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Atmospheric oxidation of α,β-unsaturated ketones: kinetics and mechanism of the OH radical reaction

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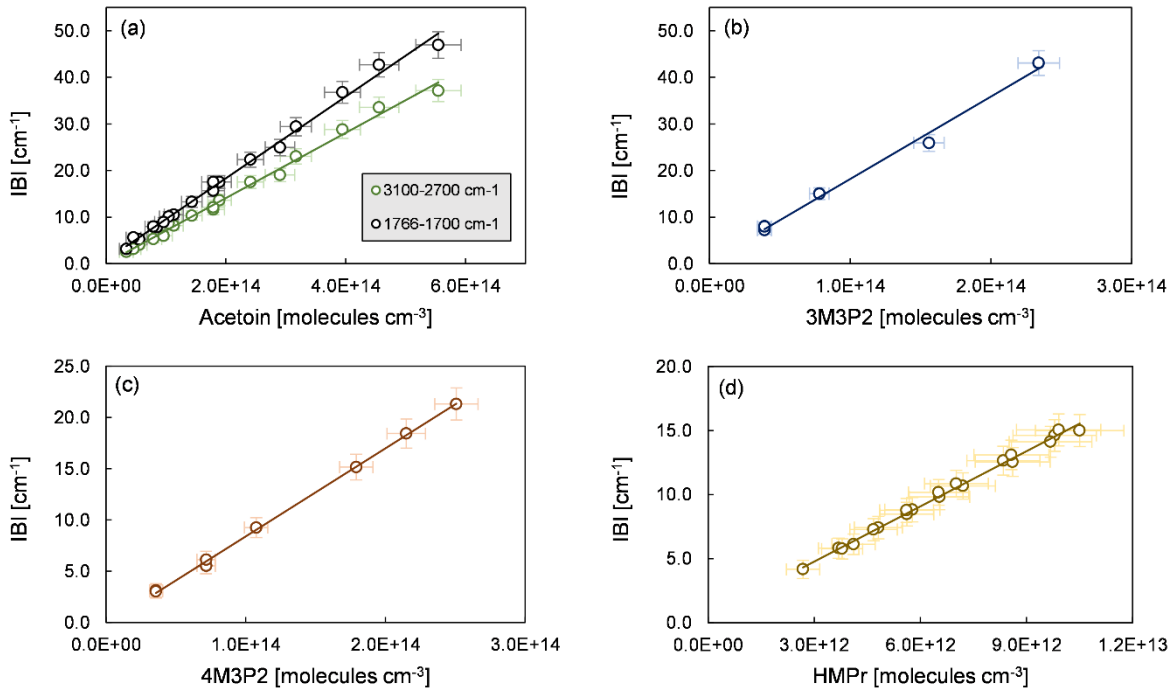

Figure S1. Calibration plots for (a) acetoin, (b) 3M3P2, (c) 4M3P2, and (d) HMPr. The calibrations were performed at an optical path length of 50.4 ± 0.2 m for acetoin, 3M3P2, and 4M3P2 and 484.7 ± 0.9 m for HMPr, respectively.

