acyclic alkenes are ethene, propene, but-1-ene, pent-1-ene, hex-1-ene, cis-but-2-ene, trans-but-2-ene, trans-pent-2-ene*, trans-hex-2-ene*, 2-methylbut-2-ene, 2,4,4-trimethylpent-2-ene. The cyclic alkenes are cyclopentene, cyclohexene, and cycloheptene. The oxygenates are but-2-en-1-ol, 1-vinyl oxyethane and 1-vinyl oxybutane. (*Isomeric mixture used, which is dominated by trans-isomer).
S2. Reanalysis of the data of Dark and Nash

The table below reproduces the experimental data of Dark and Nash (1970) for the selected alkenes presented in Fig. 1 of the main paper. The effects on the *Escherichia coli* population were reported as a survival fraction ($f$) following a 10 minute experimental exposure time, and a first-order loss rate constant, $k_{\text{loss}}$ (in units of min$^{-1}$) is inferred here, representing the average removal rate over the 10 minute period.

**Table S1.** Survival fractions ($f$) of *Escherichia coli* reported by Dark and Nash (1970) for selected ozone-alkene experiments and the inferred loss rates ($k_{\text{loss}}$) of *Escherichia coli*.

| [O$_3$]$_0$/ppb | Survival fraction ($f$)$^a$ | $k_{\text{loss}}$/min$^{-1}$$^b$ |
|-----------------|-----------------------------|---------------------------------|
|                 | 33 ppb | 11 ppb | 4 ppb | 33 ppb | 11 ppb | 4 ppb |
| cyclohexene     | 0.02   | 0.07   | 0.35  | 0.391  | 0.266  | 0.105 |
| hex-2-ene$^c$   | 0.05   | 0.20   | 0.70  | 0.300  | 0.161  | 0.036 |
| pent-1-ene      | 0.05   | 0.20   | 0.65  | 0.300  | 0.161  | 0.043 |
| pent-2-ene$^c$  | 0.10   | 0.50   | 0.80  | 0.230  | 0.069  | 0.022 |
| trans-but-2-ene | 0.10   | 0.30   | 0.85  | 0.230  | 0.120  | 0.016 |
| propene         | 0.20   | 0.70   | 0.70  | 0.161  | 0.036  | 0.036 |
| hex-1-ene       | 0.20   | 0.70   | 0.75  | 0.161  | 0.036  | 0.029 |
| cis-but-2-ene   | 0.20   | 0.75   | 1.00  | 0.161  | 0.029  | 0.000 |
| but-1-ene       | 0.35   | 0.35   | 0.90  | 0.105  | 0.105  | 0.011 |
| 2-methylbut-2-ene | 0.55 | 0.75   | 1.00  | 0.060  | 0.029  | 0.000 |
| 2,4,4-trimethylpent-2-ene | 1.00 | 1.00   | 1.00  | 0.000  | 0.000  | 0.000 |

**Notes:**

$^a$ Survival fraction of *Escherichia coli* at the end of each 10 minute experiment, as reported by Dark and Nash (1970);

$^b$ The inferred average first-order loss rate, $k_{\text{loss}}$, determined from $k_{\text{loss}} = \ln(1/f)/10$ and thus assumes that mixing of gases was rapid compared to the 10 minute timescale over which the E-coli were exposed.

$^c$ Isomeric mixture dominated by trans isomer.
S3. Characteristics of outside air at Porton Down

(a) Concentrations of NOx and volatile organic compounds (VOCs)

The experiments reported by Druett and May (1968) sampled night-time outside air at Porton Down, a rural location in southern England about 8 km north-east of Salisbury, Wiltshire (51.131, -1.704). The air composition would likely have been influenced by both local-scale chemical processes occurring shortly before sampling and regional-scale chemical processes occurring over time scales of up to a day or more prior to sampling, superimposed on northern hemispheric background air (e.g., Jenkin, 2008). Although there is no detailed information available on the air composition at that time, it is possible to estimate the approximate concentrations of some key components (NOx and hydrocarbons) for rural southern England using more recent monitoring data from comparable rural locations (https://uk-air.defra.gov.uk/data/), and the documented trends in the emissions of air quality pollutants (https://naei.beis.gov.uk/).

The examples below (Fig. S2) show that annual mean NOx mixing ratios have generally followed the documented trend in road transport emissions, showing a progressive decline since the early 1990s in response to EU controls of anthropogenic emissions. Based on the estimated historical trend in UK emissions shown, it can therefore be inferred that the annual mean NOx mixing ratios at such rural locations was probably about 5 – 10 ppb at the beginning of the series in 1970. The monitoring data also show that NO accounts for about 20 % of NOx on average at these NOx levels, i.e., an annual mean NO mixing ratio of about 1 – 2 ppb. It should be noted that the partitioning of NOx into NO and NO2 shows a strong diurnal variation, with NO suppressed to very low levels at night (when regeneration by NO2 photolysis cannot occur) by virtue of its reaction with excess O3 (typically 20 – 25 ppb).

Figure S2. Comparison of the trend in UK NOx emissions from road transport (https://naei.beis.gov.uk/) with annual mean NOx mixing ratios measured at rural locations in the UK Automatic Urban and Rural Network, AURN (https://uk-air.defra.gov.uk/data/): Harwell, Oxfordshire (51.573, -1.316), Ladybower, Derbyshire (53.403, -1.752) and Yarner Wood, Devon (50.598, -3.717).

Concentrations of light (C2-C8) hydrocarbons at UK monitoring sites have also been reported to reflect the documented trend in road transport emissions, again showing a progressive decline since the early 1990s in response to EU controls of anthropogenic emissions (Dollard et al., 2007). Based again on rural measurements from the Harwell site (Fig. S3), emissions trend estimates, and additionally speciation information for non-methane VOC emissions in the UK
(Passant, 2002), it is possible to estimate an associated HO reactivity of about $4 - 5 \text{ s}^{-1}$ for anthropogenic non-methane VOCs in the rural southern England in 1970. The HO reactivity is expected to have been significantly further elevated by contributions from biogenic VOCs, and from oxygenated products of VOC degradation in general. It was therefore likely to have been substantially greater than the value of about $1 \text{ s}^{-1}$, associated with reaction with methane and CO in the remote background lower troposphere.

The experiments of Druett and May (1968) were carried out after nightfall. As indicated above, the composition of the sampled air would likely have been particularly influenced by both local-scale chemical processes (e.g., O$_3$ and NO$_3$ initiated alkene oxidation), and by the air mass history over the period of a day or more, i.e., regional-scale chemical processes, including photochemically-driven HO initiated VOC chemistry. The air would therefore have been expected to contain oxygenated organic products containing a variety functional groups (including -OH, -OOH, -O$_2^-$, -C(=O)O$^-$, -ONO$_2^-$, -NO$_2^-$ and -C(=O)OOONO$_2^-$) in addition to the radical intermediates involved in their formation mechanisms (e.g., HO, HO$_2$, RO$_2$, NO$_3$ and sCl).

(b) Formation of hydroperoxides and peroxy acids
In the present work, we have focused species containing -OOH (hydroperoxide) and -C(=O)OOH (peroxy acid) groups (in conjunction with other groups in bi- and multifunctional species), because they are known germicides. They are formed via a number of routes, including bimolecular RO$_2$ + HO$_2$ reactions, RO$_2$ isomerization (auto-oxidation) reactions, and from the reactions of stabilized Criegee intermediates (sCIs) with H$_2$O and (H$_2$O)$_2$.

The formation rate of hydroperoxides and peroxy acids from the bimolecular RO$_2$ + HO$_2$ reactions is determined by the ambient concentrations of the precursor RO$_2$ and HO$_2$ radicals. It is well established from modelling studies that
these concentrations are relatively insensitive to the NOx level over a wide range in the background (“methane and CO”) atmosphere, with RO2 entirely as CH3O2 (e.g., Logan et al., 1981; Lightfoot et al., 1992) up to about 1 ppb NOx. At higher NOx levels, the presence of co-emitted VOCs allows radical levels to be sustained, because reaction of HO with VOCs (forming a suite of RO2 radicals) continues to compete with radical loss via the HO + NO2 reaction. As indicated above, a typical HO reactivity significantly in excess of 4−5 s−1 can be estimated for rural southern England in 1970, compared with an average reactivity of about 1−2 s−1 for reaction with 4−8 ppb NO2 (i.e. the corresponding average estimated above). Under these conditions, conversion of HO to RO2 and HO2 through reaction with VOCs approximately balances the conversion of RO2 and HO2 to HO through reaction with NO, and the concentrations of RO2 and HO2 radicals thus continue to be sustained at these NOx levels. This has been confirmed by measurements of peroxy radicals at a UK rural site by Fleming et al. (2006), which demonstrated sustained concentrations of peroxy radicals up to about 5−10 ppb NOx during day and night in both summer and winter. In addition, gaseous H2O2 was routinely monitored at several UK rural network sites during the late 1980s and early 1990s (i.e., the period when UK rural NOx levels were likely at their highest), consistent with its formation (at least partially) through the operation of the HO2 + HO2 reaction (Dollard and Davies, 1992; PORG, 1993; 1997), and measurements of peroxides have been reported in many other studies at comparable NOx levels (e.g., Zhang et al., 2012; Wang et al., 2016; Watanabe et al., 2018). Hydroperoxides and peroxy acids formed from bimolecular RO2 + HO2 reactions would therefore be expected to have been present, both in the rural air sampled by Druett and May (1968), and more generally over the intervening years. It is also noted that some relevant species (in particular peracetic acid, CH3C(O)OOH: Berasategui et al., 2020) are sufficiently long-lived that their formation may have occurred on a regional-scale during the preceding day(s). Auto-oxidation mechanisms involving RO2 isomerization reactions (i.e., HOM formation) can also contribute to the formation of hydroperoxide and peroxy acid species, although these mechanisms can be inhibited at high NOx by the reactions of RO2 with NO. The pseudo-first order loss rate of peroxy radicals with respect to reaction with 1−2 ppb NO (i.e., the average estimated above for rural southern England in 1970) is about 0.2−0.4 s−1. Because peroxy radical isomerization rates are very strongly structure dependent, this can compete with or dominate over some of the possible isomerization reactions. However, a large proportion of those calculated for peroxy radicals formed from the ozonolysis of cyclohexene (e.g., see Sect. 6) and related cyclic terpenoids are sufficiently rapid to compete with reaction with NO at this level, and all of them will certainly be competitive under the night-time conditions in the vicinity of the Druett and May (1968) sampling location, when [NO] is heavily suppressed.

The reactions H2O and (H2O)2 with stabilized Criegee intermediates (sCIs) formed from O3 + alkene reactions provide additional sources of both H2O2 and α-hydroxy hydroperoxides (e.g., Nguyen et al., 2016; Sheps et al., 2017). As discussed by Cox et al. (2020), and further below, these reactions are major loss routes for sCIs for rural conditions typical of southern England. The very rapid reactions of sCIs with organic acids (e.g., HC(O)OH: Cox et al., 2020 and references therein) and inorganic acids (HNO3 and HCl: Foreman et al., 2016) also provide routes to products containing hydroperoxide groups (hydroperoxy-esters, nitro-oxy-hydroperoxides and chloro-hydroperoxides, respectively). Based on UK measurements of HC(O)OH (Le Breton et al., 2014; Bannan et al., 2017), HNO3 (Le Breton et al., 2014; Tang et al., 2018) and HCl (Tang et al., 2018), these may provide minor supplementary hydroperoxide sources for conditions typical of southern England.
(c) Concentrations and lifetimes of sCI

Cox et al. (2020) have recently estimated seasonally-averaged winter and summer production rates, removal rates and steady-state concentrations of sCIs, using recent observational data from the Chilbolton Observatory, Hampshire (51.150, -1.438), which is about 15 km to the east of MRE Porton Down and in a similarly rural location. Full details are available in section 8 and Supplement C of Cox et al. (2020). The calculations made use of measured or inferred concentrations of a series of C₁–C₆ alkenes, isoprene, α-pinene, limonene, O₃, NO₂, SO₂ and HC(O)OH, in conjunction with H₂O and (H₂O)₂ concentrations based on modelled temperature and relative humidity data typical of the region. Production of sCIs from the ozonolysis of the C₁–C₆ alkenes, isoprene, α-pinene and limonene was therefore represented, with removal by unimolecular decomposition and bimolecular reactions with H₂O, (H₂O)₂, NO₂, SO₂ and HC(O)OH. These are expected to be the most important source and sink reactions (Cox et al., 2020).

Table S2. Representative ambient concentrations and lifetimes of a core set of sCIs calculated by Cox et al. (2020) for average winter conditions at the Chilbolton observatory in south-east England (T = 278 K; RH = 85 %).

| sCI                          | Ambient concentration/ molecule cm⁻³ | Lifetime/ s   | Main removal reaction         |
|------------------------------|--------------------------------------|---------------|------------------------------|
| CH₂OO                        | 5.3                                  | 5.3 × 10⁻⁴    | Reaction with (H₂O)₂         |
| Z-CH₃CHOO                    | 300                                  | 1.5 × 10⁻²    | Thermal decomposition        |
| E-CH₃CHOO                    | 2.0                                  | 9.6 × 10⁻⁵    | Reaction with (H₂O)₂ and H₂O|
| (CH₃)₂COO                    | 28                                   | 5.1 × 10⁻¹    | Thermal decomposition        |
| Z-(CH=CH₂)(CH₃)COO a         | 0.010                                | 2.8 × 10⁻⁴    | Thermal decomposition        |
| E-(CH=CH₂)(CH₃)COO a         | 4.9                                  | 5.8 × 10⁻²    | Thermal decomposition        |
| Z-(C(CH₃)=CH₃)CHOO a         | 0.0042                               | 2.7 × 10⁻⁴    | Thermal decomposition        |
| E-(C(CH₃)=CH₃)CHOO a         | 0.57                                 | 1.6 × 10⁻²    | Reaction with (H₂O)₂ and H₂O|

Notes:
a Derived specifically from isoprene.

Tables S2 and S3 show the calculated ambient concentrations and lifetimes of a core set of sCIs for winter and summer conditions, with the total sCI concentrations being about 380 molecule cm⁻³ in both summer and winter. The core set accounted for 91 % and 76 % of the winter and summer totals, with a particularly important contribution from Z-CH₃CHOO, which is formed from all linear alk-2-enes in the alkene speciation and has a relatively long atmospheric lifetime. The main sCI removal reactions were either thermal decomposition or reaction with (H₂O)₂ (supplemented by reaction with H₂O), each accounting for approximately half of total sCI loss. The calculated ambient lifetimes for all sCIs were < 60 ms in the winter and < 30 ms in the summer, with many being orders of magnitude shorter lived. The calculations of Cox et al. (2020) were based on data reported in recent years. Taking account of the trends in
anthropogenic pollutant emissions discussed above (particularly for the precursor alkenes), total sCl concentrations about a factor of three higher (i.e., about $10^4$ molecule cm$^{-3}$) can be inferred for 1970, but with their removal still dominated by the reactions shown in Tables S2 and S3 such that the lifetimes are approximately unchanged.

Table S3. Representative ambient concentrations and lifetimes of a core set of sCIs calculated by Cox et al. (2020) for average summer conditions at the Chilbolton observatory in south-east England (T = 288 K; RH = 70 %).

| sCl                  | Ambient concentration (molecule cm$^{-3}$) | Lifetime (s) | Main removal reaction          |
|----------------------|-------------------------------------------|--------------|--------------------------------|
| CH$_2$OO             | 4.5                                       | $4.2 \times 10^4$ | Reaction with (H$_2$O)$_2$     |
| Z-CH$_3$CHOO         | 220                                       | $9.1 \times 10^3$ | Thermal decomposition          |
| E-CH$_3$CHOO         | 1.5                                       | $6.0 \times 10^5$ | Reaction with (H$_2$O)$_2$ and H$_2$O |
| (CH$_3$)$_2$COO      | 19                                        | $3.4 \times 10^3$ | Thermal decomposition          |
| Z-(CH=CH$_2$)(CH$_3$)COO $^a$ | 0.025                                    | $1.4 \times 10^4$ | Thermal decomposition          |
| E-(CH=CH$_2$)(CH$_3$)COO $^a$ | 11                                        | $2.7 \times 10^2$ | Thermal decomposition          |
| Z-(C(CH$_3$)=CH$_2$)CHOO $^a$ | 0.010                                    | $1.3 \times 10^4$ | Thermal decomposition          |
| E-(C(CH$_3$)=CH$_2$)CHOO $^a$ | 1.3                                       | $7.7 \times 10^3$ | Reaction with (H$_2$O)$_2$ and H$_2$O |

Notes:

$^a$ Derived specifically from isoprene.
Based on the information given by Druett and May (1968), the gas flow through the \( l = 12.8 \) m long and \( d = 11.4 \) cm inner diameter long brass tube was \( 171 \) m\(^3\) h\(^{-1}\) giving a gas residence time \( 2.75 \) s. The slope of the exponential decay of the viable cells as a function of the operation time of the flow tube at these positions was \( k_{\text{cell}} = 3.3 \pm 0.3, 1.6 \pm 0.2, \) and \( 0.9 \pm 0.7 \) h\(^{-1}\), respectively. Assuming that \( k_{\text{cell}} \) is linearly related to the OAF concentration, we can estimate the first order loss rate of OAF along the brass tube from a plot of \( k_{\text{cell}} \) as a function of the residence time in the brass tube, shown in Fig. S4. From Fig. S4 we see that the decay of bactericidal activity decreased non-exponentially, reasons for which could be manifold. First, the outdoor concentration of OAF (and its precursors) may have varied over time of operation of the flow tube. Second, the OAF is likely to be a group of individual species with variable life-times. Third, OAF may have been generated along the tube as the precursor chemistry continued. Rough values for the loss rate coefficients \( k_{\text{OAF}} \) from the first two points, the second and third points and all three combined are \( 0.9, 0.3 \) and \( 0.5 \) s\(^{-1}\), respectively.

