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SUPLEMENTARY INFORMATION

Identification of the Acetaldehyde Oxide Criegee Intermediate Reaction Network in the Ozone-Assisted Low-Temperature Oxidation of *trans*-2-Butene

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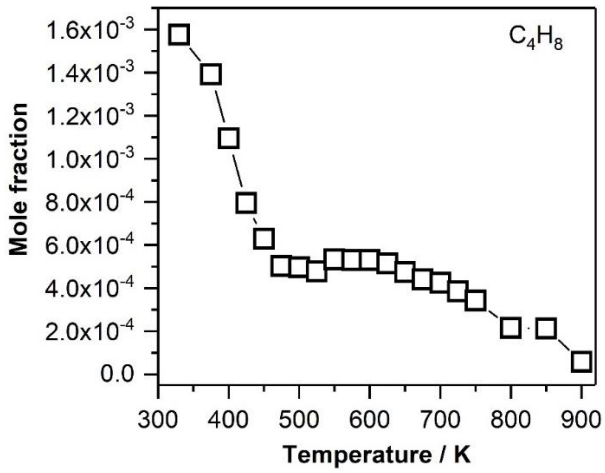

Figure S1: Mole fraction temperature profile of *trans*-2-butene concentration.

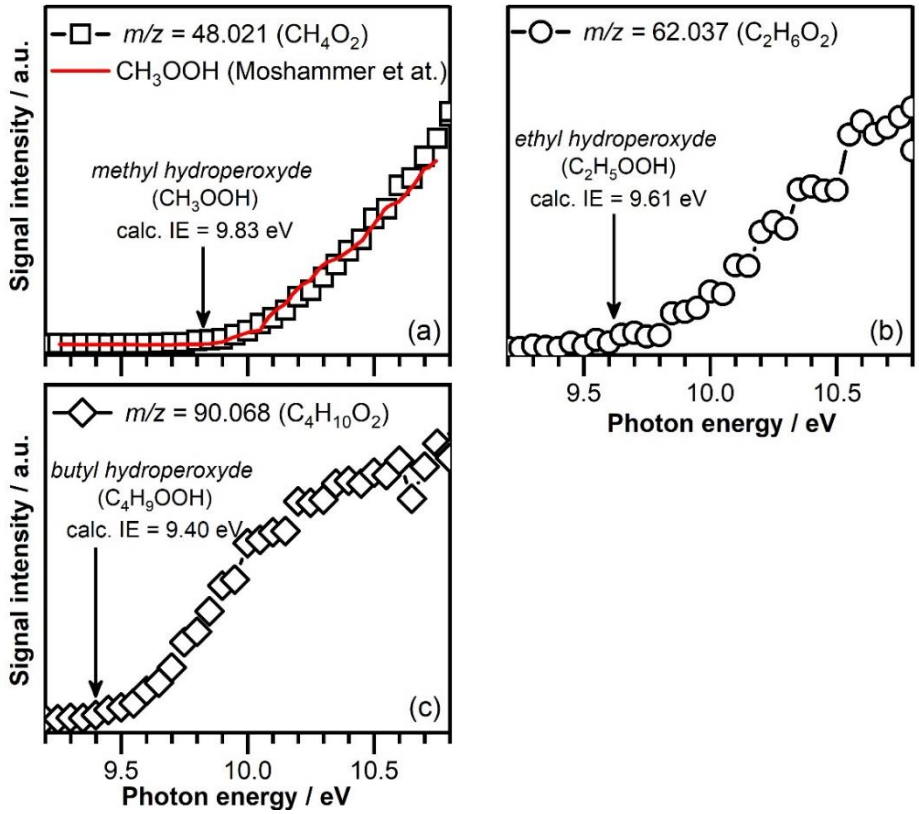

Figure S2. PIE scans of the signal recorded at (a) *m/z* = 48.021 (CH_4O_2), (b) *m/z* = 62.037 ($C_2H_6O_2$), and (c) *m/z* = 90.068 at a temperature of 425 K. The observed ionization thresholds are close to the calculated values for CH_3OOH, C_2H_5OOH, and C_4H_9OOH, respectively. The observed PIE curve of the CH_4O_2 signal resembles the one sampled by Moshammer et al.[1]