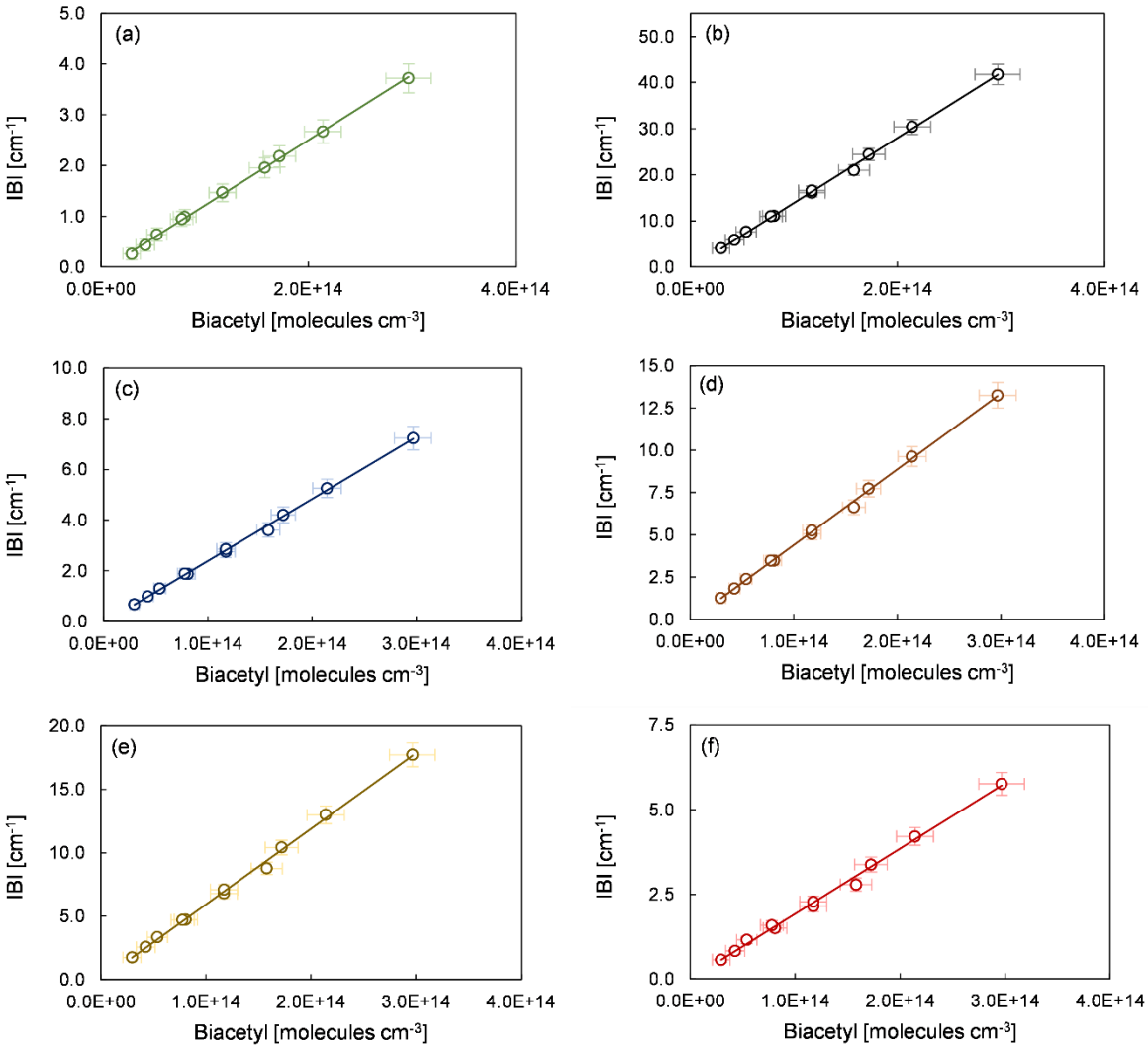

Figure S2. Calibration plots for biacetyl for absorption features in the range (a) 3053–2905 cm^{-1}, (b) 1769–1690 cm^{-1}, (c) 1492–1392 cm^{-1}, (d) 1392–1297 cm^{-1}, (e) 1154–1078 cm^{-1}, and (f) 994–870 cm^{-1}. All calibrations were performed at an optical path length of 50.4 ± 0.2 m.