Figure S4: Decay of OAF driven bactericidal activity along the brass tube of the Druett and May (1968) study.

We next consider that the decreasing activity of OAF along the tube was controlled by its loss to the walls. Highly oxygenated VOC exhibit substantial partitioning to walls in tubes, via both reversible and irreversible loss processes (Deming et al., 2019). For the impact on bacterial viability over the relevant time scales, it seems that the loss was of rather of irreversible nature as reversible adsorption would have led to slow migration of the responsible species along the tube. The large flow rate implies turbulent flow conditions (Reynolds number > 30000). If we first assume perfect mixing and interaction of the agent with the wall purely driven by gas kinetics, the observed loss rate coefficient corresponds to an uptake coefficient (\( \gamma \)), the net, fractional efficiency (per collision) of loss from the gas-phase: \( \gamma = \frac{k_{\text{OAF}}}{\omega} \), where \( \omega \) is the mean thermal velocity of the OAF ‘molecule’. Assuming a molecular weight between 50 and
150 g mole⁻¹ and the range for \( k_{\text{OAF}} \) obtained above, \( \gamma \) is in the range \((1 - 5) \times 10^{-4}\). However, even under highly turbulent conditions, a quasi-stagnant boundary layer persists that effectively limits mass transport and could lead to an effective wall loss rate that is up to two orders of magnitude smaller (Seeley et al., 1996; Seeley et al., 1993; Donahue et al., 1996; Herndon et al., 2001). As this near-surface resistance to uptake cannot be readily assessed retrospectively for the Druett and May experiment, we conservatively conclude that the loss of OAF to the brass walls in the experiment of Druett and May is consistent with an uptake coefficient in the range of \( 10^{-4} \) to \( 10^{-2} \).

Peroxides could fit into this range for the wall loss. For example, \( \text{H}_2\text{O}_2 \) is readily destroyed on metal and metal-oxide surfaces, for which a \( \gamma \) value of \( 1 \times 10^{-4} \) has been recommended (Crowley et al., 2010). Similar uptake coefficients were observed for peracetic acid (Wu et al., 2015), and also a range of hydroperoxides from isoprene and terpene ozonolysis efficiently partition and react on or in condensed phases (Riva et al., 2017). Peroxy-radicals, with \( \gamma \) values ranging between \( 10^{-4} \) and \( 10^{-2} \) depending on the substrate (Ammann et al., 2013; Lakey et al., 2015; Lakey et al., 2016) also fit into this range, with higher values obtained in the presence of transition metals that may also be present in a brass tube exposed to acidifying gases. We note that the analysis of Hood (1974) did not consider the possibility that only a fraction of the collisions of the OAF with the wall may lead to its loss, which implies that the molecular weight may be overestimated so that smaller molecules and radicals considered here might remain candidates.
The chamber experiments of Dark and Nash (1970) were reanalysed using a detailed chemical model based on the present version of the Master Chemical Mechanism (MCMv3.2, http://mcm.york.ac.uk/). Simulations of reactant loss and product formation were performed for six different alkenes (propene, but-1-ene, trans-but-2-ene, cis-but-2-ene, pent-1-ene and hex-1-ene) for an experiment time of 10 minutes. Initial ozone and alkene concentrations and the conditions (T =293 K and RH = 80 %) of the ozonolysis experiments were as given by Dark and Nash (1970). In total, 18 model runs were performed for the six different alkenes and the three different initial O₃ concentrations listed by Dark and Nash (1970). Concentration profiles of HO radicals, HO₂ radicals, hydrogen peroxide (H₂O₂), organic peroxides (ROOHs), aldehydes (RCHOs), alcohols (ROH), carboxylic acids (RC(O)OH) and organic peroxy radicals (RO₂) were computed (https://chemie.tropos.de/images/Zusatzmaterial/CoxACP2021.zip). Note, groups such as RCHO contain all different aldehydes formed in the specific cases, i.e. for propene (HCHO, CH₃CHO) and for hexane (HCHO, CH₃(CH₂)xCHO with x = 0,1,2,3). Figure S5 shows the modelled data for the 11 ppbv initial ozone experiments.

To examine possible relationships between the product median concentration levels and the observed bactericidal effects, correlation coefficients and slopes between the two quantities were calculated. However, a greater slope may not necessarily imply a stronger causal relationship because of the underlying variation within the three different ozone concentrations. Similarly, owing to the small number of datapoints, statistical analyses for each specific ozone concentration revealed no clear correlation.

It is highly likely that not only the concentration but also the rate of transfer of a gas-phase product to the aqueous phase (containing the bacteria) play an important role in defining germicidal efficiency. This is manifest in the well-established principle that an efficient air-borne disinfectant must have a very low vapour pressure (Nash, 1951). For this reason, assuming that the germicidal effect of a trace-gas is proportional to its concentration and inversely proportional to p₀, we calculated the ratio (r_p) of the median concentration (expressed as a pressure) and the saturation vapour pressure (p₀) of trace gas product. Values of p₀ were taken from databases (https://chemie.tropos.de/images/Zusatzmaterial/SI Tables Cox et al.pdf), www.dguv.de/ifa/stoffdatenbank) or calculated (Compernolle et al., 2011). Values of r_p were found to increase at higher ozone conditions (i.e. higher product concentrations) and for the larger olefins.

In order to eliminate the effect of varying the ozone concentration on the relationship between the experimentally derived death fraction df (df = (1 - f) · 100) and r_p, the absolute differences between df and r_p for the various ozone concentrations were used; e.g. Δdf₁₁⁻₄ = df₁₁ - df₄ and Δr_p₁₁⁻₄ = r_p₁₁ - r_p₄ represents the differences in both parameters for the model run with 11 and 4 ppbv ozone, respectively. In this way, the relationship of the change in the predicted product concentrations (change in the cause) to the change in the observed death fraction (change in the effect) was studied. Figure S6 shows the relationship between Δdf and Δr_p for two inorganic (HO₂, H₂O₂) and two organic (RC(O)OOH, RCHO) trace-gases. While a positive slope is generally observed, the data is very scattered and with the exception of HO₂, the correlation coefficients are < 0.5. All other trace-gases display correlations similar to that of RCHO with correlation coefficients of about 0.1.
The probability that a trace-gas partitioned to the surface region is able to penetrate through the bacterial membrane can be a key factor in determining germicidal effects. Partitioning coefficients such as the octanol-water-coefficient ($K_{OW}$) are often used as a proxy because the cell membrane permeability is typically linearly proportional to it (Levin et al., 1984). $K_{OW}$ values for all oxidation products were taken from the EPIsuite database or estimated by the KOWWIN v1.67 estimation method (EPA, 2021; US-EPA, 2012). The values obtained (https://chemie.tropos.de/images/Zusatzmaterial/SI_Tables_Cox_et_al.pdf) indicate an increasing value of $K_{OW}$ with increasing carbon chain length. From the values of $K_{OW}$ thus obtained and the modelled concentration of each trace-gas product we calculated $f_{KOW}$, which is the median simulated concentration (expressed as a partial pressure) of a product multiplied by its value of $K_{OW}$. As for the analysis using the saturation vapour pressure, $f_{KOW}$ was not strongly correlated with germicidal efficiency.

Possible reasons for the lack of correlation (with the exception of HO$_2$) between the germicidal efficiency $\Delta f$ and the $\Delta r_p$ or $\Delta f_{KOW}$ of a trace gas may be related to missing chemistry in the MCM mechanism used or in the assumption of a linear relationship between germicidal efficiency and either $r_p$ or $K_{OW}$.
Figure S5: Concentration profiles for HO radicals, HO$_2$ radicals, H$_2$O$_2$, organic hydroperoxides (ROOH), aldehydes (RCHO), alcohols (ROH), carboxylic acids (ROOH), and RO$_2$ radicals in six different olefin-ozone experiments conducted by Dark and Nash (1970).
S6. Calculations using updated alkene degradation chemistry

(a) Construction of new chemical schemes
The chemistry of small alkenes, as represented in the MCM, is currently based on the rules defined by Jenkin et al. (Jenkin et al., 1997). To take account of recent advances in understanding, updated chemical schemes were constructed for the 11 alkenes shown in Fig. 1 of the main paper, the ozonolysis of which resulted in the wide range of germicidal impacts reported by Dark and Nash (Dark and Nash, 1970). Importantly, this included chemical schemes for cyclohexene and 2,4,4-trimethylpent-2-ene, for which the reported impacts were at the extremes of the range, these alkenes not being treated in the MCM. The new and updated schemes represented explicitly the O₃ and HO-initiated gas-phase chemistry of the series of alkenes to first-generation products under NOₓ-free conditions, with the rate coefficients for these initiation reactions taken from Cox et al. (Cox et al., 2020), Mellouki et al. (Mellouki et al., 2021, 2020) and McGillen et al. (McGillen et al., 2020). The schemes included excited Criegee intermediate (CI*) chemistry designed to recreate recommended HO and sCI yields (e.g. as reported by Cox et al. (Cox et al., 2020)), primary carbonyl yields (e.g. as summarized by Calvert et al. (Calvert et al., 2015) and Cox et al. (Cox et al., 2020)), and reported yields of other products formed from the prompt decomposition of CI* (e.g. HO₂, ketenes, etc.), where available, e.g. Tuazon et al. (Tuazon et al., 1997) for propene, cis-but-2-ene, trans-but-2-ene and 2-methylbut-2-ene; Aschmann et al. (Aschmann et al., 2003) and Hansel et al. (Hansel et al., 2018) for cyclohexene.
The sCl chemistry was based on, or inferred from the recommendations of Cox et al. (2020) and the theoretical/structure-activity relationship (SAR) methods of Vereecken et al. (Vereecken et al., 2017). This includes unimolecular decomposition (e.g. to form HO and organic radical co-products), reaction with H2O and (H2O)2, and reaction with the primary carbonyl and carboxylic acid products formed in each alkene system to form secondary ozonides and hydroperoxy-esters.

The bimolecular reactions of peroxy (RO2) radicals formed from the O3 and HO-initiated chemistry was based on the recommendations of Jenkin et al. (Jenkin et al., 2019), with a parameterized representation of RO2 permutation reactions. In the specific case of the complex C6 RO2 radicals formed from cyclohexene oxidation, unimolecular isomerization reactions were included, based on the methods of Vereecken and Nozière (Vereecken and Nozière, 2020), allowing rapid formation of HOMs via the resultant autooxidation mechanism, and the formation of the main series of products reported by Aschmann et al. (Aschmann et al., 2003) and Hansel et al. (Hansel et al., 2018). Where appropriate, the decomposition and isomerization chemistry of the oxy (RO) radicals formed in the various systems was based on the methods of Vereecken and Peeters (Vereecken and Peeters, 2010, 2009). The new mechanisms are listed in Table S4, along with a key to species identity in Table S5.

(b) Results

Simulations of the 11 alkene systems were carried out for each of the three ozone regimes for the 10 minute experiment duration, using the initial conditions reported by Dark and Nash (1970). The average gas-phase concentrations of a series of products or product classes were plotted against the average E. coli loss rates (kloss) summarised in Table S1. The products included sCIs, the radical species HO, HO2 and RO2, and the closed-shell products, RCHO, RC(O)R, H2O2, ROOH, RC(O)OOH, RC(O)OH, ketenes and secondary ozonides. No clear correlations were observed for any product, as shown in Figs. S7 and S8. Figure 2a of the main text also shows example results for species containing -OOH groups (including H2O2, ROOH, RC(O)OOH and total -OOH) for the 33 ppb ozone experiments, showing that the concentrations of -OOH species generated from alkenes with low (or zero) germicidal impacts (2-methylbut-2-ene and 2,4,4-trimethylpent-2-ene) are comparable with those generated from cyclohexene, which has the highest germicidal impact.

It is noted, however, that the broad product classes formed in the various systems can include a structurally diverse set of compounds, which may possess different propensities to penetrate the protective membrane of the microorganisms and initiate oxidation. Peroxidic compounds such as H2O2 and peracetic acid (CH3C(O)OOH) are known germicides (e.g. (McDonnell and Russell, 1999)), and the speciation was considered in more detail. Figure 2b,c,d of the main text and Fig. S9 shows the simulated speciation of peroxidic compounds generated from the ozonolysis of 2-methylbut-2-ene, 2,4,4-trimethylpent-2-ene and cyclohexene (33 ppb ozone experiments). For 2-methylbut-2-ene and 2,4,4-trimethylpent-2-ene, the most important contributors are the β-hydroxy species formed from secondary attack of HO on the parent alkenes (accounting of 75 % and 63 % of the peroxide burden, respectively) with additional contributions resulting mainly from the chemistry of the organic co-radical(s) formed with HO from the ozonolysis mechanism (e.g. CH3C(O)CH2OOH, CH3C(O)OOH and CH3OOH from the chemistry of CH3C(O)CH2 co-radical, and HC(O)CH2OOH from the chemistry of HC(O)CH2 co-radical in the 2-methylbut-2-ene system). As a
result, the peroxide concentrations for the complete series of acyclic alkenes broadly follow the trend in HO yields, with underlying contributions from \( \alpha \)-hydroxy ROOH and \( \text{H}_2\text{O}_2 \) formed from the reactions of some sCIs with \( \text{H}_2\text{O} \) and \( (\text{H}_2\text{O})_2 \). In the case of cyclohexene, however, important additional contributions result from autooxidation chemistry involving peroxy radicals formed from the organic co-radical, HC(O)CH\(_2\)CH\(_2\)CH\(_2\)CHCHO. This leads to additional rapid formation of a number of multi-functional species (HOMs) containing \( -\text{OOH} \) and \( -\text{C(O)}\text{OOH} \) groups, resulting from sequential H-shift isomerisation reactions, as also reported experimentally (e.g. Hansel et al., 2018). It is probable that such multifunctional species may show an increased propensity for uptake to surfaces. In contrast, it is noted that the majority of hydroperoxide species formed from 2-methylbut-2-ene and 2,4,4-trimethylpent-2-ene are either tertiary and/or contain bulky \( \beta \)-substituents which may have an influence on uptake and/or the decomposition rates and pathways in the condensed phase. Clearly further work is required on the structural dependence of germicidal properties of hydroperoxides and other oxygenated products of alkene ozonolysis.

**Figure S7:** Simulated concentrations of HO, \( \text{HO}_2 \), RO\(_2\), sCI, secondary ozonide (SOZ) and ketene products vs. \( k_{\text{loss}} \) for *E. coli* in 33 ppb O\(_3\) experiments for the series of 11 alkenes shown in Fig. 1 of the main paper; and linear regression of the data.
Figure S8: Simulated concentrations of H₂O₂, ROOH, RC(O)OOH, RC(O)OH, RCHO and RC(O)R products vs. $k_{loss}$ for *E. coli* in 33 ppb O₃ experiments for the series of 11 alkenes shown in Fig. 1 of the main paper; and linear regression of the data.
Figure S9. Simulated speciation of peroxidic compounds generated from 2-methylbut-2-ene, 2,4,4-trimethylpent-2-ene and cyclohexene in the 33 ppb O₃ experiments. The total -OOH concentrations in the three cases were $2.8 \times 10^{11}$, $3.2 \times 10^{11}$ and $3.7 \times 10^{11}$ molecule cm$^{-3}$. Species in red ellipses are those formed from the HO + alkene reactions. A key to species identity is given in Table S5.

(c) Uncertainties
Mechanistic uncertainties: The new chemical schemes are designed to incorporate up-to-date kinetic and mechanistic information, as described above. Despite this, there are remaining uncertainties in the chemistry of alkene ozonolysis, as discussed in recent reviews, e.g., Osborn and Taatjes (2015); Vereecken et al. (2017); Khan et al. (2018); Cox et al. (2020); Caravan et al. (2021). A particular area of uncertainty for the current study is the product distribution formed from the reactions of sCIs with H₂O and (H₂O)₂. As illustrated above in section 3c, these reactions are major atmospheric loss routes for CH₂OO and generally for $E$- mono-substituted sCIs, and they are also important loss routes for the conditions of the Dark and Nash (1970) experiments. The product channel contributions have only been fully characterized for the reactions of CH₂OO with H₂O (Nguyen et al., 2016) and (H₂O)₂ (Nguyen et al., 2016; Sheps et al., 2017). Although both these studies report significant formation of the α-hydroxy hydroperoxide product, HOCH₂OOH, for the (H₂O)₂ reaction (40% and 55%, respectively), there is substantial disagreement on the
importance of the channels forming HCHO + H2O2 (6% and 40%) and HC(O)OH (54% and <10%), and IUPAC currently makes no recommendations for the product channel branching ratios for either the H2O or (H2O)2 reaction (Cox et al., 2020). In the present work, we have adopted the product channels reported by Nguyen et al. (2016), because they report branching ratios for both reactions under chamber conditions. Furthermore, the same product channel contributions are applied to all sCIs by analogy, in the absence of reported information, and this assumption could mask any trends in the formation of H2O2, α-hydroxy hydroperoxides and carboxylic acids from these sources. Clearly, additional studies are required to reduce uncertainty in this area and to identify any systematic dependences in the branching ratios from one sCI to another.

