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Supplement of

On the importance of atmospheric loss of organic nitrates by aqueous-phase ·OH oxidation

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S1

Iodoacetone, α-nitrooxyacetone and 1-nitrooxy-2-propanol synthesis

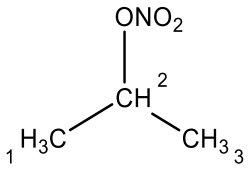
1.2 eq-mol of KI was added to a solution of chloroacetone in acetone. The solution was stirred in the dark at room temperature for 20 h. The mixture was filtered, and acetone was dried under vacuum leading to a brown viscous liquid. Iodoacetone was purified with a short chromatography column. To an acetonitrile solution of iodoacetone 1.5 eq-mol of $AgNO_3$ was slowly added under dark conditions at 273 K and then stirred for 20 h at room temperature. The precipitate was filtered and dried under vacuum. α-Nitrooxyacetone was purified with a chromatography column (pentane 1:1 ethyl acetate). A yellow pale viscous liquid was formed and was identified by NMR and GC-MS. 1-Nitrooxy-2-propanol was synthesized by reducing the carbonyl group of α-nitrooxyacetone. α-Nitrooxyacetone was dissolved in ethanol where a 0.4 eq-mol of $NaBH_4$ and a 0.2 eq-mol $NaHCO_3$ were added at 273 K. The mixture was stirred at room temperature for 4 hours. It has been purified with a silica gel column and identified by NMR and GC-MS.

S2

SAR Examples. Calculations of k_{OH} for the studied organic nitrates.

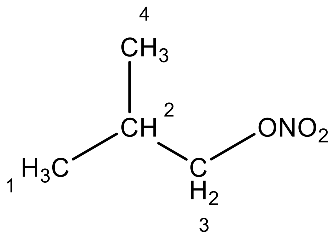
Organic nitrates aqueous-phase k_{OH} values using the extended SAR were calculated according to Eq. (4). Each number detailed in the molecule structure corresponds to a different reactive site, it numbers the order in the corresponding equation.

Isopropyl nitrate



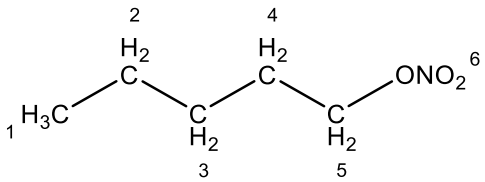
$$k_{OH} = k_{CH_3} \cdot F(CH) \cdot G(CH_3) \cdot G(ONO_2) + k_{CH} \cdot (F(CH_3))^2 \cdot F(ONO_2) + k_{CH_3} \cdot F(CH) \cdot G(CH_3) \cdot G(ONO_2)$$

Isobutyl nitrate



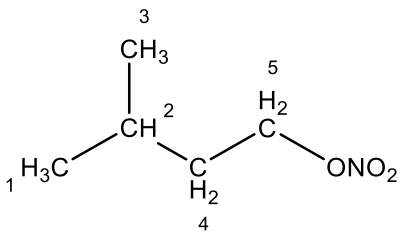
$$k_{OH} = k_{CH_3} \cdot F(CH) \cdot G(CH_2) \cdot G(CH_3) \cdot H(ONO_2) + k_{CH} \cdot (F(CH_3))^2 \cdot F(CH_2) \cdot G(ONO_2) + k_{CH_2} \cdot F(ONO_2) \cdot F(CH) \cdot (G(CH_3))^2 + k_{CH_3} \cdot F(CH) \cdot G(CH_3) \cdot G(ONO_2) + k_{CH_3} \cdot F(CH) \cdot G(CH_2) \cdot G(CH_3) \cdot H(ONO_2)$$

1-Pentyl nitrate



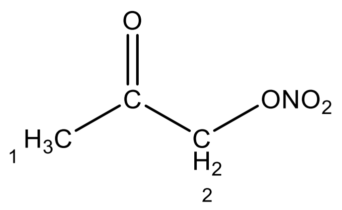
$$k_{OH} = k_{CH_3} \cdot F(CH_2) \cdot G(CH_2) + k_{CH_2} \cdot F(CH_3) \cdot F(CH_2) \cdot G(CH_2) + k_{CH_2} \cdot (F(CH_2))^2 \cdot G(CH_2) \cdot G(CH_3) \cdot H(ONO_2) + k_{CH_2} \cdot (F(CH_2))^2 \cdot G(CH_2) \cdot G(ONO_2) + k_{CH_2} \cdot F(ONO_2) \cdot F(CH_2) \cdot G(CH_2)$$