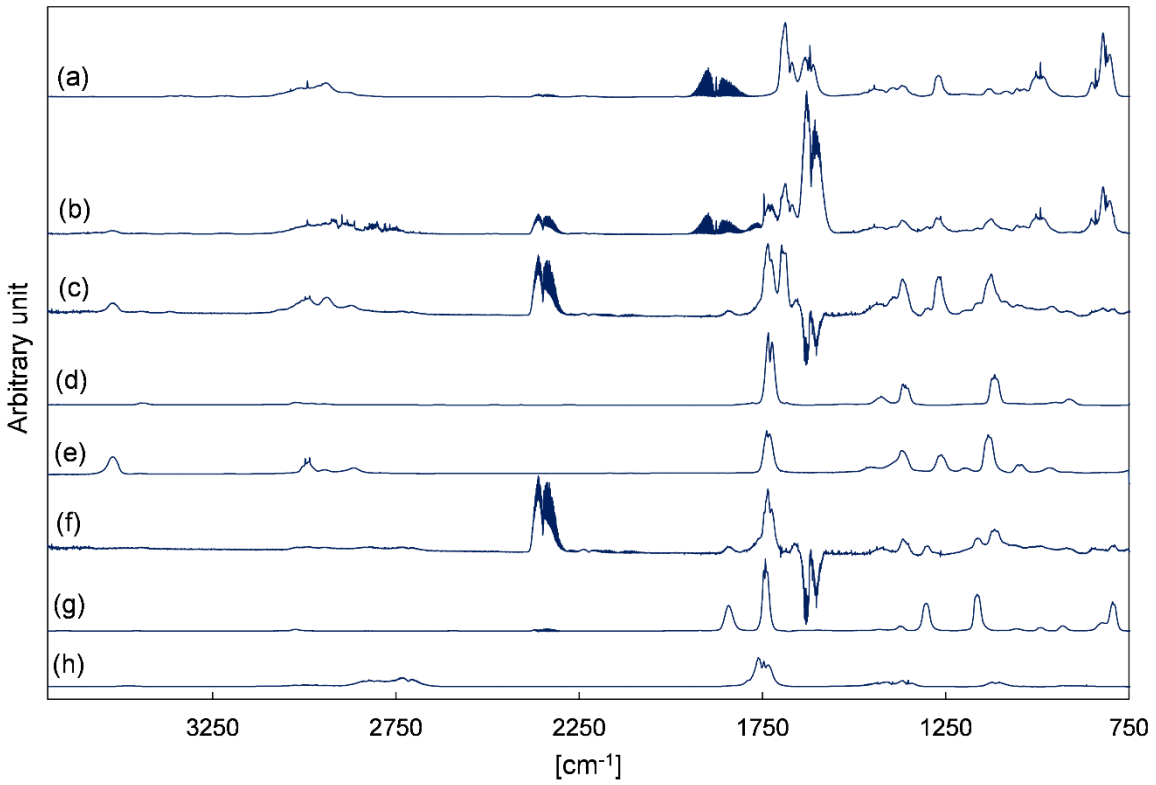

Figure S3. Exemplary FTIR spectra of a product study experiment of 3M3P2 + OH: (a) reaction mixture before irradiation, (b) reaction mixture at the end of the irradiation period, (c) residual spectrum after subtraction of methyl nitrite, methyl nitrate, HNO_3, HONO, NO, NO_2 and HCHO from (b), (d) reference spectrum of 2,3-butanedione (biacetyl), (e) reference spectrum of 3-hydroxy-2-butanone (acetoin), (f) residual spectrum after subtraction of 3M3P2 and acetoin from (c), (g) reference spectrum of peroxyacetyl nitrate (PAN), and (h) reference spectrum of acetaldehyde. The spectra are shifted and scaled individually for a better overview.