As indicated above, the mechanisms also include the formation of secondary ozonides from the reactions of sCIs with the primary carbonyl products formed in each alkene system. The results show that the gas phase formation of secondary ozonides (SOZs) is unimportant for most of the alkene systems considered (see Fig. S7). This is because removal of the stabilized Criegee intermediates (sCIs) formed is generally dominated by either thermal decomposition or reaction with H2O and (H2O)2, thereby precluding significant formation of SOZs from their secondary reactions with the product aldehydes or ketones. The only exceptions are the 2,4,4-trimethylpent-2-ene and cyclohexene systems, which have the lowest and highest germicidal impacts of the alkene systems considered. In the former case, both thermal decomposition and reaction with H2O and (H2O)2 are predicted to be relatively slow for one sCI (Z-pivaldehyde oxide, Z-(CH3)3CCHOO) (Vereecken et al., 2017), allowing its reaction with the product pivaldehyde (in particular) to compete to some extent, forming a C10 SOZ (about 150 ppt in the 33 ppb ozone experiment).

In the case of cyclohexene, the small yield (3 %) of the E- and Z-carbonyl-substituted sCIs is represented to react exclusively by ring-closure to form an SOZ, this being based on the extremely rapid rate coefficients calculated by Long et al. (2019). This results in about 600 ppt SOZ in the 33 ppb ozone experiment (see Fig. S7). However, it is noted that Berndt et al. (2017) reported detection of the cyclohexene-derived carbonyl-substituted sCI(s), and tentative rate coefficients for the bimolecular reactions with added SO2, acetone and acetic acid – suggesting that rapid SOZ formation does not occur. Either way, the trend of gas-phase SOZ formation for the series of alkenes considered cannot explain the variation of germicidal impact observed by Dark and Nash (1970), although further work is required to establish the extent of intramolecular SOZ formation from small cyclic alkenes with low sCI yields. We note that, in some contrast, in the condensed phase, typical fates of the sCI are 1,3-dipolar cycloaddition with the carbonyl containing product that was formed from the decomposition of the primary ozonide (Zahardis and Petrucci, 2007). The products of these reactions are SOZ or polymeric ozonides. Cycloaddition with another sCI leads to diperoxides and peroxidic polymers. In presence of protic solvents, hydroperoxides are formed (Bailey, 1958). Thus, the formation of SOZ is strongly depending on the polarity of the condensed-phase matrix. As already mentioned in the submitted manuscript, the germicidal effects of ozonized unsaturated oils were suggested to be related to the presence of SOZ (Travagli et al., 2010). But since the alkenes considered as OAF precursors in the Dark and Nash (1970) work are not being oxidised to an appreciable degree in the condensed phase, condensed phase SOZ are not relevant there. In addition, since peroxides generally contribute to the health impact of particulate matter, it is important that any potential direct health effects of airborne germicides contributing to the OAF are also identified and investigated.
Mechanistic simplifications: The schemes written here also contain some simplifications, the possible effects of which were assessed. The HO-initiated chemistry takes account of the major product channels resulting from HO addition to the C=C bonds but, for expediency, omits the minor channels resulting from H atom abstraction from the substituent groups. These are estimated to account for between 1% and 22% of the reaction for the series of alkenes (8% on average), based on the structure-activity relationship methods of Jenkin et al. (2018), being systematically more important for cyclohexene and the larger acyclic alkenes. These reactions would tend to generate unsaturated mono-functional oxygenated products, in particular alk-1-enyl oxygenates (e.g., allyl hydroperoxide and acrolein in the case of the simplest alkene, propene), in place of the corresponding β-hydroxy substituted product classes formed from the HO addition chemistry. In addition, unimolecular ring-closure reactions might be operative for some of the unsaturated RO$_2$ formed (Vereecken et al., 2021), potentially providing minor routes to highly oxygenated products. A broad assessment of the trend in formation of such unsaturated and highly oxygenated products was carried out (based on HO yields of the O$_3$ + alkene reactions and the H atom abstraction fractions), but there was no correlation with the reported germicidal impacts reported by Dark and Nash (1970) (Table S1), largely reflecting that the impacts do not correlate with alkene size.

For simplicity, the schemes applied here also use a parameterized representation of the RO$_2$ permutation reactions (i.e., RO$_2$ + RO$_2$ and RO$_2$ + R'O$_2$) in which each RO$_2$ reacts with the pool of peroxy radicals in a pseudo-unimolecular reaction (Jenkin et al., 2019), as shown in Table S4. As a result, it was not possible to represent the product channels forming ROOR (or ROOR') + O$_2$, because part of the ROOR/ROOR' product derives from the peroxy radical pool rather than from the reacting RO$_2$ (see discussion in Jenkin et al., 2019). In practice, the contributions of these channels, and their dependence on peroxy radical structure, are not generally well characterized, and even an explicit representation of the reactions would therefore have substantial uncertainties associated with the yields of these products. However, assuming only a modest structural dependence, their collective formation efficiency might be expected to be mainly governed by the peroxy radical concentration which, as indicated above and shown in Fig. S7, shows no correlation with the reported germicidal impacts.

Potential impact of impurity NOx: Finally, the analysis we have carried out assumes that the Dark and Nash (1970) experiments were carried out under NO$_x$-free conditions. Their chamber experiments were nominally carried out in the absence of NO (which could otherwise have a provided a major reaction partner for the peroxy radicals, RO$_2$ and HO$_2$) and alkene impurities, and they report a systematic procedure for minimizing the impacts of such impurities. However, their procedure would result in any NO$_4$ present being in the form of NO$_2$ rather than NO, and we therefore cannot rule out the possibility of trace levels of NO$_2$ being present in their experiments. Peroxy radicals also react with NO$_2$, but the impact of these reactions is limited in the majority of cases because the product peroxy-nitrates (RO$_2$NO$_2$) are generally thermally unstable, decomposing rapidly to regenerate RO$_2$ and NO$_2$. Based on the generic rate coefficients recommended by Jenkin et al. (2019), this occurs on the timescale of about 200 ms for a typical RO$_2$NO$_2$ (298 K, 760 Torr). As a result, an approximately unchanged steady state concentration of RO$_2$ is rapidly established, with RO$_2$NO$_2$ present at about 4% of the RO$_2$ concentration at an example level of 1 ppb NO$_2$ (and systematically higher at higher levels of NO$_2$). In the specific cases of acyl peroxy radicals (RC(O)O$_2$), however, the product peroxy-acyl nitrates (PANs) are effectively stable species on the experimental timescale, and the presence of NO$_2$ could inhibit
the formation of products from their alternative reaction pathways, including peroxy acids (RC(O)OOH) formed from
the reactions with HO2 or by unimolecular isomerization. For the linear alkene systems considered, acyl peroxy
radicals are not formed from the first-generation ozonolysis chemistry, and no significant effect of trace levels of NO2
would be expected. In the cases of cyclohexene (at the high end of the germicidal impact range), and to a lesser extent
2-methylbut-2-ene and 2,4,4-trimethylpent-2-ene (at the low end of the germicidal impact range), however, acyl
peroxy radicals are formed from the first-generation chemistry. As shown in Fig. S8, significant formation of
RC(O)OOH is simulated to occur in these systems under NOx-free conditions, particularly for cyclohexene (the mean
concentrations are about $1.4 \times 10^{11}$ molecule cm$^{-3}$ for cyclohexene, and about $2.7 \times 10^{9}$ molecule cm$^{-3}$ for each of 2-
methylbut-2-ene and 2,4,4-trimethylpent-2-ene). Reaction of RC(O)O2 with $\geq 1$ ppb NO2 can generally compete with
the other bimolecular reactions for RC(O)O2 (i.e., with HO2 and RO2) and would therefore have an impact on the
formation of RC(O)OOH and other bimolecular reaction products. In the particularly important case of cyclohexene,
however, a significant proportion of the RC(O)OOH (and other -OOH species) is formed from the auto-oxidation
chemistry, involving peroxy radical isomerization reactions. These reactions are generally sufficiently rapid that the
presence of ppb levels of NO2 is predicted to have a reduced effect compared with its impact on the bimolecular
reaction products. It is also noted that when the corresponding PANs may be formed, they are generally
multifunctional species also containing -OOH groups. Whilst these considerations of the possible effects of NOx are
important, they do not allow any further insight into the likely identity (or identities) of the germicidal agent
responsible for the open-air factor. Highly-instrumented chamber studies would be valuable to help relate germicidal
impacts systematically to particular classes of reaction product formed in simulated atmospheric systems.
Table S4: Updated chemical schemes for the 11 alkenes shown in Fig. 1 of the main paper. A key to species identity is provided in Table S5.\(^a\)

| Rate coefficient\(^b\) | Reaction |
|------------------------|----------|
| **Propene** | |
| **O\(_3\) initiation reactions** | |
| 5.77E-15*EXP(-1880/T)*0.35 | O\(_3\) + C\(_3\)H\(_6\) = CH\(_2\)OOA + CH\(_3\)CHO |
| 5.77E-15*EXP(-1880/T)*0.32 | O\(_3\) + C\(_3\)H\(_6\) = ZCH\(_3\)CHOOA + H\(_2\)CO |
| 5.77E-15*EXP(-1880/T)*0.33 | O\(_3\) + C\(_3\)H\(_6\) = ECH\(_3\)CHOOA + H\(_2\)CO |
| **Excited CI chemistry** | |
| KDEC*0.6\(^c\) | CH\(_2\)OOA = CH\(_2\)OO |
| KDEC*0.118 | CH\(_2\)OOA = CO + HO\(_2\) + OH |
| KDEC*0.124 | CH\(_2\)OOA = CO |
| KDEC*0.124 | CH\(_2\)OOA = H\(_2\) |
| KDEC*0.034 | CH\(_2\)OOA = HO\(_2\) + HO\(_2\) |
| KDEC*0.13 | ZCH\(_3\)CHOOA = ZCH\(_3\)CHO |
| KDEC*0.87 | ZCH\(_3\)CHOOA = HCOCH\(_2\)O\(_2\) + OH |
| KDEC*0.13 | ECH\(_3\)CHOOA = ECH\(_3\)CHO |
| KDEC*0.334 | ECH\(_3\)CHOOA = CH\(_4\) |
| KDEC*0.192 | ECH\(_3\)CHOOA = CH\(_3\)OH + CO |
| KDEC*0.125 | ECH\(_3\)CHOOA = CH\(_2\)CO |
| KDEC*0.219 | ECH\(_3\)CHOOA = CH\(_3\)O\(_2\) + HO\(_2\) |
| **Stabilized sCI chemistry** | |
| 2.8E-16*[H\(_2\)O]*0.73 | CH\(_2\)OO = HOCH\(_2\)OOC |
| 2.8E-16*[H\(_2\)O]*0.06 | CH\(_2\)OO = HCHO + H\(_2\)O |
| 2.8E-16*[H\(_2\)O]*0.21 | CH\(_2\)OO = HCOOH |
| 7.35E-18*EXP(4076/T)*[(H\(_2\)O)\(_2\)]*0.40 | CH\(_2\)OO = HOCH\(_2\)OOC |
| 7.35E-18*EXP(4076/T)*[(H\(_2\)O)\(_3\)]*0.06 | CH\(_2\)OO = HCHO + H\(_2\)O |
| 7.35E-18*EXP(4076/T)*[(H\(_2\)O)\(_3\)]*0.54 | CH\(_2\)OO = HCOOH |
| 1.52E-11*EXP(590/T) | CH\(_2\)OO + HCOOH = HPMEFORM |
| 1.30E-10 | CH\(_2\)OO + CH\(_3\)CO\(_2\)H = HPMEACET |
| 1.70E-12 | CH\(_2\)OO + HCHO = CSOZC |
| 1.70E-12 | CH\(_2\)OO + CH\(_3\)CHO = C\(_2\)SOZC |
| 7.4E+6*EXP(-3220/T) | ZCH\(_3\)CHO = HCOCH\(_2\)O + OH |
| 6.84E-19*[H\(_2\)O]*0.73 | ZCH\(_3\)CHOO = CH\(_3\)CHO + HO\(_2\) |
| 6.84E-19*[H\(_2\)O]*0.06 | ZCH\(_3\)CHOO = CH\(_3\)CHO + HO\(_2\) |

\(^{a}\) Key to species identity is provided in Table S5.

\(^{b}\) Rate coefficients are in units of s\(^{-1}\).

\(^{c}\) KDEC is the rate coefficient in units of s\(^{-1}\) for the reaction.
| Rate | Reaction |
|------|-----------|
| 6.84E-19*[H_2O]*0.21 | ZCH3CHOO = CH3CO2H |
| 2.05E-15*[H_2O_2]*0.40 | ZCH3CHOO = CH3CHOHOOH |
| 2.05E-15*[H_2O_2]*0.06 | ZCH3CHOO = CH3CHO + H2O2 |
| 2.05E-15*[H_2O_2]*0.54 | ZCH3CHOO = CH3CO2H |
| 2.50E-10 | ZCH3CHOO + HCOOH = HP1ETFORM |
| 1.70E-10 | ZCH3CHOO + CH3CO2H = HP1ETACET |
| 1.70E-12 | ZCH3CHOO + HCHO = C2SOZC |
| 1.70E-12 | ZCH3CHOO + CH3CHO = C2SOZC2 |
| 1.94E+09*T^{1.35}*EXP(-7445/T) | ECH3CHOO = CH3CO2H |
| 1.3E-14*[H_2O]*0.73 | ECH3CHOO = CH3CHOHOOH |
| 1.3E-14*[H_2O]*0.06 | ECH3CHOO = CH3CHO + H2O2 |
| 1.3E-14*[H_2O]*0.21 | ECH3CHOO = CH3CO2H |
| 4.4E-11*[H_2O_2]*0.40 | ECH3CHOO = CH3CHOHOOH |
| 4.4E-11*[H_2O_2]*0.06 | ECH3CHOO = CH3CHO + H2O2 |
| 4.4E-11*[H_2O_2]*0.54 | ECH3CHOO = CH3CO2H |
| 5.00E-10 | ECH3CHOO + HCOOH = HP1ETFORM |
| 2.50E-10 | ECH3CHOO + CH3CO2H = HP1ETACET |
| 1.70E-12 | ECH3CHOO + HCHO = C2SOZC |
| 1.70E-12 | ECH3CHOO + CH3CHO = C2SOZC2 |

**OH initiation reactions**

KMT16*0.137 \(^d\) \(\text{OH} + \text{C}_3\text{H}_6 = \text{HYPROP02}\)
KMT16*0.863 \(\text{OH} + \text{C}_3\text{H}_6 = \text{IPROP0LO2}\)

**RO\(_2\) and RO chemistry**

KRO2HO2*0.498*0.82 \(^e\) \(\text{HCOCH2O2} + \text{HO2} = \text{HCOCH2O0H}\)
KRO2HO2*0.498*0.18 \(\text{HCOCH2O2} + \text{HO2} = \text{HCOCH2O} + \text{OH}\)
1.00E-13*EXP(974/T)*0.2*[RO\(_2\)] \(^f\) \(\text{HCOCH2O2} = \text{GLYOX}\)
1.00E-13*EXP(974/T)*0.6*[RO\(_2\)] \(\text{HCOCH2O2} = \text{HCOCH2O}\)
1.00E-13*EXP(974/T)*0.2*[RO\(_2\)] \(\text{HCOCH2O2} = \text{HOCCH2CHO}\)
KDEC \(\text{HCOCH2O} = \text{HCHO} + \text{CO} + \text{HO2}\)
3.8E-13*EXP(780/T)*(1-(1/(1+498*EXP(-1160/T)))) \(\text{CH3O2} + \text{HO2} = \text{CH3OOH}\)
3.8E-13*EXP(780/T)*(1+(1+498*EXP(-1160/T))) \(\text{CH3O2} + \text{HO2} = \text{HCHO}\)
2.06E-13*EXP(365/T)*7.2*EXP(-885/T)*[RO\(_2\)] \(\text{CH3O2} = \text{CH3O}\)
1.03E-13*EXP(365/T)*(-1.72*EXP(-885/T))*[RO\(_2\)] \(\text{CH3O2} = \text{CH3OH}\)
1.03E-13*EXP(365/T)*(-1.72*EXP(-885/T))*[RO\(_2\)] \(\text{CH3O2} = \text{HCHO}\)
7.2E-14*EXP(-1080/T)*[O\(_2\)] \(\text{CH3O} = \text{HCHO} + \text{HO2}\)
\[
\begin{array}{|c|c|}
\hline
KRO2HO2*0.601 & HYPROPO2 + HO2 = HYPROPO2H \\
1.00E-13*\exp{(570/T)*0.2*[RO2]} & HYPROPO2 = ACETOL \\
1.00E-13*\exp{(570/T)*0.6*[RO2]} & HYPROPO2 = HYPROPO \\
1.00E-13*\exp{(570/T)*0.2*[RO2]} & HYPROPO2 = PROPGLY \\
2.00E+14*\exp{(-6410/T)} & HYPROPO = CH3CHO + HCHO + HO2 \\
\hline
KRO2HO2*0.601 & IPROPOLO2 + HO2 = IPROPOLO2H \\
1.00E-13*\exp{(942/T)*0.2*[RO2]} & IPROPOLO2 = CH3CHOHCHO \\
1.00E-13*\exp{(942/T)*0.6*[RO2]} & IPROPOLO2 = IPROPOLO \\
1.00E-13*\exp{(942/T)*0.2*[RO2]} & IPROPOLO2 = PROPGLY \\
2.00E+14*\exp{(-5505/T)} & IPROPOLO = CH3CHO + HCHO + HO2 \\
\hline
\end{array}
\]