Isopentyl nitrate



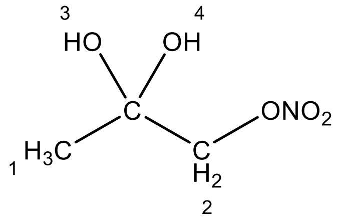
$$k_{OH} = k_{CH_3} \cdot F(CH) \cdot G(CH_3) \cdot G(CH_2) + k_{CH} \cdot (F(CH_3))^2 \cdot F(CH_2) \cdot G(CH_2) \cdot H(ONO_2) + k_{CH_3} \cdot F(CH) \cdot G(CH_3) \cdot G(CH_2) + k_{CH_2} \cdot F(CH) \cdot F(CH_2) \cdot (G(CH_3))^2 \cdot G(ONO_2) + k_{CH_2} \cdot F(CH_2) \cdot F(ONO_2) \cdot G(CH)$$

α-Nitrooxyacetone (carbonyl form)



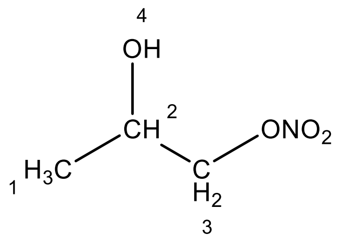
$$k_{OH} = k_{CH_3} \cdot F(C=O) \cdot G(CH_2) \cdot H(ONO_2) + k_{CH_2} \cdot F(C=O) \cdot F(ONO_2) \cdot G(CH_3)$$

α-Nitrooxyacetone (geminal diol form)



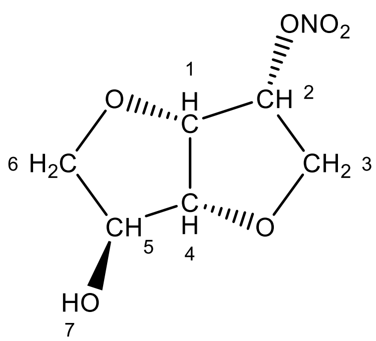
$$k_{OH} = k_{CH_3} \cdot F(C) \cdot (G(OH))^2 \cdot G(CH_2) \cdot H(ONO_2) + k_{CH_2} \cdot F(C) \cdot F(ONO_2) \cdot (G(OH))^2 \cdot G(CH_3) + k_{OH} \cdot F(C) \cdot G(gemOH) \cdot G(CH_3) \cdot G(CH_2) \cdot H(ONO_2) + k_{OH} \cdot F(C) \cdot G(gemOH) \cdot G(CH_3) \cdot G(CH_2) \cdot H(ONO_2)$$

1-Nitrooxy-2-propanol



$$k_{OH} = k_{CH_3} \cdot F(CH) \cdot G(OH) \cdot G(CH_2) \cdot H(ONO_2) + k_{CH} \cdot F(CH_3) \cdot F(CH_2) \cdot F(OH) \cdot G(ONO_2) + k_{CH_2} \cdot F(CH) \cdot F(ONO_2) \cdot G(CH_3) \cdot G(OH) + k_{OH} \cdot F(CH) \cdot G(CH_2) \cdot G(CH_3) \cdot H(ONO_2)$$

Isosorbide 5-mononitrate



$$k_{OH} = k_{CH} \cdot F(-O-) \cdot (F(CH))^2 \cdot G(-O-) \cdot (G(CH_2))^2 \cdot G(CH) \cdot G(ONO_2) \cdot (C'5(cycle))^2 + k_{CH} \cdot F(CH) \cdot F(CH_2) \cdot F(ONO_2) \cdot G(CH) \cdot (G(-O-))^2 \cdot C'5(cycle) + k_{CH_2} \cdot F(CH) \cdot F(-O-) \cdot (G(CH))^2 \cdot G(ONO_2) \cdot C'5(cycle) + k_{CH} \cdot F(-O-) \cdot (F(CH))^2 \cdot G(-O-) \cdot G(OH) \cdot (G(CH_2))^2 \cdot G(CH) \cdot H(ONO_2) \cdot (C'5(cycle))^2 + k_{CH} \cdot F(CH) \cdot F(CH_2) \cdot F(OH) \cdot G(CH) \cdot (G(-O-))^2 \cdot C'5(cycle) + k_{CH_2} \cdot F(CH) \cdot F(-O-) \cdot G(OH) \cdot (G(CH))^2 \cdot C'5(cycle) + k_{OH} \cdot F(CH) \cdot G(CH_2) \cdot G(CH)$$