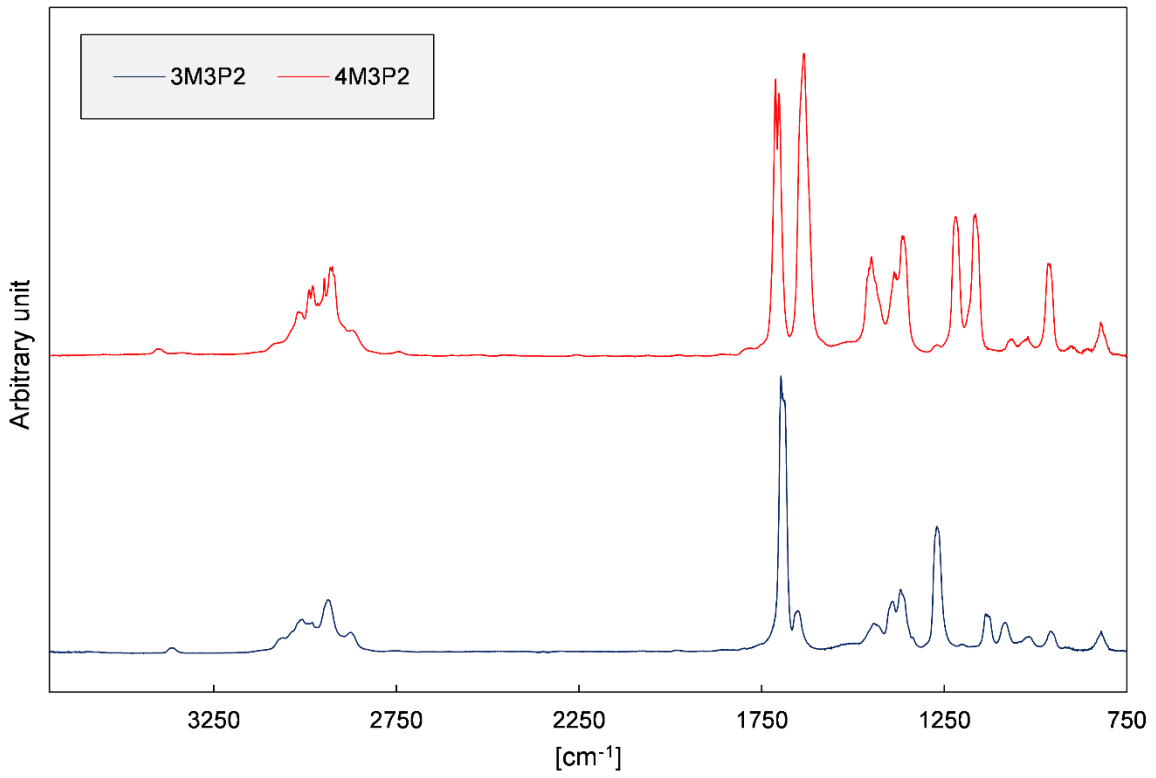

Figure S4. FTIR spectra of 3M3P2 and 4M3P2 in the gas-phase.

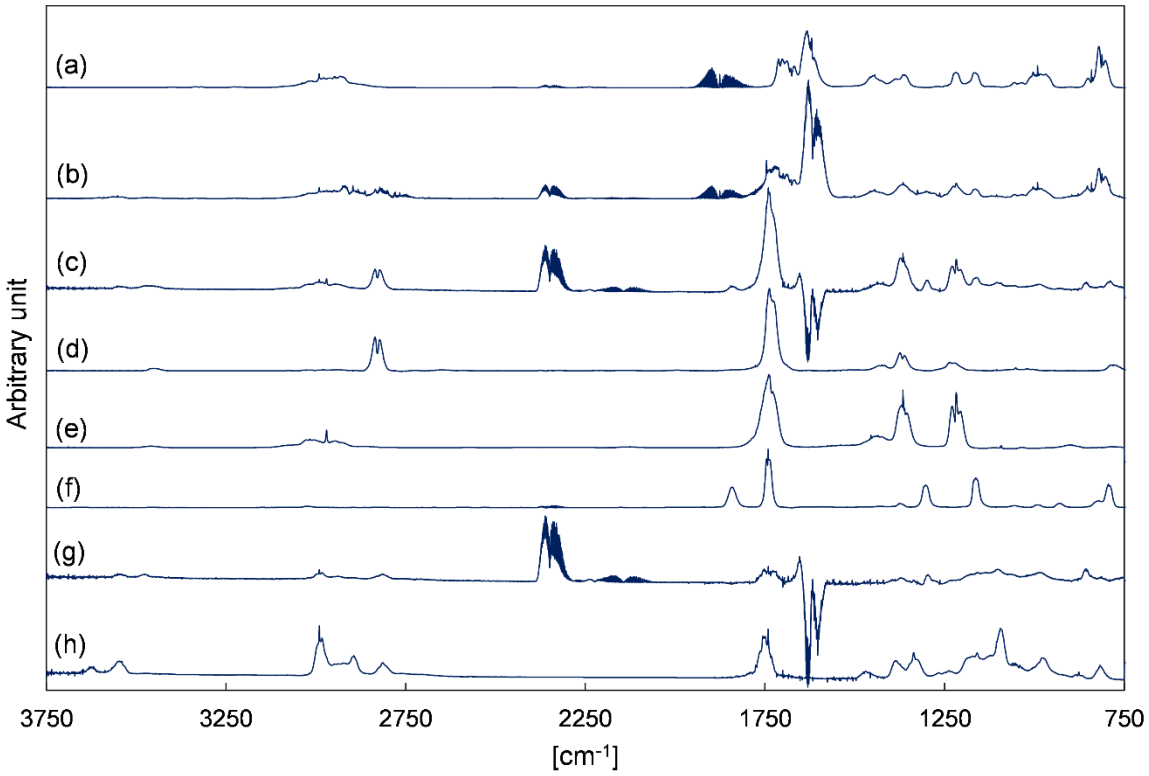

Figure S5. Exemplary FTIR spectra of a product study experiment of 4M3P2 + OH: (a) reaction mixture before irradiation, (b) reaction mixture at the end of the irradiation period, (c) residual spectrum after subtraction of 4M3P2, methyl nitrite, methyl nitrate, NO, NO_2 and HCHO from (b), (d) reference spectrum of methyl glyoxal, (e) reference spectrum of acetone, (f) reference spectrum of peroxyacetyl nitrate (PAN), (g) residual spectrum after subtracting methyl glyoxal, acetone and PAN from (c), and (h) reference spectrum of 2-hydroxy-2-methylpropanal generated in situ. The spectra are shifted and scaled individually for a better overview.

