

Synthesis of unsaturated 1,4-dicarbonyls and related compounds

(*E*)-2-butenedial

This synthetic method is based on the work of Liu¹, and Nadkarni and Sayre². To (*E*)-1,1,4,4-tetramethoxybutene (1.00 g, 5.68 mmol) in acetone (25 mL) and water (12 mL) was added Amberlyst-15 (1.80 g) and the solution was stirred at room temperature overnight. The resin was removed by filtration and the filtrate was washed with acetone (3 × 15 mL). The acetone was removed and the aqueous residue was saturated with sodium chloride. The solution was extracted with dichloromethane (5 × 30 mL), the extracts combined, washed with saturated brine (100 mL), and dried with MgSO₄ and then concentrated to give a yellow liquid. The liquid either crystallized on standing or was passed through a plug of silica, eluting with dichloromethane until the solvent ran clear. The eluent was concentrated to give (*E*)-2-butenedial as a yellow crystalline solid (0.38 g, 80%).

¹H NMR (200 MHz, CDCl₃) 6.78 (2H, dd, *J* 2.9 and 4.6, CH), 9.84 (2H, dd, *J* 2.9 and 4.6, CHO).

(*Z*)-4-oxo-2-pentenal

Method A. This synthetic method is based on the work of Adger *et al.*³. To dimethyldioxirane (69 mM in acetone, 145 mL) was added 2-methylfuran (0.82 g, 0.90 ml, 122 mmol) and the mixture was stirred at room temperature for 30 min. The solution was concentrated to give the product as a yellow liquid (0.77 g, 79%).

Method B. This synthetic method is based on the work of Liu¹. To 2-methylfuran (10.0 g, 122 mmol) in dichloromethane (100 mL) was added 3-chloroperbenzoic acid (21.0 g, 122 mmol) in dichloromethane (300 mL) drop-wise at 0 °C and the solution was stirred for 30 min. The solution was filtered and the filtrate was washed with saturated sodium hydrogen carbonate until no further evolution of gas was observed, then washed with saturated brine and dried with MgSO₄. Removal of the solvent gave the title compound (8.0 g, 67%).

¹H NMR (200 MHz, CDCl₃) 2.33 (3H, s, Me), 6.11 (1H, dd, *J* 8.0 and 11.7, H-2), 6.89 (1H, d, *J* 11.7, H-3), 10.16 (1H, d, *J* 8.0, H-1).

(*E*)-4-oxo-2-pentenal

To (*Z*)-4-oxo-2-pentenal (5.47 g, 55.8 mmol) in dichloromethane (80 mL) was added silica (5.00 g) and the solution stirred for 2 weeks while monitoring the extent of isomerization by ¹H NMR spectroscopy. The resulting mixture was filtered and concentrated to give the product as an orange/brown liquid (4.73 g, 86 %). The characteristic signal for the CHO moiety (9.80 ppm 1H, d, *J* 11.0, H-1) was monitored during the isomerization process.

2(3*H*)-furanone

To 2-furaldehyde (5.00 g, 4.30 ml, 52.0 mmol) in dichloromethane (30 ml), was added formic acid (2.95 ml, 104 mmol) and sodium sulfate (7.50 g). Hydrogen peroxide (28 %, 4.40 ml) was added and the solution was stirred for 45 min. The remaining hydrogen peroxide (10 ml) was added drop-wise and the resulting solution was heated at reflux for 5 hours and finally stirred at room temperature for 12

hours. The organic layer was separated and the aqueous layer was washed with dichloromethane (50 ml). The dichloromethane extracts were combined and stirred with saturated sodium thiosulfate solution (50 mL) for 1 hour. The organic layer was dried with MgSO_4 and concentrated to give the product as a yellow liquid (1.83 g, 42 %).

^1H NMR (200 MHz, CDCl_3) 3.10 (2H, t, J 2.4 Hz, H-3), 5.50 (1H, dt, J 2.4 and 3.6 Hz, H-5), 6.73 (1H, dt, J 2.4 and 3.6 Hz, H-4).

5-methyl-2(5H)-furanone (β -angelicalactone)

5-methyl-2(3H)-furanone (α -angelicalactone) (5.0 g, 4.6 mL, 51.0 mmol) and triethylamine (1.0 mL) were heated at 100°C for 4 hours. After cooling to room temperature, diethyl ether (100 ml) was added and the resulting solution washed with a saturated aqueous solution of sodium sulfate containing 8 ml concentrated sulfuric acid (100 mL) and then saturated aqueous potassium carbonate (100 mL). The ethereal solution was dried with MgSO_4 , filtered and concentrated to give a yellow liquid that was purified by preparative gas chromatography to yield colourless oil (3.42 g, 67 %).