S3

α-Nitrooxyacetone k_{hyd} determination

The equilibrium constant, K_{hyd}, is defined, as in Eq. (5) (considering water activity as unity).

$$K_{hyd} = \frac{[gem-diol]}{[carbonyl]}$$

After synthesis and purification of α-nitrooxyacetone an ^{1}H-NMR spectra was recorded in D_2O. Peaks at 5.31 and 2.30 ppm correspond to the protons of the carbonyl form while more right-shifted peaks (4.55 and 1.50 ppm) correspond to the gem-diol protons. The integration ratio results in a $K_{hyd} = 0.048 \pm 0.002$. An additional ^{1}H-NMR spectra was recorded after the addition of some drops of D_2SO_4 to reach a pH similar to the one in the aqueous-phase reactor. Comparable values were obtained in both cases suggesting that the K_{hyd} does not depend significantly on the pH.

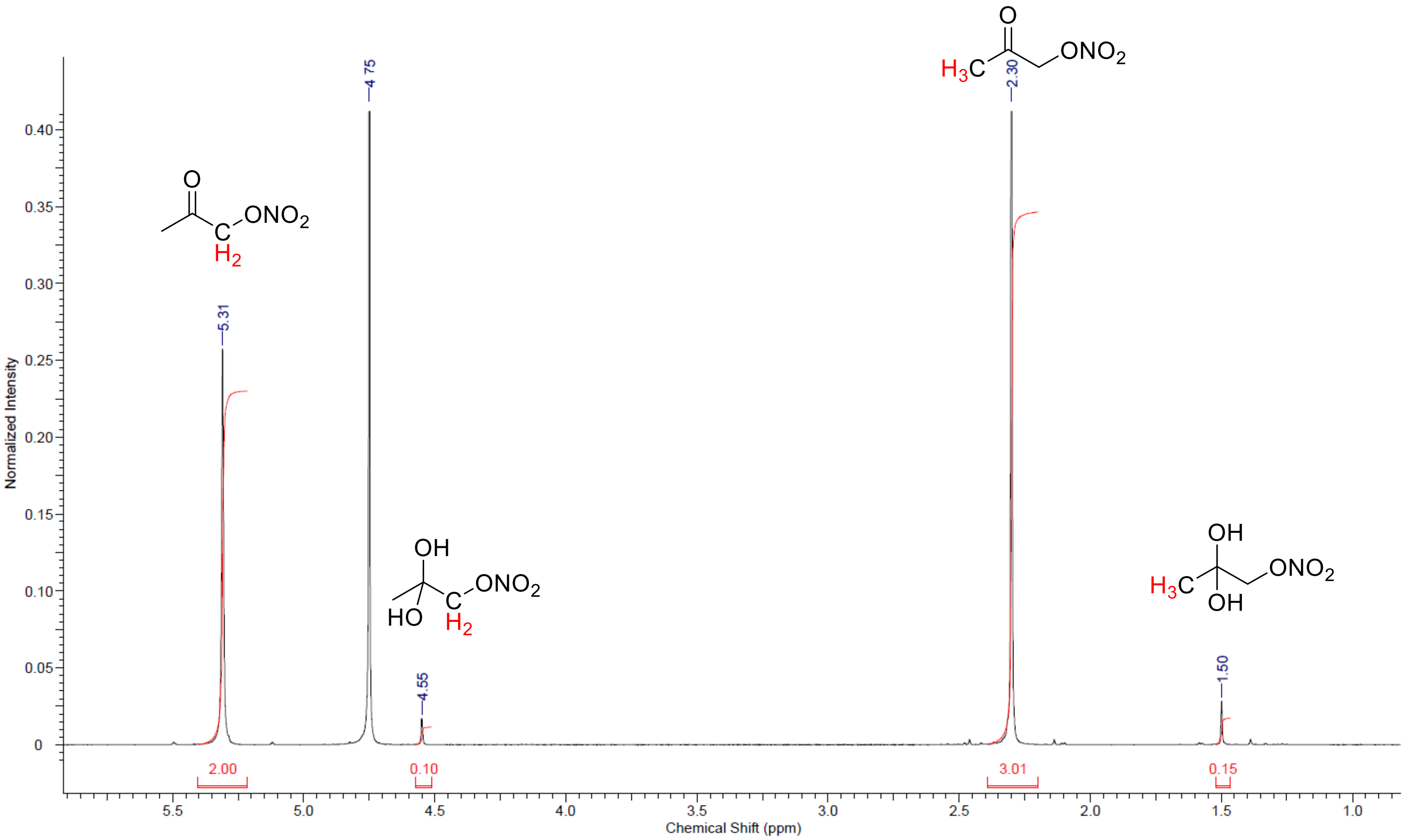


Table S1

Aqueous-phase rate constant of ·OH-oxidation of methanol, isopropanol, acetone, thiocyanate, ethanol and iron II (reported in the literature).

Compound	k_{OH} / $\cdot 10^9$ M^{-1} s^{-1}	Reference
Methanol	0.95 (± 0.22)	Adams et al., 1965
	0.83 (± 0.01)	Neta, 1968
	0.95 (± 0.23)	Baxendale and Khan, 1969
	0.97 (± 0.10)	Willson et al., 1971
	1.00 (± 0.10)	Wolfenden and Willson, 1982a
	0.83 (± 0.04)	Motohashi and Saito, 1993
	1.30 (± 0.42)	George et al., 2003
	0.90 (± 0.05)	Alam et al., 2003
	0.97 (± 0.15)	**Average value**
Isopropanol	1.9 (± 0.4)	Thomas, 1965
	1.9 (± 0.3)	Greenstock et al., 1968
	2.1 (± 0.2)	Willson et al., 1971
	1.9 (± 0.1)	Wolfenden and Willson, 1982b
	2.3 (± 0.1)	Elliot and Simsons, 1984
	1.9 (±0.2)	Buxton et al., 1988
	1.6 (± 0.1)	Motohashi and Saito, 1993