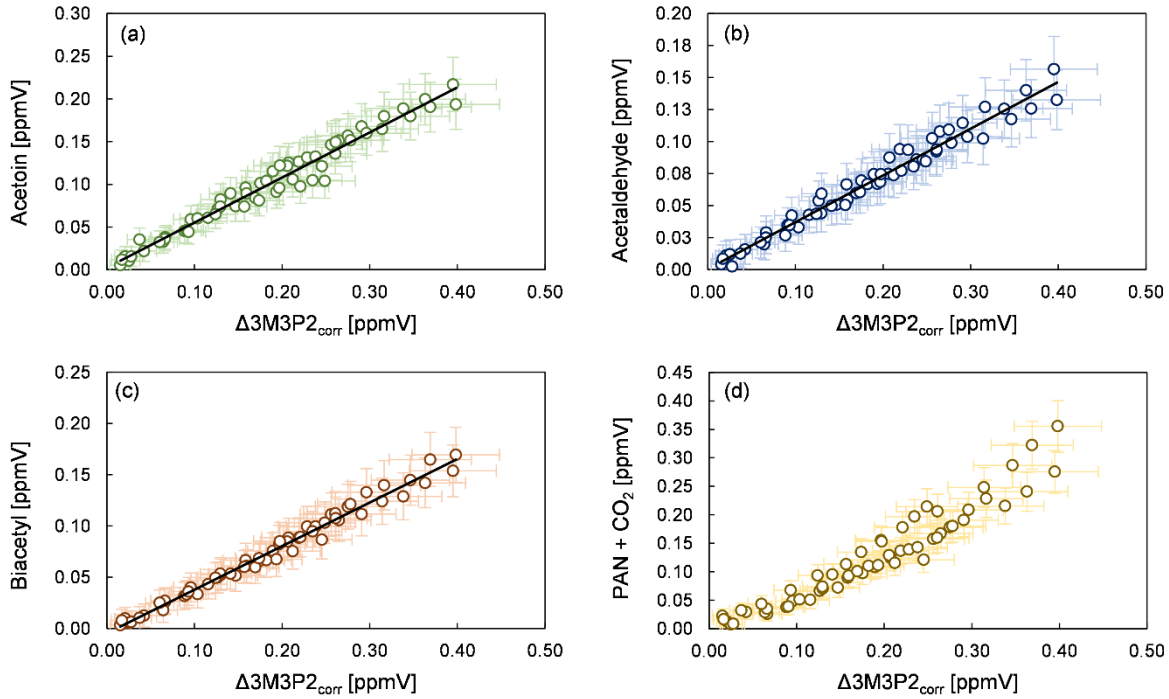

Figure S6. Yield plots of (a) acetoin, (b) acetaldehyde, (c) biacetyl, and (d) the sum of PAN and CO_2 in the 3M3P2 + OH reaction where the consumption of 3M3P2 is corrected for the wall loss. Mixing ratios of the 480 L chamber experiments are multiplied by a factor of 0.1 to fit within the scale of the 1080 L chamber experiments.