^1H NMR (200 MHz, CDCl_3) 1.46 (3H, d, J 11.8 Hz, Me), 5.25 (1H, m, H-5), 6.11 (1H, dd, J 1.9 and 5.7 Hz, H-3), 7.45 (1H, dd, J 1.5 and 5.7 Hz, H-4).

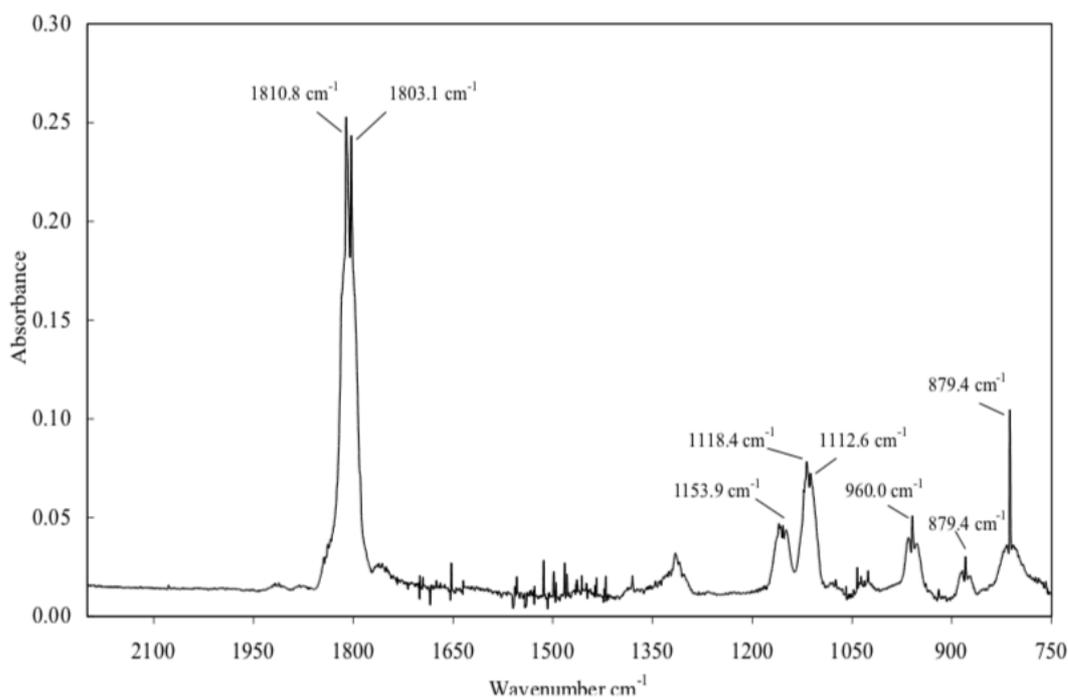


Figure S1 Gas-phase FTIR spectrum of 5-methyl-2(5H)-furanone (β -angelicalactone).