**But-1-ene**

\textit{O}_3\textit{initiation reactions}

\[
\begin{align*}
3.55E-15*\exp{(-1750/T)*0.35} & \quad O3 + BUT1ENE = CH2OOB + C2H5CHO \\
3.55E-15*\exp{(-1750/T)*0.325} & \quad O3 + BUT1ENE = ZC2H5CHOOA + HCHO \\
3.55E-15*\exp{(-1750/T)*0.325} & \quad O3 + BUT1ENE = EC2H5CHOOA + HCHO \\
\end{align*}
\]

\textit{Excited CI chemistry}

\[
\begin{align*}
KDEC*0.7 & \quad CH2OOB = CH2OO \\
KDEC*0.088 & \quad CH2OOB = CO + HO2 + OH \\
KDEC*0.093 & \quad CH2OOB = CO \\
KDEC*0.093 & \quad CH2OOB = H2 \\
KDEC*0.026 & \quad CH2OOB = HO2 + HO2 \\
KDEC*0.15 & \quad ZC2H5CHOOA = ZC2H5CHOO \\
KDEC*0.85 & \quad ZC2H5CHOOA = PROPALO2 + OH \\
KDEC*0.15 & \quad EC2H5CHOOA = EC2H5CHOO \\
KDEC*0.326 & \quad EC2H5CHOOA = C2H6 \\
KDEC*0.188 & \quad EC2H5CHOOA = C2H5OH + CO \\
KDEC*0.122 & \quad EC2H5CHOOA = CH3CHCO \\
KDEC*0.214 & \quad EC2H5CHOOA = C2H5O2 + HO2 \\
\end{align*}
\]

\textit{Stabilized sCI chemistry}

\[
\begin{align*}
1.30E-10 & \quad CH2OO + PROPACID = HPMEPROP \\
1.70E-12 & \quad CH2OO + C2H5CHO = C3SOZC \\
2.41E-62*T^{2.333}\exp{(2571/T)} & \quad ZC2H5CHOO = PROPALO2 + OH \\
1.51E-18*[H2O]*0.73 & \quad ZC2H5CHOO = ETCHOHOOH \\
1.51E-18*[H2O]*0.06 & \quad ZC2H5CHOO = C2H5CHO + H2O2 \\
1.51E-18*[H2O]*0.21 & \quad ZC2H5CHOO = PROPACID \\
\end{align*}
\]
| Reaction | Rate Constant | Products |
|----------|---------------|----------|
| \(4.31 \times 10^{-15} \times [(H_2O)_2]^*0.40\) | | ZC2H5CHO = ETCHOHOOH |
| \(4.31 \times 10^{-15} \times [(H_2O)_2]^*0.06\) | | ZC2H5CHO = C2H5CHO + H2O2 |
| \(4.31 \times 10^{-15} \times [(H_2O)_2]^*0.54\) | | ZC2H5CHO = PROPACID |
| | | |
| \(2.50 \times 10^{-10}\) | | ZC2H5CHO + HCOOH = HP1PRFORM |
| \(1.70 \times 10^{-12}\) | | ZC2H5CHO + PROPACID = HP1PROP |
| \(1.70 \times 10^{-12}\) | | ZC2H5CHO + HCHO = C3SOZC |
| \(1.70 \times 10^{-12}\) | | ZC2H5CHO + C2H5CHO = C3SOZC3 |
| \(1.57 \times 10^{10} \times T^{1.83} \times \exp(-7464/T)\) | | EC2H5CHO = PROPACID |
| \(1.58 \times 10^{-12} \times [H_2O]^*0.73\) | | EC2H5CHO = ETCHOHOOH |
| \(1.58 \times 10^{-12} \times [H_2O]^*0.06\) | | EC2H5CHO = C2H5CHO + H2O2 |
| \(1.58 \times 10^{-12} \times [H_2O]^*0.21\) | | EC2H5CHO = PROPACID |
| \(1.75 \times 10^{-11} \times [(H_2O)_2]^*0.40\) | | EC2H5CHO = ETCHOHOOH |
| \(1.75 \times 10^{-11} \times [(H_2O)_2]^*0.06\) | | EC2H5CHO = C2H5CHO + H2O2 |
| \(1.75 \times 10^{-11} \times [(H_2O)_2]^*0.54\) | | EC2H5CHO = PROPACID |
| \(5.00 \times 10^{-10}\) | | EC2H5CHO + HCOOH = HP1PRFORM |
| \(2.50 \times 10^{-10}\) | | EC2H5CHO + PROPACID = HP1PROP |
| \(1.70 \times 10^{-12}\) | | EC2H5CHO + HCHO = C3SOZC |
| \(1.70 \times 10^{-12}\) | | EC2H5CHO + C2H5CHO = C3SOZC3 |

**OH initiation reactions**

| Reaction | Rate Constant | Products |
|----------|---------------|----------|
| \(6.6 \times 10^{-12} \times \exp(465/T) \times 0.137\) | | BUT1ENE + OH = HO3C4O2 |
| \(6.6 \times 10^{-12} \times \exp(465/T) \times 0.863\) | | BUT1ENE + OH = NBUTOLAO2 |

**RO2 and RO chemistry**

| Reaction | Rate Constant | Products |
|----------|---------------|----------|
| \(6.4 \times 10^{-13} \times \exp(710/T)\) | | C2H5O2 + HO2 = C2H5OOH |
| \(1.00 \times 10^{-13} \times \exp(353/T) \times 0.6 \times [RO_2]\) | | C2H5O2 = C2H5O |
| \(1.00 \times 10^{-13} \times \exp(353/T) \times 0.2 \times [RO_2]\) | | C2H5O2 = C2H5OH |
| \(1.00 \times 10^{-13} \times \exp(353/T) \times 0.2 \times [RO_2]\) | | C2H5O2 = CH3CHO |
| \(2.4 \times 10^{-14} \times \exp(-325/T) \times [O_2]\) | | C2H5O = CH3CHO + HO2 |
| \(KRO2HO2 \times 0.601 \times 0.82\) | | PROPALO2 + HO2 = PROPALOOGH |
| \(KRO2HO2 \times 0.601 \times 0.18\) | | PROPALO2 + HO2 = PROPALO + OH |
| \(1.00 \times 10^{-13} \times \exp(674/T) \times 0.2 \times [RO_2]\) | | PROPALO2 = CH3CHOCHO |
| \(1.00 \times 10^{-13} \times \exp(674/T) \times 0.2 \times [RO_2]\) | | PROPALO2 = MGLYOX |
| \(1.00 \times 10^{-13} \times \exp(674/T) \times 0.6 \times [RO_2]\) | | PROPALO2 = PROPALO |
| \(KDEC\) | | PROPALO = CH3CHO + HO2 + CO |
| \(KRO2HO2 \times 0.683\) | | HO3C4O2 + HO2 = HO3C4OOH |
| \(1.00 \times 10^{-13} \times \exp(983/T) \times 0.2 \times [RO_2]\) | | HO3C4O2 = HO3C3CHO |
| Reaction Description | Reaction | Rate Constant | Product(s) |
|----------------------|----------|---------------|------------|
| KRO2HO2*0.683        |          |               | NBUTOLAO2 + HO2 = NBUTOLAOOH |
| KRO2HO2*0.748        |          |               | HO34C4O2 + HO2 = HO34C4OOH |
| Pent-1-ene O3 initiation reactions | 2.13E-15*EXP(-1580/T)*0.35 | PENT1ENE + O3 = CH2OOC + C3H7CHO |
|                      | 2.13E-15*EXP(-1580/T)*0.325 | PENT1ENE + O3 = ZC3H7CHOOA + HCHO |
|                      | 2.13E-15*EXP(-1580/T)*0.325 | PENT1ENE + O3 = EC3H7CHOOA + HCHO |
| Excited CI chemistry | KDEC*0.9 | CH2OOC = CH2OO |
|                      | KDEC*0.029 | CH2OOC = CO + HO2 + OH |
|                      | KDEC*0.031 | CH2OOC = CO |
|                      | KDEC*0.031 | CH2OOC = H2 |
|                      | KDEC*0.009 | CH2OOC = HO2 + HO2 |
|                      | KDEC*0.19 | ZC3H7CHOOA = ZC3H7CHOO |
|                      | KDEC*0.81 | ZC3H7CHOOA = BUTALAO2 + OH |
|                      | KDEC*0.19 | EC3H7CHOOA = EC3H7CHOO |
|                      | KDEC*0.311 | EC3H7CHOOA = C3H8 |
|                      | KDEC*0.179 | EC3H7CHOOA = NPROPOL + CO |
|                      | KDEC*0.116 | EC3H7CHOOA = C2H5CHCO |
|                      | KDEC*0.204 | EC3H7CHOOA = NC3H7O2 + HO2 |
| Stabilized sCI chemistry | 1.30E-10 | CH2OO + BUTACID = HPMEBUTR |
|                      | 1.70E-12 | CH2OO + C3H7CHO = C4SOZC |
| Reaction | Rate Constant | Products |
|----------|-------------|----------|
| \(2.41 \times 10^{-62} \times \exp(2571/T)\) | \(ZC3H7CHOO = BUTALAO2 + OH\) |
| \(1.51 \times 10^{-18} \times [H_2O]^{0.73}\) | \(ZC3H7CHOO = PRCHOHOOH\) |
| \(1.51 \times 10^{-18} \times [H_2O]^{0.06}\) | \(ZC3H7CHOO = C3H7CHO + H2O2\) |
| \(4.31 \times 10^{-15} \times [(H_2O)_2]^{0.40}\) | \(ZC3H7CHOO = PRCHOHOOH\) |
| \(4.31 \times 10^{-15} \times [(H_2O)_2]^{0.06}\) | \(ZC3H7CHOO = C3H7CHO + H2O2\) |
| \(4.31 \times 10^{-15} \times [(H_2O)_2]^{0.54}\) | \(ZC2H5CHO = BUTACID\) |
| \(2.50 \times 10^{-10}\) | \(ZC3H7CHOO + HCOOH = HP1BUFORM\) |
| \(1.70 \times 10^{-12}\) | \(ZC3H7CHOO + BUTACID = HP1BUBUTR\) |
| \(1.70 \times 10^{-12}\) | \(ZC3H7CHOO + C3H7CHO = C4SOZC\) |
| \(1.57 \times 10^{-11} \times \exp(-7464/T)\) | \(EC3H7CHOO = BUTACID\) |
| \(1.58 \times 10^{-14} \times [H_2O]^{0.73}\) | \(EC3H7CHOO = PRCHOHOOH\) |
| \(1.58 \times 10^{-14} \times [H_2O]^{0.06}\) | \(EC3H7CHOO = C3H7CHO + H2O2\) |
| \(1.58 \times 10^{-14} \times [H_2O]^{0.21}\) | \(EC3H7CHOO = BUTACID\) |
| \(1.75 \times 10^{-1} \times [(H_2O)_2]^{0.40}\) | \(EC3H7CHOO = PRCHOHOOH\) |
| \(1.75 \times 10^{-1} \times [(H_2O)_2]^{0.06}\) | \(EC3H7CHOO = C3H7CHO + H2O2\) |
| \(1.75 \times 10^{-1} \times [(H_2O)_2]^{0.54}\) | \(EC3H7CHOO = BUTACID\) |
| \(5.00 \times 10^{-10}\) | \(EC3H7CHOO + HCOOH = HP1BUFORM\) |
| \(2.50 \times 10^{-10}\) | \(EC3H7CHOO + BUTACID = HP1BUBUTR\) |
| \(1.70 \times 10^{-12}\) | \(EC3H7CHOO + C3H7CHO = C4SOZC\) |
| \(1.70 \times 10^{-12}\) | \(EC3H7CHOO + C3H7CHO = C4SOZC\) |

**OH initiation reactions**

| Reaction | Rate Constant | Products |
|----------|-------------|----------|
| \(5.86 \times 10^{-12} \times \exp(500/T) \times 0.863\) | \(PENT1ENE + OH = PE1ENEAO2\) |
| \(5.86 \times 10^{-12} \times \exp(500/T) \times 0.137\) | \(PENT1ENE + OH = PE1ENEBO2\) |

**RO2 and RO chemistry**

| Reaction | Rate Constant | Products |
|----------|-------------|----------|
| \(KRO2HO2 \times 0.498\) | \(NC3H7O2 + HO2 = NC3H7OOH\) |
| \(1.00 \times 13 \times \exp(559/T) \times 0.2 \times [RO_2]\) | \(NC3H7O2 = C2H5CHO\) |
| \(1.00 \times 13 \times \exp(559/T) \times 0.6 \times [RO_2]\) | \(NC3H7O2 = NC3H7O\) |
| \(1.00 \times 13 \times \exp(559/T) \times 0.2 \times [RO_2]\) | \(NC3H7O2 = NPROPOL\) |
| \(2.6 \times 14 \times \exp(-255/T) \times [O_2]\) | \(NC3H7O = C2H5CHO + HO2\) |
| \(KRO2HO2 \times 0.683 \times 0.82\) | \(BUTALAO2 + HO2 = BUTALAOOH\) |
| \(KRO2HO2 \times 0.683 \times 0.18\) | \(BUTALAO2 + HO2 = BUTAL2O + OH\) |
| \(1.00 \times 13 \times \exp(779/T) \times 0.6 \times [RO_2]\) | \(BUTALAO2 = BUTAL2O\) |
| \(1.00 \times 13 \times \exp(779/T) \times 0.2 \times [RO_2]\) | \(BUTALAO2 = EGLYOX\) |
| Term                                      | Equation                                      | Result                              |
|-------------------------------------------|-----------------------------------------------|-------------------------------------|
| 1.00E-13*EXP(779/T)*0.2*[RO₂]            | BUTALAO² = HO3C3CHO                           |                                    |
| KDEC                                      | BUTAL2O = C2H5CHO + HO2 + CO                 |                                    |
| KRO2HO²*0.748                            | PE1ENEAO² + HO2 = C51OH2OOH                   |                                    |
| 1.00E-13*EXP(731/T)*0.2*[RO₂]            | PE1ENEAO² = C51OH2CO                         |                                    |
| 1.00E-13*EXP(731/T)*0.2*[RO₂]            | PE1ENEAO² = HO12C5                           |                                    |
| 1.00E-13*EXP(731/T)*0.6*[RO₂]            | PE1ENEAO² = PE1ENEAO                         |                                    |
| 1.80E+13*EXP(-4076/T)                    | PE1ENEAO = C3H7CHO + HCHO + HO2             |                                    |
| KRO2HO²*0.748                            | PE1ENEBO² + HO2 = C52OH1OOH                  |                                    |
| 1.00E-13*EXP(1007/T)*0.2*[RO₂]           | PE1ENEBO² = C4OHCHO                          |                                    |
| 1.00E-13*EXP(1007/T)*0.2*[RO₂]           | PE1ENEBO² = HO12C5                           |                                    |
| 1.00E-13*EXP(1007/T)*0.6*[RO₂]           | PE1ENEBO² = PE1ENEBO                         |                                    |
| 1.80E+13*EXP(-5234/T)                    | PE1ENEBO = C3H7CHO + HCHO + HO2             |                                    |
| 8.00E+10*EXP(-3010/T)                    | PE1ENEBO = HO12C54O2                         |                                    |
| KRO2HO²*0.800                            | HO12C54O2 + HO2 = HO12C54OOH                 |                                    |
| 1.00E-13*EXP(373/T)*0.2*[RO₂]            | HO12C54O2 = C51OH                            |                                    |
| 1.00E-13*EXP(373/T)*0.2*[RO₂]            | HO12C54O2 = HO12C5                           |                                    |
| 1.00E-13*EXP(373/T)*0.6*[RO₂]            | HO12C54O2 = HO12C54O                        |                                    |
| 8.00E+10*EXP(-2417/T)                    | HO12C54O = HO24C4CHO + HO2                  |                                    |
| Hex-1-ene                                 |                                               |                                    |
| O₃ initiation reactions                   |                                               |                                    |
| 1.33E-15*EXP(-1480/T)*0.35               | HEX1ENE + O₃ = CH2OO + C4H9CHO               |                                    |
| 1.33E-15*EXP(-1480/T)*0.325              | HEX1ENE + O₃ = HCHO + ZC4H9CHOOA             |                                    |
| 1.33E-15*EXP(-1480/T)*0.325              | HEX1ENE + O₃ = HCHO + EC4H9CHOOA             |                                    |
| Excited CI chemistry                      |                                               |                                    |
| KDEC*0.25                                | ZC4H9CHOOA = ZC4H9CHOO                       |                                    |
| KDEC*0.75                                | ZC4H9CHOOA = C4CHOAO2 + OH                   |                                    |
| KDEC*0.25                                | EC4H9CHOOA = EC4H9CHOO                       |                                    |
| KDEC*0.288                               | EC4H9CHOOA = NC4H10                          |                                    |
| KDEC*0.166                               | EC4H9CHOOA = NBUTOL + CO                     |                                    |
| KDEC*0.107                               | EC4H9CHOOA = C3H7CHCO                        |                                    |
| KDEC*0.189                               | EC4H9CHOOA = NC4H9O2 + HO2                  |                                    |
| Stabilized sCI chemistry                  |                                               |                                    |
| 1.30E-10                                 | CH2OO + PENTACID = HPMEPENT                   |                                    |
| 1.70E-12                                 | CH2OO + C4H9CHO = C5SOZC                     |                                    |
| Reaction | Rate Constant | Product
|----------|---------------|---------|
| ZC4H9CHOO = C4H9CHO + H2O2 | 4.31E-15*[H2O]2*0.06 *EXP(-7464/T) | EC4H9CHOO = C4H9CHO + H2O2
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.58E-14*[H2O]*0.73 *EXP-13*EXP(667/T)*0.6*[RO2] | NC4H9O = C3H7CHO + HO2
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.75E-11*[H2O]2*0.54 *EXP(-3570/T) | NC4H9O = HO1C4O2
| ZC4H9CHOO = C4H9CHO + H2O2 | 5.00E-10 | EC4H9CHOO + HCOOH = HP1PEFORM
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.70E-10 | EC4H9CHOO + PENTACID = HP1PEPENT
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.70E-12 | EC4H9CHOO + HCHO = C5SOZC
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.70E-12 | EC4H9CHOO + C4H9CHO = C5SOZC5
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.58E-14*[H2O]*0.73 *EXP-13*EXP(667/T)*0.2*[RO2] | NC4H9O = C3H7CHO
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.75E-11*[H2O]2*0.21 *EXP(-550/T)*[O2] | NC4H9O = C3H7CHO + HO2
| ZC4H9CHOO = C4H9CHO + H2O2 | 4.6D10*EXP(-3570/T) | NC4H9O = HO1C4O2
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.00E-13*EXP(746/T)*0.6*[RO2] | KRO2HO2*0.683
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.00E-13*EXP(746/T)*0.6*[RO2] | HO1C4O2 + HO2 = HO1C4O0H
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.00E-13*EXP(746/T)*0.2*[RO2] | HO1C4O2 = HO1C4O
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.00E-13*EXP(746/T)*0.2*[RO2] | HO1C4O2 = HOC3H6CHO
| ZC4H9CHOO = C4H9CHO + H2O2 | 1.00E-13*EXP(746/T)*0.2*[RO2] | HO1C4O2 = HOC4H8OH