	2.0 (± 0.1)	Alam et al., 2003
	1.9 (± 0.2)	Monod et al., 2005
	1.9 (± 0.3)	**This work**
Acetone	0.08 (± 0.02)	Thomas, 1965
	0.14 (± 0.03)	Willson et al., 1971
	0.13 (± 0.01)	Wolfenden and Willson, 1982b
	0.10 (± 0.01)	Williams et al., 2002
	0.15 (± 0.07)	Herrmann, 2003
	0.13 (± 0.01)	Herrmann, 2003
	0.11 (± 0.05)	Monod et al., 2005
	0.18 (± 0.04)	Gligorovski et al., 2009
	0.13	Schaefer et al., 2012
	0.10 (± 0.06)	**This work**
SCN-	6.6	Thomas, 1965
	20.0 *	Baxendale and Stott, 1967
	28.0 *	Baxendale et al., 1968
	10.5 (± 0.7)	Zehavi and Rabani, 1971
	10.8 (± 1.0)	Ellison et al., 1972

	11.7 (± 0.4)	Elliot and Simsons, 1984
	10.0	Tanaka et al., 1984
	12.4	Chin and Wine, 1992
	12.1	Motohashi and Saito, 1993
	12.0	Chin and Wine, 1994
	11.9	Zhu et al., 2003
	14.0	Milosavljevic and LaVerne, 2005
	11.2 (± 2.0)	**Average value**
Ethanol	2.0 (± 0.2)	Adams et al. 1965
	1.67 (± 0.07)	Matthews and Sangster, 1965
	2.0	Heckel et al., 1966
	1.8 (± 0.2)	Neta, 1968
	1.6 (± 0.4)	Baxendale and Khan, 1969
	2.1 (± 0.3)	Buxton, 1970
	2.1	Willson et al. 1971
	1.9	Matheson et al., 1973
	1.9 (± 0.1)	Wolfenden and Willson, 1982b
	1.9 (± 0.1)	Park and Getoff, 1992
	2.2	Motohashi et al. 1993
	2.1 (± 0.1)	Ervens et al., 2003
	1.9 (± 0.5)	George et al. 2003
	2.1 (± 0.2)	Monod et al. 2005
	1.4 (± 0.6)	Kwon et al., 2009
	2.2 (± 0.1)	Alam et al. 2003
	1.9 (± 0.2)	**Average value**
Fe^{2+}	0.35	Zehavi and Rabani, 1971
	0.23 (± 0.02)	Jayson et al., 1972
	0.43	Christensen and Sehested, 1981
	0.32	Stuglik and PawełZagórski, 1981
	0.33 (± 0.08)	**Average value**

* Outliers values discarded one by one using the Dixon’s Q Test.