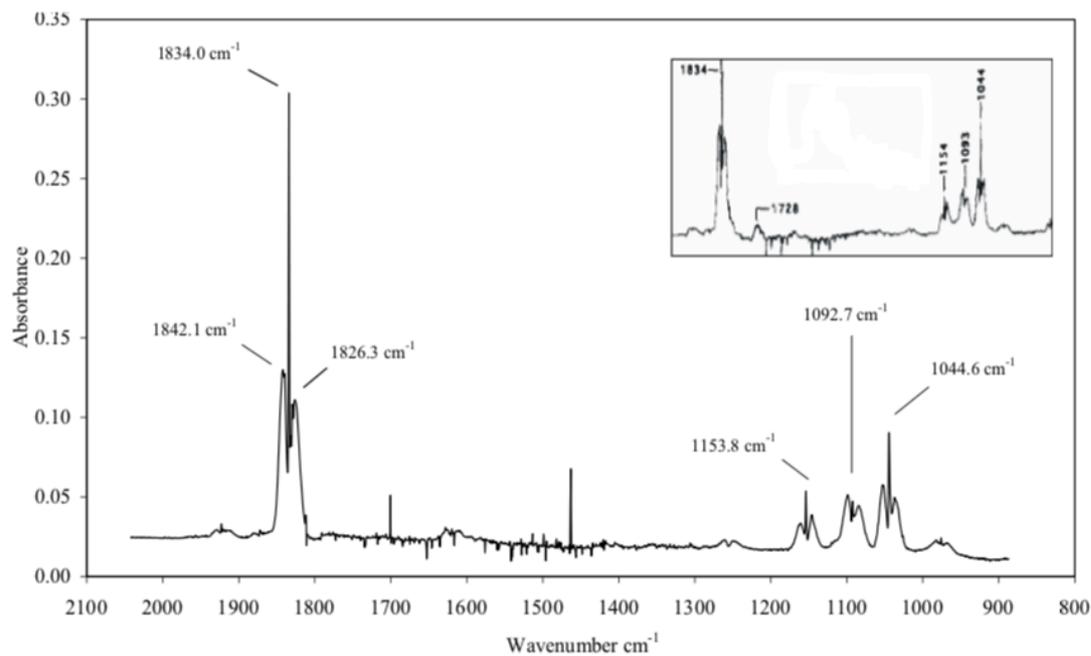


Figure S2 Gas-phase FTIR spectrum of 2(3H)-furanone. Inset: Corresponding spectrum reported by Bierbach *et al.*⁴.

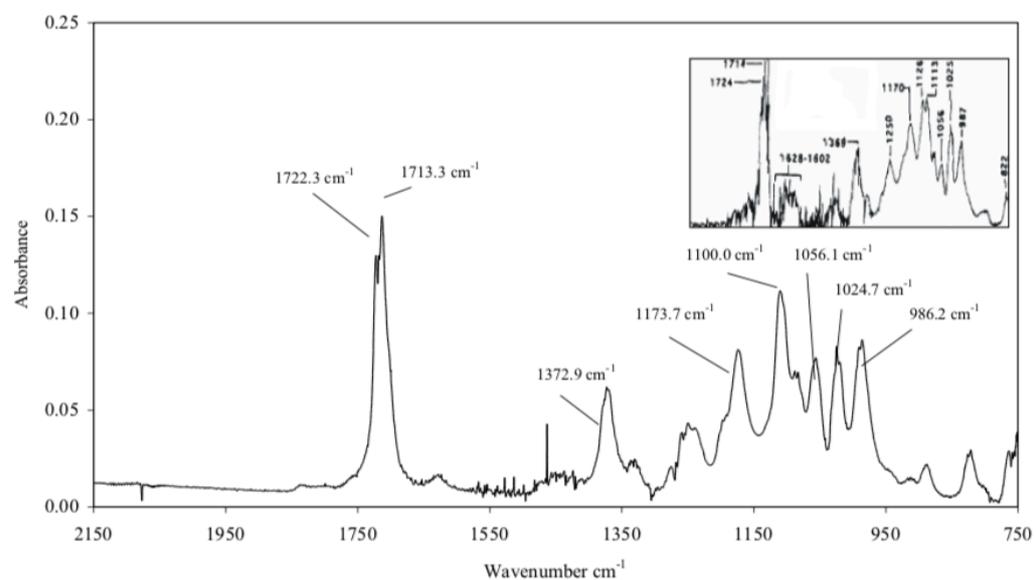


Figure S3 Gas-phase FTIR spectrum of synthesized (*E*)-4-oxo-2-pentenal. Inset: Spectrum of (*Z*)-4-oxo-2-pentenal reported by Bierbach *et al.*⁴.

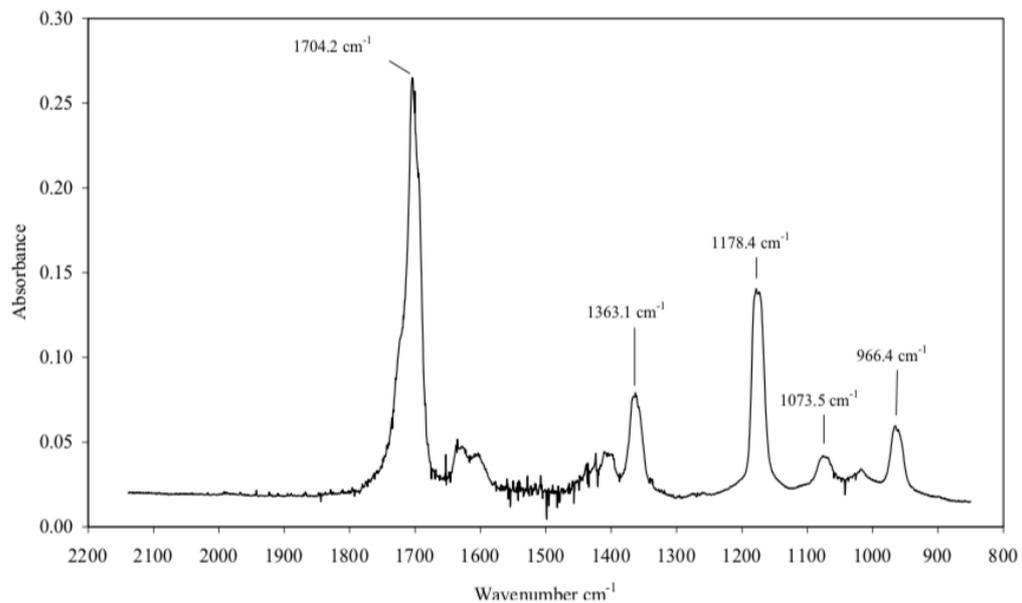


Figure S4 Gas-phase FTIR spectrum of synthesized (Z)-4-oxo-2-pentenal.