**OH initiation reactions**

| Reaction | Rate Constant | Product
|----------|---------------|---------|
| HEX1ENE + OH = C6OH5O2 | 3.70E-11*0.863 | NC4H9O2 = C3H7CHO
| HEX1ENE + OH = C6OH5O2 | 3.70E-11*0.137 | NC4H9O2 = C3H7CHO

**RO2 and RO chemistry**

| Reaction | Rate Constant | Product
|----------|---------------|---------|
| KRO2HO2*0.601 | NC4H9O2 + HO2 = NC4H9OOH
| 1.00E-13*EXP(667/T)*0.2*[RO2] | NC4H9O2 = C3H7CHO
| 1.00E-13*EXP(667/T)*0.2*[RO2] | NC4H9O2 = NBUTOL
| 1.00E-13*EXP(667/T)*0.6*[RO2] | NC4H9O2 = NC4H9O
| 8.9E-14*EXP(-550/T)*[O2] | NC4H9O = C3H7CHO + HO2
| 4.6D10*EXP(-3570/T) | NC4H9O = HO1C4O2
| KRO2HO2*0.683 | HO1C4O2 + HO2 = HO1C4O0H
| 1.00E-13*EXP(746/T)*0.6*[RO2] | HO1C4O2 = HO1C4O
| 1.00E-13*EXP(746/T)*0.2*[RO2] | HO1C4O2 = HOC3H6CHO
| 1.00E-13*EXP(746/T)*0.2*[RO2] | HO1C4O2 = HOC4H8OH
- $8.74 \times 10^{11} \exp\left(-3430/T\right)$  
  \[ \text{HO1C4O} = \text{HOC3H6CHO} + \text{HOO2} \]

- $\text{KRO2HO2} \times 0.748 \times 0.82$  
  \[ \text{C4CHOAO2} + \text{HOO2} = \text{C4CHOAOOH} \]

- $\text{KRO2HO2} \times 0.748 \times 0.18$  
  \[ \text{C4CHOAO2} + \text{HOO2} = \text{C4CHO2O} + \text{OH} \]

- $1.00 \times 10^{-13} \exp\left(834/T\right) \times 0.748 \times 0.82$  
  \[ \text{C4CHOAO2} = \text{C4CHO2O} \]

- $1.00 \times 10^{-13} \exp\left(834/T\right) \times 0.748 \times 0.18$  
  \[ \text{C4CHOAO2} = \text{C4OHCHO} \]

- $1.00 \times 10^{-13} \exp\left(834/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{C4CHOAO2} = \text{PGLYOX} \]

- $\text{KDEC}$  
  \[ \text{C4CHO2O} = \text{C3H7CHO} + \text{HOO2} + \text{CO} \]

- $\text{KRO2HO2} \times 0.800$  
  \[ \text{C6OH5O2} + \text{HOO2} = \text{C6OH5OOH} \]

- $1.00 \times 10^{-13} \exp\left(760/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{C6OH5O2} = \text{C4COMEOH} \]

- $1.00 \times 10^{-13} \exp\left(760/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{C6OH5O2} = \text{C656OHH} \]

- $1.00 \times 10^{-13} \exp\left(760/T\right) \times 0.6 \times \text{[RO2]}$  
  \[ \text{C6OH5O2} = \text{C6OH5O} \]

- $1.80 \times 10^{13} \exp\left(-4076/T\right)$  
  \[ \text{C6OH5O} = \text{C4H9CHO} + \text{HCHO} + \text{HO2} \]

- $8.00 \times 10^{10} \exp\left(-3010/T\right)$  
  \[ \text{C6OH5O} = \text{HO12C65O2} \]

- $\text{KRO2HO2} \times 0.800$  
  \[ \text{HO5C6O2} + \text{HOO2} = \text{HO5C6OOH} \]

- $1.00 \times 10^{-13} \exp\left(1021/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{HO5C6O2} = \text{C656OHH} \]

- $1.00 \times 10^{-13} \exp\left(1021/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{HO5C6O2} = \text{HO5C5CHO} \]

- $1.00 \times 10^{-13} \exp\left(1021/T\right) \times 0.6 \times \text{[RO2]}$  
  \[ \text{HO5C6O2} = \text{HO5C6O} \]

- $4.00 \times 10^{10} \exp\left(-1871/T\right)$  
  \[ \text{HO12C65O2} = \text{HO15C62CO} + \text{HO2} \]

- $\text{KRO2HO2} \times 0.841$  
  \[ \text{HO12C64O2} + \text{HOO2} = \text{HO12C65OOH} \]

- $1.00 \times 10^{-13} \exp\left(399/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{HO12C65O2} = \text{HO12C65CO} \]

- $1.00 \times 10^{-13} \exp\left(399/T\right) \times 0.2 \times \text{[RO2]}$  
  \[ \text{HO12C65O2} = \text{HO12C65C6} \]

- $1.00 \times 10^{-13} \exp\left(399/T\right) \times 0.6 \times \text{[RO2]}$  
  \[ \text{HO12C65O2} = \text{HO12C65O} \]

- $4.00 \times 10^{10} \exp\left(-1871/T\right)$  
  \[ \text{HO12C65O} = \text{HO15C62CO} + \text{HO2} \]

- $\text{cis-But-2-ene}$

- $O_3$ initiation reactions

- $3.37 \times 10^{-15} \exp\left(-970/T\right) \times 0.33$  
  \[ \text{CBUT2ENE} + \text{O3} = \text{CH3CHO} + \text{ZCH3CHOOB} \]

- $3.37 \times 10^{-15} \exp\left(-970/T\right) \times 0.67$  
  \[ \text{CBUT2ENE} + \text{O3} = \text{CH3CHO} + \text{ECH3CHOOB} \]

- **Excited CI chemistry**

- $\text{KDEC} \times 0.50$  
  \[ \text{ZCH3CHOOB} = \text{ZCH3CHOO} \]
| Reaction | Rate Constant | Product(s)   |
|----------|---------------|--------------|
| KDEC*0.50 | ZCH3CHOOB = HCOCH2O2 + OH |
| KDEC*0.32 | ECH3CHOOB = ECH3CHOO |
| KDEC*0.268 | ECH3CHOOB = CH4 |
| KDEC*0.138 | ECH3CHOOB = CH3OH + CO |
| KDEC*0.104 | ECH3CHOOB = CH2CO |
| KDEC*0.170 | ECH3CHOOB = CH3O2 + HO2 |

**OH initiation reactions**

1.10E-11*EXP(487/T) CBUT2ENE + OH = BUT2OLO2

**RO2 and RO chemistry**

| Reaction | Rate Constant | Product(s)   |
|----------|---------------|--------------|
| KRO2HO2*0.683 | BUT2OLO2 + HO2 = BUT2OLOOH |
| 1.00E-13*EXP(675/T)*0.6*[RO2] | BUT2OLO2 = BUT2OLAO |
| 1.00E-13*EXP(675/T)*0.2*[RO2] | BUT2OLO2 = BUT2OLO |
| 1.00E-13*EXP(675/T)*0.2*[RO2] | BUT2OLO2 = BUT2LOH |
| 1.80E+13*EXP(-2528/T) | BUT2OLAO = CH3CHO + CH3CHO + HO2 |

**trans-But-2-ene**

**O3 initiation reactions**

6.64E-15*EXP(-1059/T)*0.6 TBUT2ENE + O3 = CH3CHO + ZCH3CHOOB
6.64E-15*EXP(-1059/T)*0.4 TBUT2ENE + O3 = CH3CHO + ECH3CHOOC

**Excited Cl chemistry**

| Reaction | Rate Constant | Product(s)   |
|----------|---------------|--------------|
| KDEC*0.32 | ECH3CHOOC = ECH3CHOO |
| KDEC*0.288 | ECH3CHOOC = CH4 |
| KDEC*0.175 | ECH3CHOOC = CH3OH + CO |
| KDEC*0.115 | ECH3CHOOC = CH2CO |
| KDEC*0.102 | ECH3CHOOC = CH3O2 + HO2 |

**OH initiation reactions**

1.01E-11*EXP(550/T) TBUT2ENE + OH = BUT2OLO2

**trans-Pent-2-ene**

**O3 initiation reactions**

7.10E-15*EXP(-1132/T)*0.25 TPENT2ENE + O3 = ZC2H5CHOOB + CH3CHO
7.10E-15*EXP(-1132/T)*0.25 TPENT2ENE + O3 = EC2H5CHOOB + CH3CHO
7.10E-15*EXP(-1132/T)*0.25 TPENT2ENE + O3 = ZCH3CHOOC + C2H5CHO
7.10E-15*EXP(-1132/T)*0.25 TPENT2ENE + O3 = ECH3CHOOD + C2H5CHO

**Excited Cl chemistry**

KDEC*0.58 ZCH3CHOOC = ZCH3CHOO
| KDEC*0.42 | ZCH3CHOOC = HCOCH2O2 + OH |
| KDEC*0.58 | ECH3CHOOD = ECH3CHOO |
| KDEC*0.178 | ECH3CHOOD = CH4 |
| KDEC*0.108 | ECH3CHOOD = CH3OH + CO |
| KDEC*0.071 | ECH3CHOOD = CH2CO |
| KDEC*0.063 | ECH3CHOOD = CH3O2 + HO2 |
| KDEC*0.45 | ZC2H5CHOOB = ZC2H5CHOO |
| KDEC*0.55 | ZC2H5CHOOB = PROPALO2 + OH |
| KDEC*0.45 | EC2H5CHOOB = EC2H5CHOO |
| KDEC*0.233 | EC2H5CHOOB = C2H6 |
| KDEC*0.141 | EC2H5CHOOB = C2H5OH + CO |
| KDEC*0.093 | EC2H5CHOOB = CH3CHCO |
| KDEC*0.083 | EC2H5CHOOB = C2H5O2 + HO2 |
| **Stabilized sCI chemistry** |
| 1.70E-10 | ZCH3CHOO + PROPACID = HP1ETPROP |
| 1.70E-12 | ZCH3CHOO + C2H5CHO = C3SOZC2 |
| 2.50E-10 | ECH3CHOO + PROPACID = HP1ETPROP |
| 1.70E-12 | ECH3CHOO + C2H5CHO = C3SOZC2 |
| 1.70E-10 | ZC2H5CHOO + CH3CO2H = HP1PRACET |
| 1.70E-12 | ZC2H5CHOO + CH3CHO = C3SOZC2 |
| 2.50E-10 | EC2H5CHOO + CH3CO2H = HP1PRACET |
| 1.70E-12 | EC2H5CHOO + CH3CHO = C3SOZC2 |
| **OH initiation reactions** |
| 6.69E-11*0.5 | TPENT2ENE + OH = PE2ENEAO2 |
| 6.69E-11*0.5 | TPENT2ENE + OH = PE2ENEBO2 |
| **RO2 and RO chemistry** |
| KRO2HO2*0.748 | PE2NEAO2 + HO2 = C52OH3OOH |
| 1.00E-13*EXP(731/T)*0.2*[RO2] | PE2NEAO2 = C523OH |
| 1.00E-13*EXP(731/T)*0.2*[RO2] | PE2NEAO2 = DIEKAOH |
| 1.00E-13*EXP(731/T)*0.6*[RO2] | PE2NEAO2 = PE2NEAO |
| 1.80E+13*EXP(-2528/T) | PE2NEAO = C2H5CHO + CH3CHO + HO2 |
| Reaction | Rate Constant |
|----------|--------------|
| KHRO2HO2*0.748 | PE2ENEBO2 + HO2 = C53OH2O2OH |
| 1.00E-13*EXP(731/T)*0.2*[RO2] | PE2ENEBO2 = C53OH |
| 1.00E-13*EXP(731/T)*0.2*[RO2] | PE2ENEBO2 = MPRKAOH |
| 1.00E-13*EXP(731/T)*0.6*[RO2] | PE2ENEBO2 = PE2ENEBO |
| 1.80E+13*EXP(-2528/T) | PE2ENEBO = CH3CHO + C2H5CHO + HO2 |

**trans-Hex-2-ene**

**O₃ initiation reactions**

| Rate Constant | Reaction |
|---------------|----------|
| 7.60E-15*EXP(-1163/T)*0.25 | THEX2ENE + O₃ = C3H7CHO + ZCH3CHOOD |
| 7.60E-15*EXP(-1163/T)*0.25 | THEX2ENE + O₃ = C3H7CHO + ECH3CHOOE |
| 7.60E-15*EXP(-1163/T)*0.25 | THEX2ENE + O₃ = CH3CHO + ZC3H7CHOOB |
| 7.60E-15*EXP(-1163/T)*0.25 | THEX2ENE + O₃ = CH3CHO + EC3H7CHOOB |

**Excited CI chemistry**

| Rate Constant | Reaction |
|---------------|----------|
| KDEC*0.80 | ZCH3CHOOD = ZCH3CHOO |
| KDEC*0.20 | ZCH3CHOOD = HCOCH2O2 + OH |
| KDEC*0.80 | ECH3CHOOE = ECH3CHOO |
| KDEC*0.085 | ECH3CHOOE = CH4 |
| KDEC*0.051 | ECH3CHOOE = CH3OH + CO |
| KDEC*0.034 | ECH3CHOOE = CH2CO |
| KDEC*0.030 | ECH3CHOOE = CH3O2 + HO2 |
| KDEC*0.40 | ZC3H7CHOOB = ZC3H7CHOO |
| KDEC*0.60 | ZC3H7CHOOB = BUTALAO2 + OH |
| KDEC*0.40 | ECH3CHOOB = ECH3CHOO |
| KDEC*0.254 | ECH3CHOOB = C3H8 |
| KDEC*0.155 | ECH3CHOOB = NPROPOL + CO |
| KDEC*0.101 | ECH3CHOOB = C2H5CHCO |
| KDEC*0.090 | ECH3CHOOB = NC3H7O2 + HO2 |