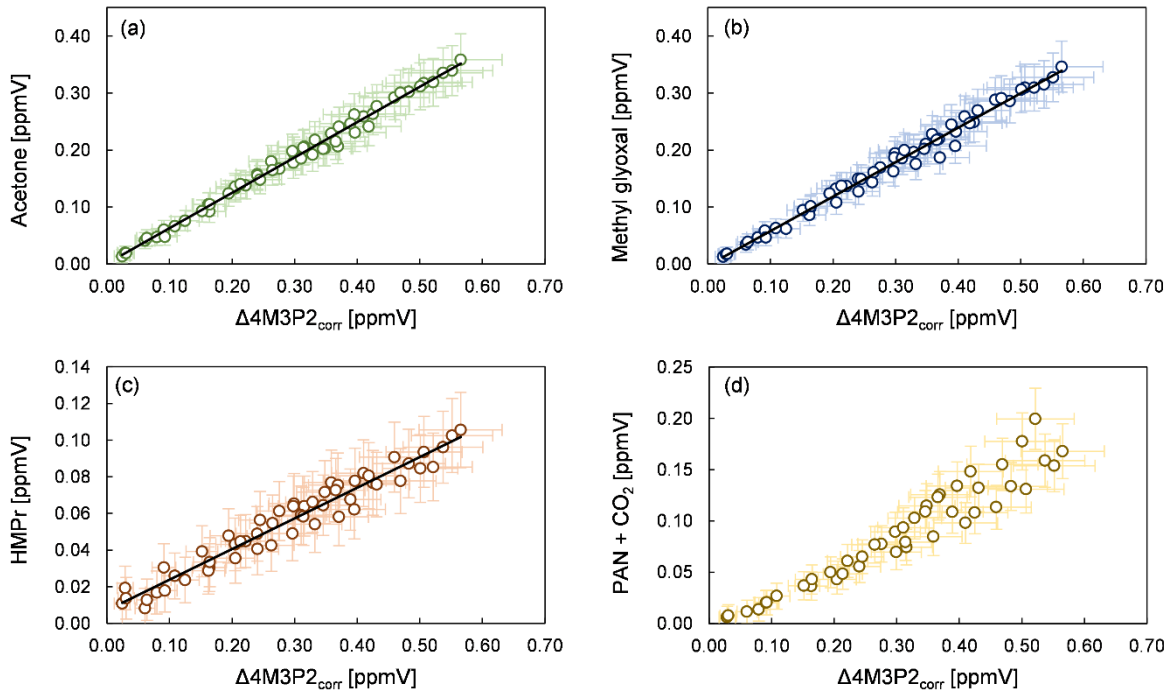

Figure S7. Yield plots of (a) acetone, (b) methyl glyoxal, (c) 2-hydroxy-2-methylpropanal (HMPr), and (d) the sum of PAN and CO_2 in the 4M3P2 + OH reaction where the consumption of 4M3P2 is corrected for the wall loss. Mixing ratios of the 480 L chamber experiments are multiplied by a factor of 0.1 to fit within the scale of the 1080 L chamber experiments.

Table S1. Parameters used in the model for the correction for secondary reactions in the 3M3P2 + OH reaction system.

Reaction	*k*	*y*	Reference
3M3P2 + wall	$\leq 6 \times 10^{-5}$ s^{-1}		
$CH_3C(OH)C(O)CH_3 + OH \rightarrow CH_3C(O)C(O)CH_3$	1.0×10^{-11} cm^3 molecule^{-1} s^{-1}	0.8	Aschmann et al., (2000)
$CH_3C(OH)C(O)CH_3$ + wall	$\leq 2.5 \times 10^{-4}$ s^{-1}		
$CH_3C(O)H + OH \rightarrow CH_3C(O)$	1.5×10^{-11} cm^3 molecule^{-1} s^{-1}	0.95	Calvert et al., (2011)
$CH_3C(O)H$ + wall	$\leq 3.5 \times 10^{-4}$ s^{-1}		
$CH_3C(O)C(O)CH_3 + h\nu \rightarrow CH_3C(O)$	$3.6 \times 10^{-2} \times J(NO_2)$	2.0	Klotz et al., (2001)
$CH_3C(O)C(O)CH_3$ + wall	$\leq 7 \times 10^{-5}$ s^{-1}		

Table S2. Parameters used in the model for the correction for secondary reactions in the 4M3P2 + OH reaction system.

Reaction	*k*	*y*	Reference
4M3P2 + wall	$\leq 8 \times 10^{-5}$ s^{-1}		
$CH_3C(O)C(O)H + OH \rightarrow CH_3C(O)$	1.3×10^{-11} cm^3 molecule^{-1} s^{-1}	1.0	Calvert et al., (2011)
$CH_3C(O)C(O)H$ + wall	$\leq 1.0 \times 10^{-4}$ s^{-1}		
$CH_3C(O)CH_3 + OH \rightarrow CH_3C(O)$	1.8×10^{-13} cm^3 molecule^{-1} s^{-1}	1.0	Calvert et al., (2011)
$CH_3C(O)CH_3$ + wall	$\leq 2.0 \times 10^{-4}$ s^{-1}		
$(CH_3)_2C(OH)C(O)H + OH \rightarrow CH_3C(O)CH_3$	1.5×10^{-11} cm^3 molecule^{-1} s^{-1}	1.0	Carrasco et al., (2006)

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