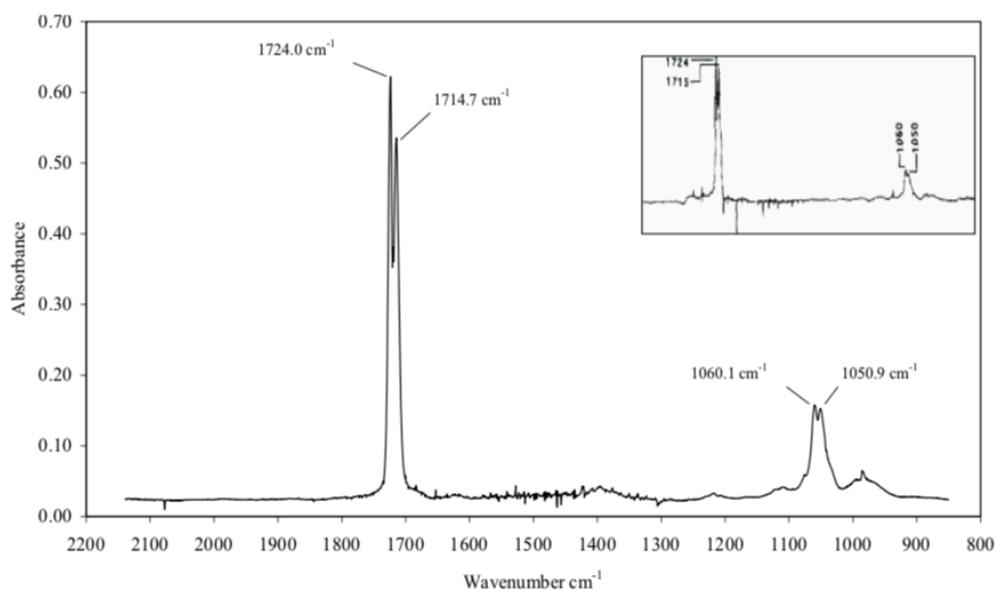


Figure S5 Gas-phase FTIR spectrum of synthesized (E)-2-butenedial. Inset: Corresponding spectrum reported by Bierbach *et al.*⁴.

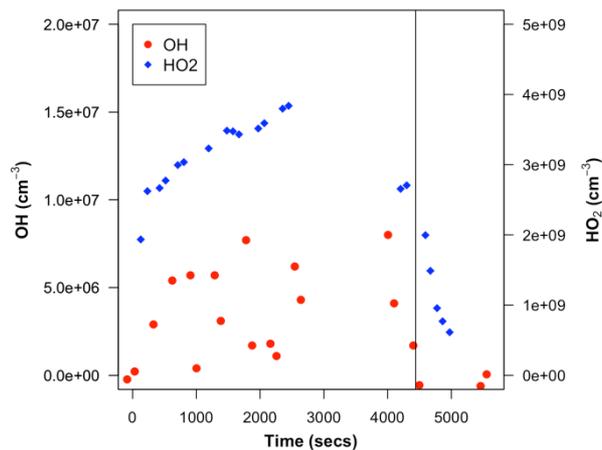


Figure S6 OH (red circles, left axis) and HO₂ (blue diamonds, right axis) concentrations measured by LIF-FAGE during experiment EBUT05. Chamber open at $t = 0$ s, chamber closed at vertical line; $t = 4440$ s.