**Stabilized sCI chemistry**

| Rate Constant | Reaction |
|---------------|----------|
| 1.70E-10 | ZCH3CHOO + BUTACID = HP1ETBUTR |
| 1.70E-12 | ZCH3CHOO + C3H7CHO = C4SOZC2 |
| 2.50E-10 | ECH3CHOO + BUTACID = HP1ETBUTR |
| 1.70E-12 | ECH3CHOO + C3H7CHO = C4SOZC2 |
| 1.70E-10 | ZC3H7CHOO + CH3CO2H = HP1BUACET |
| 1.70E-12 | ZC3H7CHOO + CH3CHO = C4SOZC2 |
| Reaction | Equation |
|----------|----------|
| EC3H7CHOO + CH3CO2H = HP1BUACET | 2.50E-10 |
| EC3H7CHOO + CH3CHO = C4SOZC2 | 1.70E-12 |
| **OH initiation reactions** | |
| THEX2ENE + OH = C64OH5O2 | 6.00E-11*0.5 |
| THEX2ENE + OH = C65OH4O2 | 6.00E-11*0.5 |
| **RO2 and RO chemistry** | |
| KRO2HO2*0.800 C64OH5O2 + HO2 = C64OH5OOH | |
| 1.00E-13*EXP(760/T)*0.2*[RO2] C64OH5O2 = C645OH | |
| 1.00E-13*EXP(760/T)*0.6*[RO2] C64OH5O2 = C64OH5O | |
| 1.00E-13*EXP(760/T)*0.2*[RO2] C64OH5O2 = CO2HO3C6 | |
| 1.80E+13*EXP(-2528/T) C64OH5O = CH3CHO + C3H7CHO + HO2 | |
| KRO2HO2*0.800 C65OH4O2 + HO2 = C65OH4OOH | |
| 1.00E-13*EXP(760/T)*0.2*[RO2] C65OH4O2 = C645OH | |
| 1.00E-13*EXP(760/T)*0.6*[RO2] C65OH4O2 = C65OH4O | |
| 1.00E-13*EXP(760/T)*0.2*[RO2] C65OH4O2 = HEX3ONCOH | |
| 1.80E+13*EXP(-2528/T) C65OH4O = C3H7CHO + CH3CHO + HO2 | |
| **2-Methyl-but-2-ene** | |
| **O3 initiation reactions** | |
| ME2BUT2ENE + O3= CH3CHO + CH3CCH3OOA | 6.51E-15*EXP(-829/T)*0.63 |
| ME2BUT2ENE + O3= CH3COCH3 + ZCH3CHOOE | 6.51E-15*EXP(-829/T)*0.22 |
| ME2BUT2ENE + O3= CH3COCH3 + ECH3CHOOF | 6.51E-15*EXP(-829/T)*0.15 |
| **Excited Cl chemistry** | |
| ZCH3CHOOE = ZCH3CHOO | KDEC*0.35 |
| ZCH3CHOOE = HCOCH2O2 + OH | KDEC*0.65 |
| ECH3CHOOF = ECH3CHOO | KDEC*0.35 |
| ECH3CHOOF = CH4 | KDEC*0.275 |
| ECH3CHOOF = CH3OH + CO | KDEC*0.167 |
| ECH3CHOOF = CH2CO | KDEC*0.110 |
| ECH3CHOOF = CH3O2 + HO2 | KDEC*0.098 |
| CH3CCH3OOA = CH3CCH3OO | KDEC*0.27 |
| CH3CCH3OOA = CH3COCH2O2 + OH | KDEC*0.73 |
| **Stabilized sCl chemistry** | |
| CH3CCH3OO = CH3COCH2O2 + OH | 7.2E+06*EXP(-2920/T) |
| Reaction | Rate | Product(s) |
|----------|------|------------|
| \(7.54 \times 10^{-18} \cdot H_2O \cdot 0.92\) | | \(CH_3CCCH_3OO = H_2IPROOH\) |
| \(7.54 \times 10^{-18} \cdot H_2O \cdot 0.08\) | | \(CH_3CCCH_3OO = CH_3COCH_3 + H_2O\) |
| \(1.82 \times 10^{-14} \cdot H_2O \cdot 0.87\) | | \(CH_3CCCH_3OO = H_2IPROOH\) |
| \(1.82 \times 10^{-14} \cdot H_2O \cdot 0.13\) | | \(CH_3CCCH_3OO = CH_3COCH_3 + H_2O\) |
| \(3.10 \times 10^{-10}\) | | \(CH_3CCCH_3OO + CH_3CO_2H = HP2PRACET\) |
| \(1.70 \times 10^{-12}\) | | \(CH_3CCCH_3OO + CH_3CHO = IC_3SOZC_2\) |
| \(3.40 \times 10^{-13}\) | | \(CH_3CCCH_3OO + CH_3COCH_3 = IC_3SOZIC_3\) |
| \(3.40 \times 10^{-12}\) | | \(ZCH_3CHO + CH_3COCH_3 = IC_3SOZC_2\) |
| \(3.40 \times 10^{-12}\) | | \(ECH_3CHO + CH_3COCH_3 = IC_3SOZC_2\) |
| \(OH\) initiation reactions | | |
| \(1.92 \times 10^{-11} \cdot \exp(450/T) \cdot 0.353\) | | \(ME_2BU2ENE + OH = ME_2BU2OLO2\) |
| \(1.92 \times 10^{-11} \cdot \exp(450/T) \cdot 0.647\) | | \(ME_2BU2ENE + OH = ME_2BUOLO2\) |
| \(RO_2\) and \(RO\) chemistry | | |
| \(1.15 \times 10^{-13} \cdot \exp(1300/T) \cdot 0.18\) | | \(CH_3COCH_2O_2 + HO_2 = CH_3COCH_2O + OH\) |
| \(1.15 \times 10^{-13} \cdot \exp(1300/T) \cdot 0.82\) | | \(CH_3COCH_2O_2 + HO_2 = HYPERACET\) |
| \(1.00 \times 10^{-13} \cdot \exp(1045/T) \cdot 0.2[RO_2]\) | | \(CH_3COCH_2O_2 = ACETOL\) |
| \(1.00 \times 10^{-13} \cdot \exp(1045/T) \cdot 0.6[RO_2]\) | | \(CH_3COCH_2O_2 = CH_3COCH_2O\) |
| \(1.00 \times 10^{-13} \cdot \exp(1045/T) \cdot 0.2[RO_2]\) | | \(CH_3COCH_2O_2 = MGLYOX\) |
| KDEC | | |
| \(4.40 \times 10^{-15} \cdot \exp(1910/T)\) | | \(CH_3CO_3 + HO_2 = CH_3CO_2H + O_3\) |
| \(1.50 \times 10^{-12} \cdot \exp(480/T)\) | | \(CH_3CO_3 + HO_2 = CH_3CO_3H\) |
| \(4.66 \times 10^{-12} \cdot \exp(235/T)\) | | \(CH_3CO_3 + HO_2 = CH_3O_2 + OH\) |
| \(2.00 \times 10^{-12} \cdot \exp(508/T) \cdot 0.2[RO_2]\) | | \(CH_3CO_3 = CH_3CO_2H\) |
| \(2.00 \times 10^{-12} \cdot \exp(508/T) \cdot 0.8[RO_2]\) | | \(CH_3CO_3 = CH_3O_2\) |
| \(KRO_2HO_2 \cdot 0.748\) | | \(ME_2BUOLO2 + HO_2 = M2BUOLOO\) |
| \(1.00 \times 10^{-13} \cdot \exp(731/T) \cdot 0.2[RO_2]\) | | \(ME_2BUOLO2 = C4ME3HO23\) |
| \(1.00 \times 10^{-13} \cdot \exp(731/T) \cdot 0.6[RO_2]\) | | \(ME_2BUOLO2 = ME2BUOLO\) |
| \(1.00 \times 10^{-13} \cdot \exp(731/T) \cdot 0.2[RO_2]\) | | \(ME2BUOLO2 = MIPKAOH\) |
| \(1.80 \times 10^{-13} \cdot \exp(-1424/T)\) | | \(ME2BUOLO = CH3COCH3 + CH3CHO + HO2\) |
| \(KRO_2HO_2 \cdot 0.748\) | | \(ME2BUOLO2 + HO_2 = ME2BUOLOOH\) |
| \(1.00 \times 10^{-13} \cdot \exp(221/T) \cdot 0.2[RO_2]\) | | \(ME2BUOLO2 = C4ME3HO23\) |
| \(1.00 \times 10^{-13} \cdot \exp(221/T) \cdot 0.8[RO_2]\) | | \(ME2BUOLO2 = ME2BUOLO\) |
| \(1.80 \times 10^{-13} \cdot \exp(-1734/T)\) | | \(ME2BUOLO = CH3COCH3 + CH3CHO + HO2\) |
| \(2,4,4\) Trimethyl-pent-2-ene | | |
| \(O_3\) initiation reactions | | |
| 1.42E-16*0.8 | $\text{TMEPEN2ENE + O}_3 = \text{TBUTCHO + CH}_3\text{CCH}_3\text{OOB}$ |
| 1.42E-16*0.1 | $\text{TMEPEN2ENE + O}_3 = \text{CH}_3\text{COCH}_3 + \text{ZTBUCHOOA}$ |
| 1.42E-16*0.1 | $\text{TMEPEN2ENE + O}_3 = \text{CH}_3\text{COCH}_3 + \text{ETBUCHOOA}$ |

**Excited CI chemistry**

| KDEC*0.6 | $\text{ZTBUCHOOA} = \text{ZTBUCHOO}$ |
| KDEC*0.212 | $\text{ZTBUCHOOA} = \text{IC}_4\text{H10}$ |
| KDEC*0.084 | $\text{ZTBUCHOOA} = \text{TBUTOL + CO}$ |
| KDEC*0.104 | $\text{ZTBUCHOOA} = \text{TC}_4\text{H}_9\text{O}_2 + \text{HO}_2$ |

| KDEC*0.6 | $\text{ETBUCHOOA} = \text{ZTBUCHOO}$ |
| KDEC*0.212 | $\text{ETBUCHOOA} = \text{IC}_4\text{H10}$ |
| KDEC*0.084 | $\text{ETBUCHOOA} = \text{TBUTOL + CO}$ |
| KDEC*0.104 | $\text{ETBUCHOOA} = \text{TC}_4\text{H}_9\text{O}_2 + \text{HO}_2$ |

| KDEC*0.6 | $\text{CH}_3\text{CCH}_3\text{OOB} = \text{CH}_3\text{CCH}_3\text{OO}$ |
| KDEC*0.4 | $\text{CH}_3\text{CCH}_3\text{OOB} = \text{CH}_3\text{COCH}_2\text{O}_2 + \text{OH}$ |

**Stabilized sCI chemistry**

| $2.58\text{E}6*\text{T}^{3.32}*\text{EXP}(-9710/\text{T})$ | $\text{ZTBUCHOO} = \text{TBUTCO}_2\text{H}$ |
| $2.40\text{E}-19*\text{H}_2\text{O}*0.73$ | $\text{ZTBUCHOO} = \text{TBUCHOOHOOH}$ |
| $2.40\text{E}-19*\text{H}_2\text{O}*0.06$ | $\text{ZTBUCHOO} = \text{TBUTCHO + H}_2\text{O}_2$ |
| $2.40\text{E}-19*\text{H}_2\text{O}*0.21$ | $\text{ZTBUCHOO} = \text{TBUTCO}_2\text{H}$ |
| $2.84\text{E}-15*\text{H}_2\text{OD}*0.40$ | $\text{ZTBUCHOO} = \text{TBUCHOOHOOH}$ |
| $2.84\text{E}-15*\text{H}_2\text{OD}*0.06$ | $\text{ZTBUCHOO} = \text{TBUTCHO + H}_2\text{O}_2$ |
| $2.84\text{E}-15*\text{H}_2\text{OD}*0.54$ | $\text{ZTBUCHOO} = \text{TBUTCO}_2\text{H}$ |

| $1.70\text{E}-10$ | $\text{ZTBUCHOO + CH}_3\text{CO}_2\text{H} = \text{HPNPACET}$ |
| $1.70\text{E}-12$ | $\text{ZTBUCHOO + CH}_3\text{CHO} = \text{NPC}_5\text{SOZC}_2$ |
| $1.70\text{E}-10$ | $\text{ZTBUCHOO + TBUTCO}_2\text{H} = \text{HPNPPIV}$ |
| $1.70\text{E}-12$ | $\text{ZTBUCHOO + TBUTCHO} = \text{NPSOZNP}$ |
| $3.40\text{E}-13$ | $\text{ZTBUCHOO + CH}_3\text{COCH}_3 = \text{NPSOZIC}_3$ |

| $8.51\text{E}9*\text{T}^{1.15}*\text{EXP}(-7357/\text{T})$ | $\text{ETBUCHOO} = \text{TBUTCO}_2\text{H}$ |
| $4.50\text{E}-14*\text{H}_2\text{O}*0.73$ | $\text{ETBUCHOO} = \text{TBUCHOOHOOH}$ |
| $4.50\text{E}-14*\text{H}_2\text{O}*0.06$ | $\text{ETBUCHOO} = \text{TBUTCHO + H}_2\text{O}_2$ |
| $4.50\text{E}-14*\text{H}_2\text{O}*0.21$ | $\text{ETBUCHOO} = \text{TBUTCO}_2\text{H}$ |
| $4.74\text{E}-11*\text{H}_2\text{OD}*0.40$ | $\text{ETBUCHOO} = \text{TBUCHOOHOOH}$ |
| $4.74\text{E}-11*\text{H}_2\text{OD}*0.06$ | $\text{ETBUCHOO} = \text{TBUTCHO + H}_2\text{O}_2$ |
| $4.74\text{E}-11*\text{H}_2\text{OD}*0.54$ | $\text{ETBUCHOO} = \text{TBUTCO}_2\text{H}$ |
| Equation                                      | Reaction Description                  |
|-----------------------------------------------|---------------------------------------|
| $2.50 \times 10^{-10}$                       | $\text{ETBUCHOO} + \text{CH}_3\text{CO}_2\text{H} = \text{HPNPACET}$ |
| $1.70 \times 10^{-12}$                       | $\text{ETBUCHOO} + \text{CH}_3\text{CHO} = \text{NPC5SOZC2}$ |
| $2.50 \times 10^{-10}$                       | $\text{ETBUCHOO} + \text{TBUTC}O_2\text{H} = \text{HPNPPIV}$ |
| $1.70 \times 10^{-12}$                       | $\text{ETBUCHOO} + \text{TBUTC}HO = \text{NPSOZNP}$ |
| $3.40 \times 10^{-13}$                       | $\text{ETBUCHOO} + \text{CH}_3\text{COCH}_3 = \text{NPSOZIC3}$ |
| $3.10 \times 10^{-10}$                       | $\text{CH}_3\text{CCH}_3\text{OO} + \text{TBUTC}O_2\text{H} = \text{HP2PRPIV}$ |
| $1.70 \times 10^{-12}$                       | $\text{CH}_3\text{CCH}_3\text{OO} + \text{TBUTC}HO = \text{NPSOZIC3}$ |
| $8.0 \times 10^{-11} \times 0.338$           | $\text{TMEPEN2ENE} + \text{OH} = \text{HOC8AO2}$ |
| $8.0 \times 10^{-11} \times 0.662$           | $\text{TMEPEN2ENE} + \text{OH} = \text{HOC8BO2}$ |
| $K\text{RO}_2\text{HO}_2 \times 0.601$       | $\text{TC4H9O2} + \text{HO}_2 = \text{TC4H9OOH}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(-662/T) \times 0.2\times[\text{RO}_2]$ | $\text{TC4H9O2} = \text{TBUTOL}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(-662/T) \times 0.8\times[\text{RO}_2]$ | $\text{TC4H9O2} = \text{TC4H9O}$ |
| $6.00 \times 14 \times \text{EXP}(-8153/T)$  | $\text{TC4H9O} = \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{O}_2$ |
| $K\text{RO}_2\text{HO}_2 \times 0.874$       | $\text{HOC8AO2} + \text{HO}_2 = \text{HOC8AOOH}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(783/T) \times 0.2\times[\text{RO}_2]$ | $\text{HOC8AO2} = \text{HOC8ACO}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(783/T) \times 0.6\times[\text{RO}_2]$ | $\text{HOC8AO2} = \text{HOC8AO}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(783/T) \times 0.2\times[\text{RO}_2]$ | $\text{HOC8AO2} = \text{HOC8AOH}$ |
| $1.80 \times 13 \times \text{EXP}(-4076/T)$  | $\text{HOC8AO} = \text{CH}_3\text{COCH}_3 + \text{TBUTC}HO + \text{HO}_2$ |
| $K\text{RO}_2\text{HO}_2 \times 0.874$       | $\text{HOC8BO2} + \text{HO}_2 = \text{HOC8BOOH}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(221/T) \times 0.2\times[\text{RO}_2]$ | $\text{HOC8BO2} = \text{HOC8AOH}$ |
| $1.00 \times 10^{-13} \times \text{EXP}(221/T) \times 0.8\times[\text{RO}_2]$ | $\text{HOC8BO2} = \text{HOC8BO}$ |
| $1.80 \times 13 \times \text{EXP}(-1734/T)$  | $\text{HOC8BO} = \text{CH}_3\text{COCH}_3 + \text{TBUTC}HO + \text{HO}_2$ |
| $2.80 \times 15 \times \text{EXP}(-1063/T) \times 0.62$ | $\text{CHEXENE} + \text{O}_3 = \text{ZC6COCHOOA}$ |
| $2.80 \times 15 \times \text{EXP}(-1063/T) \times 0.38$ | $\text{CHEXENE} + \text{O}_3 = \text{EC6COCHOOA}$ |
| $K\text{DEC} \times 0.030$                   | $\text{ZC6COCHOOA} = \text{ZC6COCHO}$ |
| $K\text{DEC} \times 0.970$                   | $\text{ZC6COCHOOA} = \text{ADIP2O2} + \text{OH}$ |
| $K\text{DEC} \times 0.030$                   | $\text{EC6COCHOOA} = \text{EC6COCHO}$ |
| $K\text{DEC} \times 0.314$                   | $\text{EC6COCHOOA} = \text{ADIPAL} + \text{O}$ |
| $K\text{DEC} \times 0.621$                   | $\text{EC6COCHOOA} = \text{C4H9CHO}$ |
| KDEC*0.035 | EC6COCHOOA = HCOC4CO2H |
|------------|------------------------|