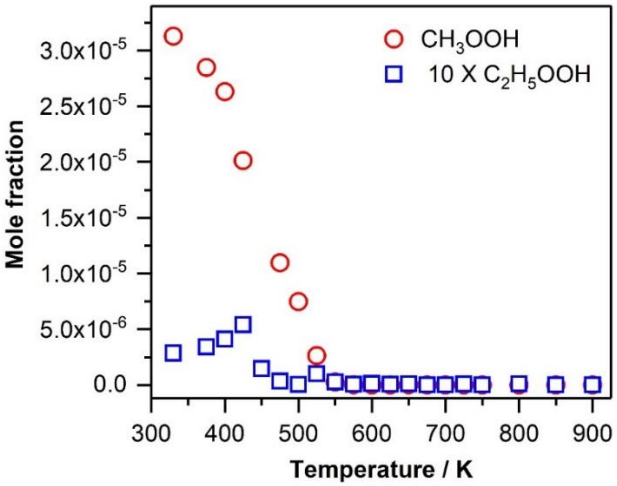

Figure S3. Experimentally measured mole fraction temperature profiles of (a) CH_3OOH and (b) C_2H_5OOH concentrations. The conversion of the mass spectra in mol fraction profiles is performed using a procedure described in literature,[2-3] using the cross section reported by Moshammer et al.[1] for CH_3OOH and Rousso et al.[4] for C_2H_5OOH. The low-temperature oxidation region and the negative-temperature coefficient region are clearly observed. CH_3OOH and C_2H_5OOH are present only in the temperature region below 600 K.

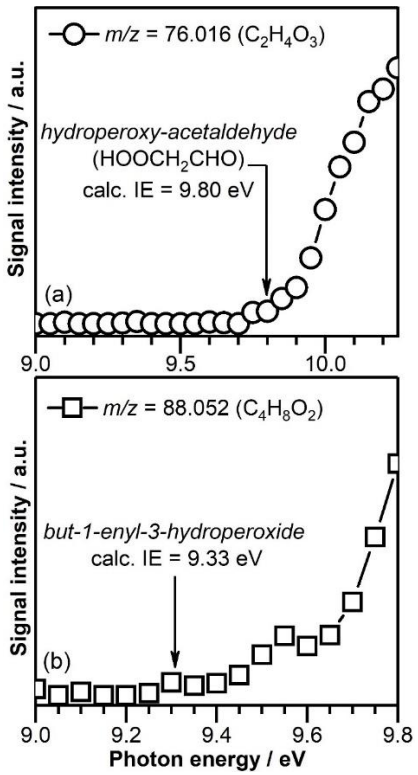

Figure S4. PIE scans of the signal recorded at (a) *m/z* = 76.016 ($C_2H_4O_3$) and (b) *m/z* = 88.052 ($C_4H_8O_2$) at a temperature of 425 K. The observed ionization thresholds match the calculated values for hydroperoxy-acetaldehyde[4] and but-1-enyl-3-hydroperoxide[5].

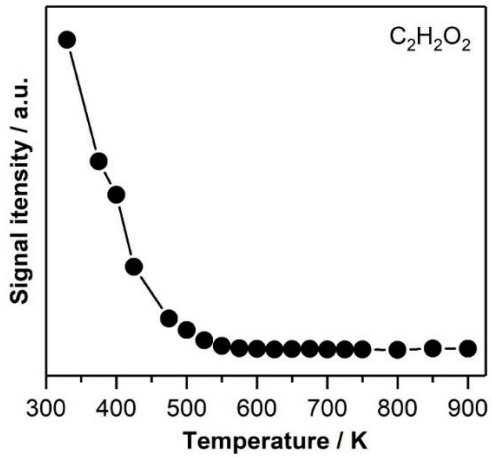

Figure S5. Experimentally measured glyoxal ($C_2H_2O_2$, *m/z* = 58.005) signal intensity as a function of temperature. The signal is recorded at a photon energy of 10.5 eV, which is slightly above the ionization energy of glyoxal.