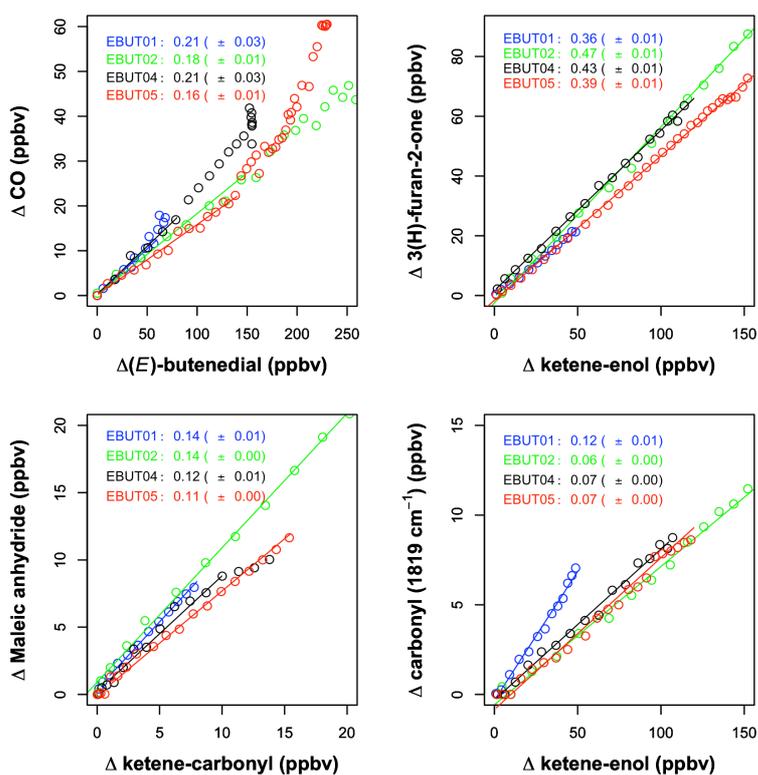


Figure S7 Rate of change (ppbv) of products plotted against reactant for the (*E*)-2-butenedial experiments. CO is assumed to be a primary photolysis product. 2(3H)-furanone and the unidentified carbonyl at 1819 cm⁻¹ are assumed to come from the ketene-enol, and maleic anhydride is assumed to come from the ketene-carbonyl.

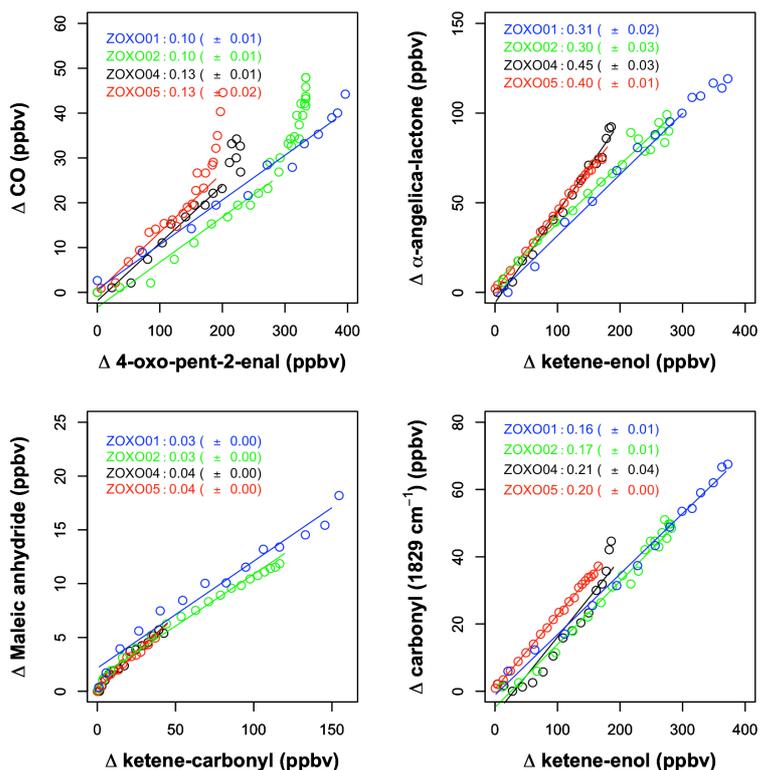


Figure S8 Rate of change (ppbv) of products plotted against reactant for the (*Z*)-4-oxo-2-pentenal experiments. CO is assumed to be a primary photolysis product. 5-methyl-2(3H)-furanone and the unidentified carbonyl at 1829 cm^{-1} are assumed to come from the ketene-enol, and maleic anhydride is assumed to come from the ketene-carbonyl.