**Stabilized sCI chemistry**

| KDEC | ZC6COCHOO = CHEXSOZ |
| KDEC | EC6COCHOO = CHEXSOZ |

**OH initiation reaction**

6.77E-11  
CHEXENE + OH = HOCHEXO2

**RO2 and RO chemistry**

| KRO2HO2*0.800 | HOCHEXO2 + HO2 = HOCHEXOOH |
|----------------|-----------------------------|
| 1.00E-13*EXP(760/T)*0.2*[RO2] | HOCHEXO2 = HOCHEXCO |
| 1.00E-13*EXP(760/T)*0.6*[RO2] | HOCHEXO2 = HOCHEXO |
| 1.00E-13*EXP(760/T)*0.2*[RO2] | HOCHEXO2 = HOCHEXOH |

| KDEC | HOCHEXO = ADIPAL + HO2 |
|----------------|---------------------|
| 2.91E-30*T12.9*EXP(-2167/T) | ADIP2O2 = CO6HP5CO3 |
| 1.08E-66*T25.23*EXP(1616/T) | ADIP2O2 = GLUTAL + CO + OH |
| 5.64E-20*T8.46*EXP(945/T) | CO6HP5CO3 = C6HOM1O2 |
| 5.64E-20*T8.46*EXP(-586/T) | C6HOM1O2 = CO6HP5CO3 |
| 2.01E-52*T15.91*EXP(1765/T) | CO6HP5CO3 = CO65CO3H + OH |
| 1.08E-66*T25.23*EXP(1616/T) | C6HOM1O2 = HCOC3CO3H + CO + OH |

| KRO2HO2*0.841*0.82 | ADIP2O2 + HO2 = ADIP2OOH |
|---------------------|---------------------------|
| 1.00E-13*EXP(878/T)*0.2*[RO2] | ADIP2O2 = ADIP2CO |
| 1.00E-13*EXP(878/T)*0.6*[RO2] | ADIP2O2 = ADIP2O |
| 1.00E-13*EXP(878/T)*0.2*[RO2] | ADIP2O2 = ADIP2OH |

| KDEC | ADIP2O = GLUTAL + CO + HO2 |
|----------------|------------------|
| 3.00E-12*EXP(480/T)*0.900 | CO6HP5CO3 + HO2 = CO6HP5CO3H |
| 8.83E-15*EXP(1910/T)*0.900 | CO6HP5CO3 + HO2 = CO6HP5CO2H + O3 |
| 9.35E-12*EXP(235/T)*0.900 | CO6HP5CO3 + HO2 = CO5HP4O2 + OH |
| 2.00E-12*EXP(508/T)*0.2*[RO2] | CO6HP5CO3 = CO6HP5CO2H |
| 2.00E-12*EXP(508/T)*0.8*[RO2] | CO6HP5CO3 = CO5HP4O2 |

| KRO2HO2*0.900*0.82 | C6HOM1O2 + HO2 = CO6HP5CO3H |
|---------------------|-----------------------------|
| 1.00E-13*EXP(891/T)*0.2*[RO2] | C6HOM1O2 = CO65CO3H |
| 1.00E-13*EXP(891/T)*0.6*[RO2] | C6HOM1O2 = C6HOM1O |
| 1.00E-13*EXP(891/T)*0.2*[RO2] | C6HOM1O2 = C6HOM1OH |
### Inorganic reactions

| Equation                                                                 | Rate Constant |
|--------------------------------------------------------------------------|---------------|
| O = O3                                                                    | 6.0E-34*[M] *(T/300)^2.6*[O₂] | O + O3 = 8.0E-12*EXP(-2060/T) | OH + O3 = 2.03E-16*(T/300)^4.57*EXP(693/T) | HO2 + O3 = 2.20E-13*EXP(600/T)*F_{H₂O} | HO2 + HO2 = 1.90E-33*[M]*EXP(980/T)*F_{H₂O} |
| HO₂ + O3 = HO₂                                                           |               |
| HO₂ + HO₂ = H₂O                                                          |               |

### Comments

*a* Reaction mechanism is designed for application to single alkene systems, but complete listing must be used for common chemistry to be represented;

*b* Units are cm³ molecule⁻¹ s⁻¹ for bimolecular reactions or s⁻¹ for unimolecular (or pseudo-unimolecular) reactions;

*c* KDEC is a generic parameter applied to selected very rapid reactions for convenience, and was assigned a value of 1.0E+06 s⁻¹ in these calculations;

*d* KMT16 is the rate coefficient for a pressure-dependent reaction in the fall-off regime, with $k_0 = 8.0E-27*[M] *(T/300)^3.5$ cm³ molecule⁻¹ s⁻¹, $k_\infty = 3.0E-11 *(T/300)^4$ cm³ molecule⁻¹ s⁻¹, and $F_z = 0.5$;

*e* KRO2HO2 = 2.80E-13*EXP(1300/T);

*f* [RO₂] represents the concentration sum of all peroxy radicals in the system;

*g* $F_{H₂O} = 1 + (1.40E-21 *EXP(2200/T)*[H₂O])$. 

---

| Parameter | Rate Constant |
|-----------|---------------|
| KDEC      | C6HOM1O = HOC3C03H + CO + HO2 |
|           | CO5HP4O2 = CO1HP5O2 |
|           | CO1HP5O2 = CO5HP4O2 |
| 3.48E-25*10.16*EXP(1327/T) | CO5HP4O2 = HP4CHO + CO + OH |
| 9.14E-15*7.6*EXP(-423/T) | CO5HP4O2 = HP5GLYOX + OH |
| 2.91E-30*T*12.9*EXP(-1458/T) | CO1HP5O2 = HP4CHO + CO + OH |
| 1.07E-66*T*25.23*EXP(1616/T) | CO1HP5O2 = HP4CHO + CO + OH |
| 3.48E-25*7.6*EXP(-25*T) | CO5HP4O2 = CO1HP5O2 |
| 9.14E-15*7.6*EXP(-15*T) | CO5HP4O2 = CO1HP5O2 |
| 2.91E-30*T*12.9*EXP(-30*T) | CO5HP4O2 = CO1HP5O2 |
| 1.07E-66*T*25.23*EXP(1616/T) | CO1HP5O2 = CO5HP4O2 |
| 3.48E-25*7.6*EXP(-25*T) | CO5HP4O2 = CO1HP5O2 |
| 9.14E-15*7.6*EXP(-15*T) | CO5HP4O2 = CO1HP5O2 |
| 2.91E-30*T*12.9*EXP(-30*T) | CO5HP4O2 = CO1HP5O2 |
| 1.07E-66*T*25.23*EXP(1616/T) | CO1HP5O2 = CO5HP4O2 |
| 3.48E-25*7.6*EXP(-25*T) | CO5HP4O2 = CO1HP5O2 |
| 9.14E-15*7.6*EXP(-15*T) | CO5HP4O2 = CO1HP5O2 |
| 2.91E-30*T*12.9*EXP(-30*T) | CO5HP4O2 = CO1HP5O2 |
| 1.07E-66*T*25.23*EXP(1616/T) | CO1HP5O2 = CO5HP4O2 |
| 3.48E-25*7.6*EXP(-25*T) | CO5HP4O2 = CO1HP5O2 |
| 9.14E-15*7.6*EXP(-15*T) | CO5HP4O2 = CO1HP5O2 |
| 2.91E-30*T*12.9*EXP(-30*T) | CO5HP4O2 = CO1HP5O2 |
| 1.07E-66*T*25.23*EXP(1616/T) | CO1HP5O2 = CO5HP4O2 |
| 3.48E-25*7.6*EXP(-25*T) | CO5HP4O2 = CO1HP5O2 |
| 9.14E-15*7.6*EXP(-15*T) | CO5HP4O2 = CO1HP5O2 |
| 2.91E-30*T*12.9*EXP(-30*T) | CO5HP4O2 = CO1HP5O2 |
| 1.07E-66*T*25.23*EXP(1616/T) | CO1HP5O2 = CO5HP4O2 |
Table S5: Identities of the organic species in the updated chemical schemes listed in Table S4.

| Species       | SMILES        | Species         | SMILES         |
|---------------|---------------|-----------------|----------------|
| C3H6          | CC=C          | C656OH          | CCCCC(O)CO     |
| CH2OOA        | C=[O+][O-]²  | C6OH5O          | CCCCC([O])CO   |
| CH2OO         | C=[O+][O-]    | HO5C6O2         | CCCCC(O)CO[O]  |
| ZCH3CHOOA     | [O-][O+]=C/C  | HO5C6OOH        | CCCCC(O)COO    |
| ZCH3CHOO      | [O-][O+]=C/C  | HO5C5CHO        | CCCCC(O)C=O    |
| ECH3CHOOA     | [O-][O+]=C/C  | HO5C6O          | CCCCC(O)[C]O   |
| ECH3CHOO      | [O-][O+]=C/C  | HO12C65O2       | CC(O(O))CC(O)CO|
| HCHO          | C=O           | HO12C65O0H      | CC(OO)CCC(O)CO|
| CH3CHO        | CC=O          | HO12C65CO       | CC(CCC(O)CO)=O|
| CH4           | C             | HO12C65O0       | CC(O)CC(O)CO   |
| CH3OH         | CO            | HO12C65O        | CC([O])CCC(O)CO|
| CH2CO         | C=C=O         | HO15C62CO       | CC(O)(CC)CO=O  |
| HOCH2OOH      | OCOO          | HO12C64O2       | CCC(O(O))CC(O)CO|
| HCOOH         | O=CO          | HO12C640O0H     | CCC(O)(O)CC(O)CO|
| HPMEFORM      | O=COCOO       | HO12C64CO       | CCC(C(C)CO)O=O |
| HPMEACET      | O=C(C)OCOO    | HO124C6         | CCC(O)CC(O)CO  |
| CS0ZC         | C10OCO1       | HO12C64O        | CCC([O])(CC)O|CO|
| C2SOZC        | CC10OCO1      | HO35C5CHO       | CCC(O)(CC)OC=O |
| CH3CHOHOOH    | CC(OO)O       | C BUT2ENE       | C=C=O          |
| CH3CO2H       | O=C(O)C       | ZCH3CHOOB       | [O-][O+]=C/C ² |
| HP1ETFORM     | O=COC(C)OO    | ECH3CHOOB       | [O-][O+]=C/C ² |
| HP1ETACET     | O=C(C)OC(C)O  | BUT2OLO2        | [O]OC(C)C(O)O  |
| C2SOZC2       | CC10OC(C)O1   | BUT2OLOO        | OOC(C)C(O)O    |
| HCOCH2O2      | O=CCO[O]      | BUT2OLO         | CC=O(C)COO    |
| HCOCH2OOH     | O=CCOO        | BUT2OLOH        | CC(O)C(C)O    |
| GLYOX         | O=CC=O        | BUT2OLAO        | CC(O)(O)C(O)  |
| HOCH2CHO      | OCC=O         | TBUT2ENE        | C=C=O          |
| HCOCH2O       | [O]CC=O       | ECH3CHOOC       | [O-][O+]=C/C ² |
| CH3O2         | CO[O]         | TPENT2ENE       | CC=C=O         |
| CH3OOH        | COO           | ZCH2H5CHOOB     | [O-][O+]=C/CC ²|
| CH3O          | C[O]          | ECH2H5CHOOB     | [O-][O+]=C/CC ²|
| HYPPOPO2      | CC(CC)O[O]    | ZCH3CHOOC       | [O-][O+]=C/CC ²|
| HYPPOPO2H     | CC(CC)OO      | ECH3CHOOD       | [O-][O+]=C/CC ²|
| ACETOL       | CC(CO)=O  | HP1ETPROP | CCC(O(C)(C)O)=O  |
|-------------|-----------|-----------|------------------|
| PROPGLY     | CC(CO)O   | C3SOZC2   | CC1OOC(CC)O1     |
| HYPROPO     | CC(CO)[O] | HP1PRACET | CC(O(CC)OO)=O    |
| IPROPOLO2   | CC(CO)[O]O| PE2ENEAO2  | CCC(O)(O)(C)C    |
| IPROPOLO2H  | CC(CO)O   | C52OH3OH  | CCC(O)(O)(C)C    |
| CH3CHOHCHO  | CC(O)=O   | C523OH    | CCC(C)(O)(C)C    |
| IPROPOLO    | CC(O)=O   | DIEKAOH   | CCC(C)(O)(C)C    |
| BUT1ENE     | CCC=C     | PE2ENEAO  | CCC([O]C(O)C)C   |
| CH2OOB      | C=[O+][O-] | PE2ENEBO2 | CCC(O)(O)(O)C    |
| ZC2H5CHOOA  | [O-][O+]=C/CC | C53OH2OH | CCC(O)(O)(O)C    |
| ZC2H5CHO0   | [O-][O+]=C/CC | MPRKAOH | CCC(O)(C)=O      |
| EC2H5CHOOA  | [O-][O+]=C/CC | PE2ENEBO | CCC(O)(C)(O)C    |
| EC2H5CHO0   | [O-][O+]=C/CC | THEX2ENE | C=C=C/ CCC       |
| C2H6        | CC        | ZCH3CHOOD | [O-][O+]=C/CC  c |
| C2H5OH      | CO        | ECH3CHOOE | [O-][O+]=C/CC  c |
| CH3CHCO     | CC=C=O    | ZC3H7CHO0B | CCC=C=[O+][O-] c |
| PROPACID    | CCC(O)=O  | EC3H7CHO0B | CCC=C=[O+][O-] c |
| C2H5CHO     | CCC=O     | HP1ETBUTR | O=C(O)(CC)OCCC  |
| HPMEPROP    | O=C(CC)OCOO | C4SOZC2 | CC1OOC(CC)O1     |
| C3SOZC      | CCC1OOCO1 | HP1BUACET | CC(OCC)(CC)O)=O  |
| ETCCHOHOOH  | OC(O)OC  | C64OH5O   | CCC(O)(O)(O)CCC  |
| HP1PRFORM   | O=COC(CC)OO | C64OH5OH | CC(O)(O)(O)CCC  |
| HP1PRPROP   | O=C(CC)OC(CC)O | C645OH | CC(O)(O)(O)CCC  |
| C3SOZC3     | CCC1OOC(CC)O1 | CO2H3O3C6 | CC(O)(O)(O)CCC  |
| C2H5O2      | CCC(O)   | C64OH5O  | CC(O)(O)(O)CCC  |
| C2H5OOH     | CCOO     | C65OH4O  | CC(O)(O)(O)CCC  |
| C2H5O       | CCC(O) | C65OH40OH | CC(O)(O)(O)CCC  |
| PROPALO2    | CC(O)(O)= | HEX3ONCOH | CC(O)(O)(O)CCC  |
| PROPALO0    | CC(O)(O)= | C65OH4O  | CC(O)(O)(O)CCC  |
| CH3CHOHCHO  | CC(O)=O  | ME2BUT2ENE | CC(C)=CC       |
| MGLYOX      | CC(C)=O  | CH3CCH30OA | CC(C)[O+][O-]  c|
| PROPALO     | CC([O]C)=O | CH3CCH300 | CC(C)[O+][O-]  c|
| H03C402     | OC(CO)(O)CC | ZCH3CHO0E | [O-][O+]=C/CC  c|
| H03C40OH    | OC(CO)(O)CC | ECH3CHOOF | [O-][O+]=C/CC  c|
| H03C3CHO    | OC(O)=OCC | CH3COCH3 | CC(C)=O         |
| NBUTOLA0H   | OC(CO)CC | H2IPROOH | CC(C)(O)(O)O    |
| Compound     | Formula   | Compound     | Formula   |
|--------------|-----------|--------------|-----------|
| HO3C4O       | OC(C(O)O)CC | HP2PRACET    | CC(C)(O)OC(C)=O |
| NIBUTOLAO2   | CCC(O(O))CO | IC3SOZC2     | CC10OC(C)(C)O1 |
| NIBUTOLAOH   | CCC(OO)CO  | IC3SOZIC3    | CC1(C)OOC(C)(C)O1 |
| MEKCOH       | O=C(CO)CC   | CH3COCH2O2   | CC(CO)(O)=O |
| NIBUTOLOAO   | [O]C(CO)CC  | HYPERACET    | CC(COO)=O |
| HO34C402     | OCC(COO)[O] | CH3COH2O     | CC(C)[O]=O |
| HO34C400H    | OCC(O)CCCO | CH3CO3       | CC(O)[O]=O |
| HO34C3CHO    | OCC(O)CCCO | CH3CO3H      | CC(OO)=O |
| HO13C40H     | OCC(O)CCO  | ME2B2OLO2    | CC(C)(O)C(O)[O]C |
| HO13C3CHO    | O=CC(O)CCO  | M2B2OLOOH    | CC(C)(O)C(O)C |
| HO34C40      | OCC(O)CCCO | C4ME3H023    | CC(C)(O)C(O)C |
| PENT1ENE     | CCC=C     | MPKAOH       | CC(C)(O)C(C)=O |
| CH20OC       | C=[O+][O-]  | ME2B2OLO     | CC(C)(O)C(O)C |
| ZC3H7CHO0A   | CCC=C=[O+]/[O-]  | ME2B2OLO2   | CC(C)(O)[O]C(O)C |
| ZC3H7CHO0    | CCC=C=[O+]/[O-]  | ME2B2OLOOH  | CC(C)(O)O(O)C |
| EC3H7CHO0A   | CCC=C=[O+]/[O-]  | ME2B2OLO    | CC(C)(O)C(O)C |
| EC3H7CHO0    | CCC=C=[O+]/[O-]  | TMEPEN2ENE  | CC(C)=CC(C)(C)C |
| C3H7CHO      | CCC=C=O    | CH3CH30OB    | CC(C)=[O+]/[O-]  |
| C3H8         | CCC       | ZTBUCCHOOA   | CC(C)(C)=C=[O+]/[O-]  |
| NPROPOL      | CCCO      | ZTBUCCHO0    | CC(C)(C)=C=[O+]/[O-]  |
| C2H5CHCO     | CCC=C=O    | ETBUCCHOOA   | CC(C)(C)=C=[O+]/[O-]  |
| BUTACID      | CCC(O)=O   | ETBUCCHO0    | CC(C)(C)=C=[O+]/[O-]  |
| HPMEBUTR     | CCCC(OOC)=O | IC4H10      | CC(C)=C |
| C4SOZC       | CCC10OCCO1 | TBUTOL       | CC(C)=O |
| PRCHOHO0H    | CCC(O)O0   | TBUTCO2H     | CC(C)(C)(O)=O |
| HP1BUTFORM   | O=COC(CCC)OO | TBUCHOHO0H  | CC(C)(C)(O)=O |
| HP1BUTFCTR   | CCC(OCC(CCC)OO)=O | TBUTCHO   | CC(C)(C)=O |
| C4SOZC4      | CCC10OCC(CCC)O1 | HPNPACET   | CC(C)(C)(O)=O |
| NC3H702      | CCCO[O]    | NPC5SOZC2    | CC10OC(C)(C)=O |
| NC3H700H     | CCCOO      | HPNPP4IV     | CC(C)(C)(O)(C)=O |
| NC3H70       | CCC[O]     | NPSOZNP      | CC(C)(C)10OC(C)=O |
| BUTALA02     | CCC(C)=O[O] | NPSOZIC3     | CC1(C)(C)OOC(C)=O |
| BUTALA00H    | CCC(C)=O[O] | HP2PRP4IV    | CC(C)(C)(C)=O |
| EGLYOX       | CCC(C)=O   | TC4H902      | CC(C)(C)=O |
| BUTAL20      | CCC(C)=O[O] | TC4H900H     | CC(C)=O |
| PE1ENEAO2    | CCC(O)[O]CO | TC4H90      | CC(C)(O)=O |
| C51OH20OH | CCC(CO)OO | HOC8A02 | CC(C)(O)C(O)[O]C(C)(C)(C)C |
| C51OH2CO | CCC(=O)CO | HOC8AOOH | CC(C)(O)C(OO)C(C)(C)(C)C |
| HO12C5   | CCC(O)CO  | HOC8ACO  | CC(C)(O)C(C)(C)(C)C=O   |
| PE1ENEAO | CCC(O)CO  | HOC8AOH  | CC(C)(O)C(O)(C)(C)(C)C |
| PE1ENEBO2| CCC(O)CO[O]| HOC8AO   | CC(C)(O)C([O])C(C)(C)(C)C |
| C520H10OH| CCC(O)COO | HOC8BO2  | CC(C)(O)[O]C(O)(C)(C)(C)C |
| C40HCHO  | CCC(O)CO  | HOC8BOOH | CC(C)(O)(O)(C)(C)(C)(C)C |
| PE1ENEBO | CCC(O)[O] | HOC8BO   | CC(C)([O])C(O)(C)(C)(C)C |
| HO12C5402| OCC(O)CC(C)O[O]| CHEXENE | C1CCCC=C1 |
| HO12C540OH| OCC(O)CC(C)O | ZC6COCHO0A | O=CCCCC=C(O)[-][O+] |
| C51OH    | OCC(O)CC(C)=O | ZC6COCHO0 | O=CCCCC=C(O)[-][O+] |
| HO124C5  | OCC(O)CC(C)=O | EC6COCHO0A | O=CCCCC=C(O)[-][O+] |
| HO24C4CHO| O=CC(O)CC(C)O | EC6COCHO0 | O=CCCCC=C(O)[-][O+] |
| HO12C54O | OCC(O)CC(C)[O] | HOC4CO2H | O=CCCCC(O)=O |
| HEX1ENE  | CCC(C)=C | CHEXSOZ | C12CCCCC(OO2)O1 |
| ZC4H9CHO0A| CCC(C)=O[O][O]- | HOCHEX02 | O1C(O)(O)(O)CCC1 |
| ZC4H9CHO0| CCC(C)=O[O][O]- | HOCHEXO0H | O1C(O)(O)(O)CCC1 |
| EC4H9CHO0A| CCC(C)=O[O][O]- | HOCHEXCO | O1C(O)(CCC1)=0 |
| EC4H9CHO0| CCC(C)=O[O][O]- | HOCHEXOH | O1C(O)(CCC1)=0 |
| C4H9CHO  | CCC=O | HOCHEXO | O1C(O)(CCC1)=0 |
| NC4H10   | CCC | ADIPAL | O=CCCCC(O)=O |
| NBUTOL   | CCCCO | ADIP2O2 | O=CCCCC(O)(O)=C=O |
| C3H7CHCO | CCC(C)=O | ADIP2OOH | O=CCCCC(OO)(O)=C=O |
| PENTACID | CCC(C)=O | ADIP2CO | O=CCCCC(O)(O)=C=O |
| HPMEPENT | OOCOC(CCCC)=O | ADIP2OH | O=CCCCC(O)(O)=C=O |
| C5SOZC   | CCC(C)OOCO1 | ADIP2O | O=CCCCC(O)(O)=C=O |
| BUCHOHOOH| OOC(O)CCC | GLUTAL | O=CCCCC(O)=C=O |
| HP1PEFORM| OOC(CCCC)(O)=O | CO6HP5CO3 | O=C(O)(O)(CCC)(OO)=C=O |
| HP1PEPENT| OOC(CCCC)(O)(CCC)=O | CO6HP5CO3H | O=C(O)(O)(CCC)(C)=O |
| C5SOZC5  | CCC(C)OOCO1 | CO6HP5CO3H | O=C(O)(O)(CCC)(O)=C=O |
| NC4H9O2  | CCC(O)[O] | CO6HP5CO2H | O=C(O)(O)(CCC)(O)=C=O |
| NC4H9OH0H| CCCOO | C6HOM102 | O=C(O)(CCC)(O)(O)=C=O |
| NC4H9O   | CCC[O] | HOC3CO3H | O=C(O)(CCC)=C=O |
| HO1C402  | OCCCC(O)[O] | C6HOM10H | O=C(O)(CCC)(O)=C=O |
| HO1C40OH | OCCCCOO | C6HOM10 | O=C(O)(CCC)(O)=C=O |
| HOC3H6CHO| OCCC(O)=O | CO5HP4O2 | O=C(O)(CCC)(O)=C=O |
## Comments