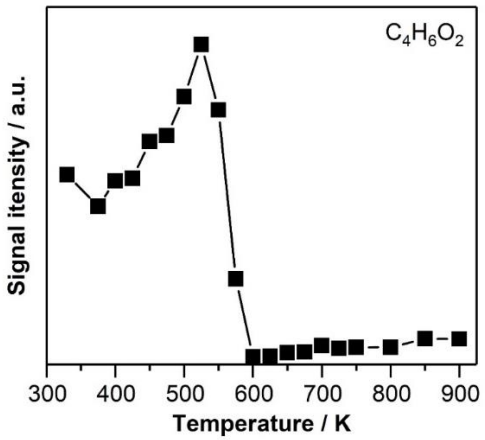

Figure S6. Experimentally measured diacetyl ($C_4H_6O_2$, *m/z* = 86.037) signal intensity as a function of temperature recorded at a photon energy of 10.0 eV.

Table S1: Products identified in the ozone-assisted oxidation reaction of *trans*-2-butene in three different temperature regions. The values of the ionization energies displayed in the table are either adapted from NIST Chemistry WebBook,[6] from literature (italicized values), or are calculated in this study (bolded values).

M (g/mol)	Compounds		Ionization energy (eV)
	Formula	***Name***	
JSR temperature < 600 K			
16.031	CH_4	methane	12.61
18.010	H_2O	water	12.62
26.015	C_2H_2	acetylene	11.40
27.994	CO	carbon monoxide	14.01
30.010	CH_2O	formaldehyde	10.88
30.046	C_2H_6	ethane	11.52
32.026	CH_4O	methanol	10.84
42.010	C_2H_2O	ketene	9.61
42.046	C_3H_6	propene	9.73
43.989	CO_2	carbon dioxide	13.77
44.026	C_2H_4O	acetaldehyde	10.22
46.005	CH_2O_2	formic acid	11.33
40.021	CH_4O	methyl hydroperoxide	*9.83*[1]
58.005	$C_2H_2O_2$	glyoxal	10.20
60.021	$C_2H_4O_2$	acetic acid glycolaldehyde	10.65 *9.98*[4]
62.036	$C_2H_6O_2$	ethyl hydroperoxide	*9.61*[1]
66.046	C_5H_6	1,3-cyclopentadiene	8.57
76.019	$C_2H_4O_3$	hydroperoxyl acetaldehyde	9.80
78.031	$C_2H_6O_3$	hydroxyethyl hydroperoxide	**9.55**
86.036	$C_4H_6O_2$	diacetyl	9.30
88.052	$C_4H_8O_2$	but-1-enyl-3-hydroperoxide	9.33
90.031	$C_3H_6O_3$	3-methyl-1,2,4-trioxolane	**9.41**
90.068	$C_4H_{10}O_2$	butyl hydroperoxide	*9.40*
104.047	$C_4H_8O_3$	3-hydroperoxybutan-2-one	**9.29**
116.083	$C_6H_{12}O_2$	4-hydroxy-3-methylpentan-2-one	**9.32**
600 K < JSR temperature < 800 K			
42.046	C_3H_6	propene	9.73
54.046	C_4H_6	1,3-butadiene	9.07
70.041	C_4H_6O	2-butenal	9.75
86.036	$C_4H_6O_2$	diacetyl	9.30
JSR temperature > 800 K			
16.031	CH_4	methane	12.61
18.010	H_2O	water	12.62
26.015	C_2H_2	acetylene	11.40
27.994	CO	carbon monoxide	14.01
28.031	C_2H_4	ethylene	10.51
30.010	CH_2O	formaldehyde	10.88
30.046	C_2H_6	ethane	11.52
40.031	C_3H_4	allene propyne	9.69 10.36

42.046	C_3H_6	propene	9.73
43.989	CO_2	carbon dioxide	13.77
54.046	C_4H_6	1,3-butadiene	9.07
66.046	C_5H_6	1,3-cyclopentadiene	8.57

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