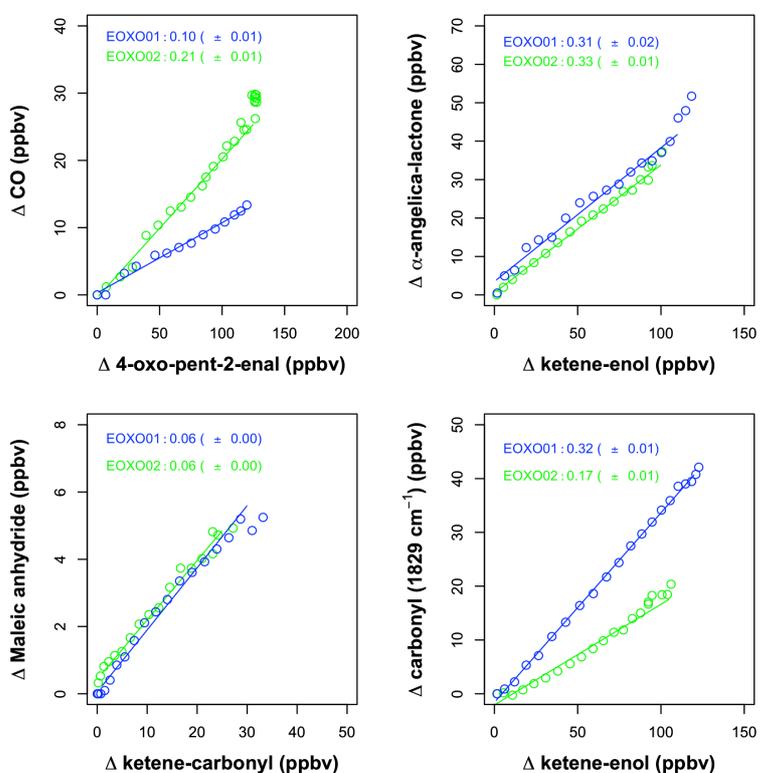


Figure S9 Rate of change (ppbv) of products plotted against reactant for the (*E*)-4-oxo-2-pentenal experiments. CO is assumed to be a primary photolysis product. 5-methyl-2(3H)-furanone and the unidentified carbonyl at 1829 cm^{-1} are assumed to come from the ketene-enol, and maleic anhydride is assumed to come from the ketene-carbonyl.

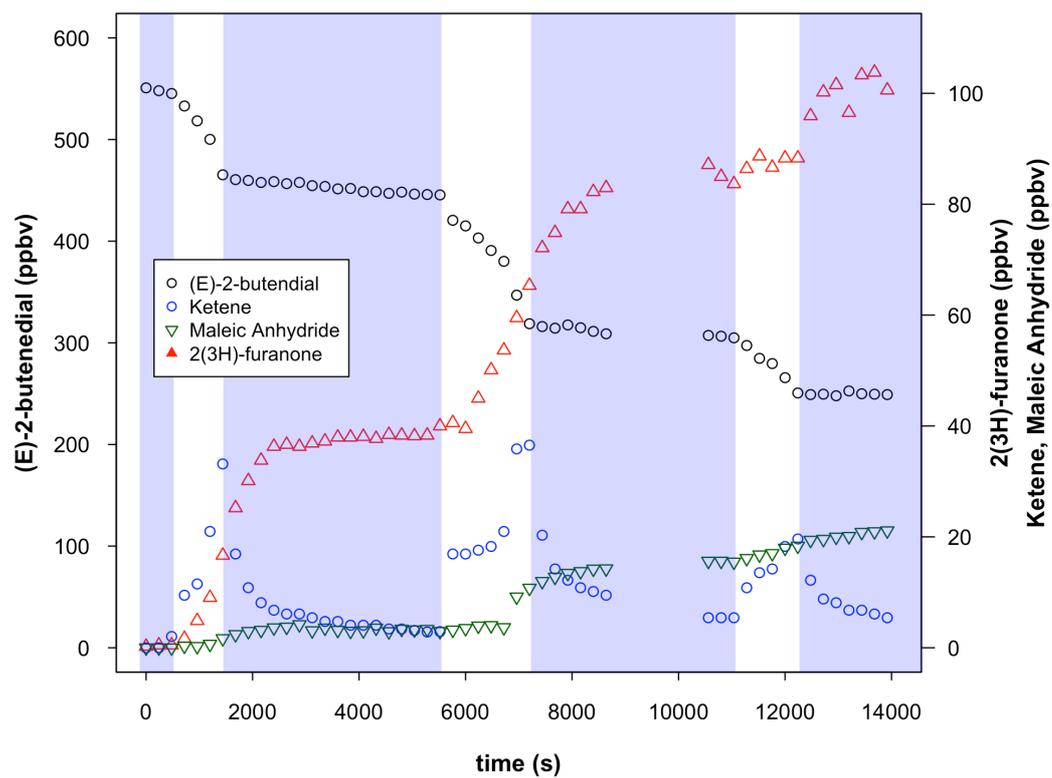


Figure S10 Experiment EBUT03. The chamber was opened (white space) and closed (blue space) several times.