*Organic species are listed. Simple inorganic species are represented as follows: Molecular hydrogen (H2), hydroxyl radical (OH), hydroperoxyl radical (HO2), hydrogen peroxide (H2O2), carbon monoxide (CO), ozone (O3) and atomic oxygen (O). Where required, the large excess concentrations of the reagents molecular oxygen, [O2], water, [H2O], water dimer, [(H2O)2], and bath gas, [M], appear as part of the rate coefficients in Table S4;*  

## References

Ammann, M., Cox, R. A., Crowley, J. N., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates, Atmos. Chem. Phys., 13, 8045-8228, 10.5194/acp-13-8045-2013, 2013.  
Ashmann, S. M., Tuazon, E. C., Arey, J., and Atkinson, R.: Products of the Gas-Phase Reaction of O3 with Cyclohexene, J. Phys. Chem. A, 107, 2247-2255, 10.1021/jp022122e, 2003.  
Bannan, T. J., Murray Booth, A., Le Breton, M., Bacak, A., Muller, J. B. A., Leather, K. E., Khan, M. A. H., Lee, J. D., Dunmore, R. E., Hopkins, J. R., Fleming, Z. E., Sheps, L., Taatjes, C. A., Shallcross, D. E. and Percival, C. J.: Seasonality of formic acid (HCOOH) in London during the ClearfLo campaign, J. Geophys. Res. Atmos., 122, 12,488-12,498 https://doi.org/10.1002/2017JD027064, 2017.  
Bailey, P. S.: The reactions of ozone with organic compounds, Chem. Rev., 58, 925–1010, 1958.  
Berasategui, M., Amedro, D., Vereecken, L., Lelieveld, J., and Crowley, J. N.: Reaction between CH3:C(O)OOH (peracetic acid) and OH in the gas phase: a combined experimental and theoretical study of the kinetics and mechanism, Atmos. Chem. Phys., 20, 13341–13355, https://doi.org/10.5194/acp-20-13341-2020, 2020.  
Calvert, J. G., Orlando, J. J., Stockwell, W. R., and Wallington, T. J.: The mechanisms of reactions influencing atmospheric ozone Oxford University Press, Oxford, UK, 2015.  
Caravan, R.L., Vansco, M.F. and Lester, M.I.: Open questions on the reactivity of Criegee intermediates, Commun. Chem., 4, 44, https://doi.org/10.1038/s42004-021-00483-5, 2021.  
Compernolle, S., Ceulemans, K., and Müller, J. F.: EVAPORATION: a new vapour pressure estimation method for organic molecules including non-additivity and intramolecular interactions, Atmos. Chem. Phys., 11, 9431-9450, 10.5194/acp-11-9431-2011, 2011.  
Cox, R. A., Ammann, M., Crowley, J. N., Herrmann, H., Jenkin, M. E., McNeill, V. F., Mellouki, A., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VII – Criegee intermediates, Atmos. Chem. Phys., 20, 13497-13519, 10.5194/acp-20-13497-2020, 2020.  
Crowley, J. N., Ammann, M., Cox, R. A., Hynes, R. G., Jenkin, M. E., Mellouki, A., Rossi, M. J., Troe, J., and Wallington, T. J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume V - Heterogeneous reactions on solid substrates, Atmos. Chem. Phys., 10, 9059-9223, 2010.
Dark, F. A., and Nash, T.: Comparative toxicity of various ozonized olefins to bacteria suspended in air, J. Hyg., 68, 245-252, 10.1017/s0022172400002710, 1970.

Deming, B. L., Pagonis, D., Liu, X., Day, D. A., Talukdar, R., Krechmer, J. E., de Gouw, J. A., Jimenez, J. L., and Ziemann, P. J.: Measurements of delays of gas-phase compounds in a wide variety of tubing materials due to gas–wall interactions, Atmos. Meas. Tech., 12, 3453-3461, 10.5194/amt-12-3453-2019, 2019.

Dollard, G. J. and Davies, T. J.: Observations of H2O2 and PAN in a rural atmosphere, Environ. Pollut., 75, 45-52, 1992.

Dollard, G. J., Dumitrescu, P., Telling, S., Dixon, J. and Derwent, R. G.: Observed trends in ambient concentrations of C2−C8 hydrocarbons in the United Kingdom over the period from 1993 to 2004, Atmos. Environ., 41(12), 2559-2569, https://doi.org/10.1016/j.atmosenv.2006.11.020, 2007.

Donahue, N. M., Clarke, J. S., Demerjian, K. L., and Anderson, J. G.: Free-Radical Kinetics at High Pressure: A Mathematical Analysis of the Flow Reactor, The Journal of Physical Chemistry, 100, 5821-5838, 10.1021/jp9525503, 1996.

Druett, H. A., and May, K. R.: Unstable Germicidal Pollutant in Rural Air, Nature, 220, 395-396, 10.1038/220395a0, 1968.

Donahue, N. M., Clarke, J. S., Demerjian, K. L., and Anderson, J. G.: Free-Radical Kinetics at High Pressure: A Mathematical Analysis of the Flow Reactor, The Journal of Physical Chemistry, 100, 5821-5838, 10.1021/jp9525503, 1996.

Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11: https://www.epa.gov/tsca-screening-tools/epi-suitetm-estimation-program-interface, 2021.

Foreman, E. S., Kapnas, K. M. and Murray, C.: Reactions between Criegee intermediates and the inorganic acids HCl and HNO3: kinetics and atmospheric implications, Angew. Chem. Int. Ed., 55, 10419-10422, https://doi.org/10.1002/anie.201604662, 2016.

Fleming, Z. L., Monks, P. S., Rickard, A. R., Bandy, B. J., Brough, N., Green, T. J., Reeves, C. E., and Penkett, S. A.: Seasonal dependence of peroxy radical concentrations at a Northern hemisphere marine boundary layer site during summer and winter: evidence for radical activity in winter, Atmos. Chem. Phys., 6, 5415–5433, https://doi.org/10.5194/acp-6-5415-2006, 2006.

Foreman, E. S., Kapnas, K. M. and Murray, C.: Reactions between Criegee intermediates and the inorganic acids HCl and HNO3: kinetics and atmospheric implications, Angew. Chem. Int. Ed., 55, 10419-10422, https://doi.org/10.1002/anie.201604662, 2016.

Lakey, P. S. J., Berkemeier, T., Krapf, M., Dommen, J., Steimer, S. S., Whalley, L. K., Ingham, T., Baeza-Romero, M. T., and Heard, D. E.: The effect of viscosity and diffusion on the HO2 uptake by sucrose and secondary organic aerosol particles, Atmos. Chem. Phys., 16, 13035-13047, 10.5194/acp-16-13035-2016, 2016.

Khan, M. A. H., Percival, C. J., Caravan, R. L., Taatjes, C. A., and Shallcross, D. E.: Criegee intermediates and their impacts on the troposphere, Environ. Sci.-Proc. Imp., 20, 437–453, 2018.

Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO2 Uptake Coefficients onto Single Component Organic Aerosols, Environ. Sci. Technol., 49, 4878-4885, 10.1021/acs.est.6b00948, 2015.

Lakey, P. S. J., Berkemeier, T., Krapf, M., Dommen, J., Steimer, S. S., Whalley, L. K., Ingham, T., Baeza-Romero, M. T., Pöschl, U., Shiraiwa, M., Ammann, M., and Heard, D. E.: The effect of viscosity and diffusion on the HO2 uptake by sucrose and secondary organic aerosol particles, Atmos. Chem. Phys., 16, 13035-13047, 10.5194/acp-16-13035-2016, 2016.

Khan, M. A. H., Percival, C. J., Caravan, R. L., Taatjes, C. A., and Shallcross, D. E.: Criegee intermediates and their impacts on the troposphere, Environ. Sci.-Proc. Imp., 20, 437–453, 2018.

Le Breton, M., Bacaak, A., Muller, J. B. A., Xiao, P., Shallcross, B. M. A., Batt, R., Cooke, M. C., Shallcross, D. E., Bauguette, S. J. -B. and Percival, C. J.: Simultaneous airborne nitric acid and formic acid measurements using a chemical ionization mass spectrometer around the UK: Analysis of primary and secondary production pathways, Atmos. Environ., 83, 166-175, https://doi.org/10.1016/j.atmosenv.2019.04.036, 2019.

Lakey, P. S. J., George, I. J., Whalley, L. K., Baeza-Romero, M. T., and Heard, D. E.: Measurements of the HO2 Uptake Coefficients onto Single Component Organic Aerosols, Environ. Sci. Technol., 49, 4878-4885, 10.1021/acs.est.6b00948, 2015.

Le Breton, M., Bacaak, A., Muller, J. B. A., Xiao, P., Shallcross, B. M. A., Batt, R., Cooke, M. C., Shallcross, D. E., Bauguette, S. J. -B. and Percival, C. J.: Simultaneous airborne nitric acid and formic acid measurements using a chemical ionization mass spectrometer around the UK: Analysis of primary and secondary production pathways, Atmos. Environ., 83, 166-175, https://doi.org/10.1016/j.atmosenv.2019.04.036, 2019.

Loew, D. A., and Nash, T.: Comparative toxicity of various ozonized olefins to bacteria suspended in air, J. Hyg., 68, 245-252, 10.1017/s0022172400002710, 1970.

Lightfoot, P. D., Cox, R. A., Crowley, J. N., Destriau, M., Hayman, G. D., Jenkin, M. E., Moortgat, G. K., and Zabel, F.: Organic peroxy radicals: kinetics, spectroscopy and tropospheric chemistry, Atmos. Environ., 26A, 1805–1964, 1992.

Logan J. A., Prather M. J., Wofsy S. C. and McElroy M. B.: Tropospheric Chemistry: A global perspective. J. Geophys. Res., 86, 7210–7254, 1981.

McCollom, G. R., Carter, W. P. L., Mellouki, A., Orlando, J. J., Picquet-Varrault, B., and Wallington, T. J.: Database for the kinetics of the gas-phase atmospheric reactions of organic compounds, Earth Syst. Sci. Data, 12, 1203-1216, 10.5194/essd-12-1203-2020, 2020.
Zahardis, J., and Petrucci, G. A.: The oleic acid-ozone heterogeneous reaction system: products, kinetics, secondary chemistry, and atmospheric implications of a model system - a review, Atmos. Chem. Phys., 7, 1237-1274, 2007.
Zhang, X., He, S. Z., Chen, Z. M., Zhao, Y., and Hua, W.: Methyl hydroperoxide (CH₃OOH) in urban, suburban and rural atmosphere: ambient concentration, budget, and contribution to the atmospheric oxidizing capacity, Atmos. Chem. Phys., 12, 8951–8962, https://doi.org/10.5194/acp-12-8951-2012, 2012.