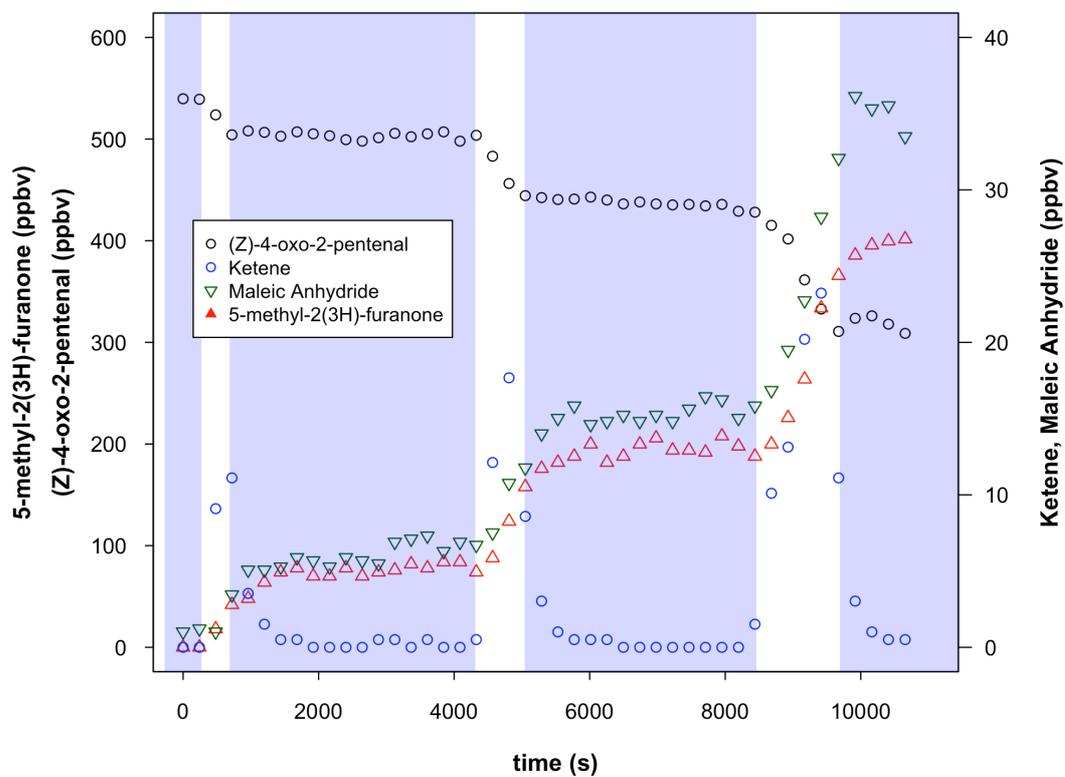


Figure S11 Experiment ZOZO03. The chamber was opened (white space) and closed (blue space) several times.

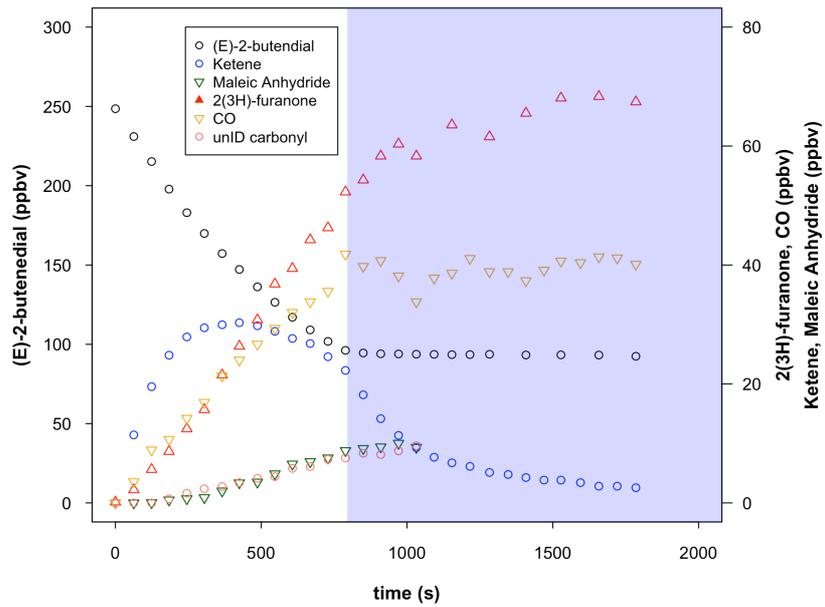


Figure S12 Experiment EBUT04. The chamber was closed at $t = 780$ s (blue space).

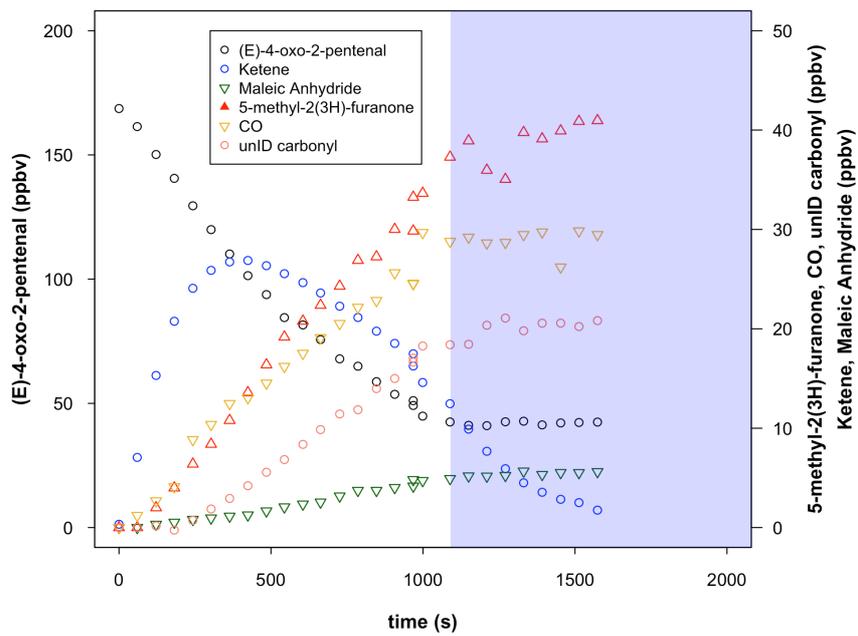


Figure S13 Experiment EOXO02. The chamber was closed at $t = 1170$ s (blue space).

Table S1 Comparison of aldehyde photolysis rates all determined in the EUPHORE chamber.

Aldehyde	j / s^{-1} ^a	$10^2 j(\text{ald.})/j(\text{NO}_2)$	Reference
n-hexanal	1.8×10^{-5}	0.2	Moortgat <i>et al.</i> ⁵
(E)-2-hexanal	1.62×10^{-4}	1.80	O'Connor <i>et al.</i> ⁶
(Z)-3-hexanal	3.60×10^{-5}	0.40	O'Connor <i>et al.</i> ⁶
Acrolein	$\leq 2.0 \times 10^{-6}$	-	Magneron <i>et al.</i> ⁷
Methacrolein	$< 2.0 \times 10^{-6}$	-	Moortgat <i>et al.</i> ⁵
(E)-crotonaldehyde	1.2×10^{-5}	-	Moortgat <i>et al.</i> ⁵
(E)-2-butenedial	1.26×10^{-3}	14.0	This work
(Z)-2-butenedial	1.8×10^{-3}	20.0	Sorenson and Barnes ⁸
(E)-4-oxo-2-pentenal	1.89×10^{-3}	21.0	This work
(Z)-4-oxo-2-pentenal	1.62×10^{-3}	18.0	This work
(E,E)-2,4-hexadienal	2.34×10^{-4}	2.60	O'Connor <i>et al.</i> ⁶
(E,E)-2,4-hexadiendial	1.02×10^{-3} ^b	11.3	Klotz <i>et al.</i> ⁹
(E,Z)-2,4-hexadienal	1.33×10^{-3}	14.8	Klotz <i>et al.</i> ⁹

^a Determined from reported $j(\text{aldehyde})/j(\text{NO}_2)$ values assuming, $j(\text{NO}_2) = 9 \times 10^{-3} \text{ s}^{-1}$.

^b (E,E)-2,4-hexadiendial photolysis was observed to follow a complex behaviour with a rapid photolytic equilibrium setup followed by slow photolysis to products¹⁰.

References

- 1 X. Liu, Ph.D. Thesis, 1999, University of North Carolina, Chapel Hill, NC.
- 2 B. M. Adger, C. Barrett, J. Brennan, M. A. McKervey and R. W. Murray, *J. Chem. Soc. Chem. Commun.*, 1991, **0**, 1553-1554.
- 3 D. V. Nadkarni, and L. M. Sayre, *Chem. Res. Toxicol.*, 1995, **8**, 284-291.
- 4 A. Bierbach, I. Barnes, K. H. Becker and E. Wiesen, *Environ. Sci. Technol.*, 1994, **28**, 715-729.
- 5 G. K. Moortgat, Important photochemical processes in the Atmosphere, *Pure and Applied Chemistry*, 2001, **73**, 487.
- 6 M. P. O'Connor, J. C. Wenger, A. Mellouki, K. Wirtz and A. Muñoz, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5236-5246.
- 7 I. Magneron, R. Thevenet, A. Mellouki, G. Le Bras, G. K. Moortgat and K. Wirtz, *J. Phys. Chem. A*, 2002, **106**, 2526-2537.
- 8 S. Sørensen and I. Barnes, EUPHORE Report 1997, Ed. Barnes, I.; Wenger, J., Department of Physical Chemistry, Bergische Universität Wuppertal, Wuppertal, Germany, 1998.
- 9 B. Klotz, I. Barnes and K. H. Becker, *Int. J. Chem. Kinet.*, 1999, **31**, 689-697.