Table S2

Initial conditions of each competition kinetics experiment. All experiments were performed at 296 ± 2 K.

Experiment number	**Target compound**	**$[X]_{(aq)}$ / $\cdot10^{-4}$ mol L^{-1}**	**$[CH_3OH]_{(aq)}$ / $\cdot10^{-4}$ mol L^{-1}**	**$[FeSO_4\cdot7H_2O]_{(aq)}$ / mol L^{-1}**	**V_{added} of $FeSO_4\cdot7H_2O$ / mL**
1	Isopropanol	3	3	0.06	10
2	Isopropanol	3	3	0.06	10
3	Isopropanol	3	3	0.06	10
4	Acetone	3	3	0.06	10
5	Acetone	3	3	0.06	10
6	Acetone	3	3	0.06	10
7	Isopropyl nitrate	6	3	0.06	10
8	Isopropyl nitrate	6	3	0.06	10
9	Isopropyl nitrate	6	3	0.06	10
10	Isopropyl nitrate	0.5	1.5	0.06	10
11	Isopropyl nitrate	0.5	1.5	0.06	10
12	Isopropyl nitrate	1	1.5	0.06	10
13	Isobutyl nitrate	0.25	1.5	0.06	5
14	Isobutyl nitrate	0.25	1.5	0.06	5
15	Isobutyl nitrate	0.25	1.5	0.03	10
16	1-Pentyl nitrate	0.5	3	0.02	10
17	1-Pentyl nitrate	0.5	3	0.02	10
18	Isopentyl nitrate	0.05	3	0.02	10
19	Isopentyl nitrate	0.05	3	0.02	10
20	Isopentyl nitrate	0.05	3	0.02	10
21	2-Ethylhexyl nitrate	0.25	1.5	0.03	10
22	2-Ethylhexyl nitrate	0.25	1.5	0.03	10
23	α-Nitrooxyacetone	10	6	0.06	10
24	α-Nitrooxyacetone	10	6	0.06	10
25	α-Nitrooxyacetone	10	6	0.06	10
26	1-nitrooxy-2-propanol	6	6	0.06	10
27	1-nitrooxy-2-propanol	6	6	0.06	10
28	1-nitrooxy-2-propanol	6	6	0.06	10
29	Isosorbide 5-mononitrate	10	6	0.06	10
30	Isosorbide 5-mononitrate	10	6	0.06	10
31	Isosorbide 5-mononitrate	10	6	0.06	10

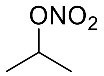
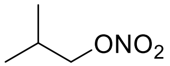
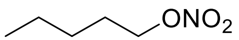
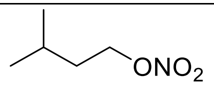
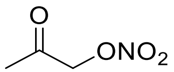
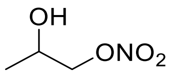
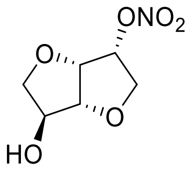
Table S3

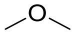
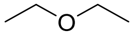
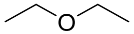
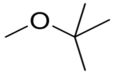
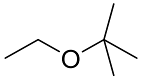
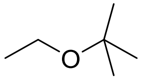
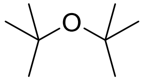
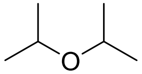
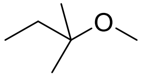
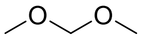
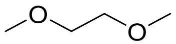
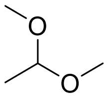
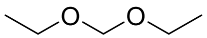
Detected fragments of the organic nitrates with PTR-MS and their relative intensities at E/N = 136 T. Minimum determined sensitivity of each compound, normalized to 10^6 H_3O^+ ions in the drift tube.

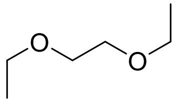
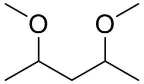
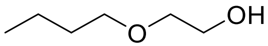
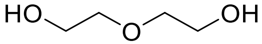
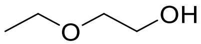
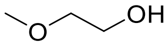
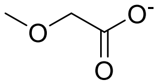
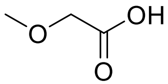
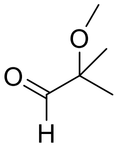
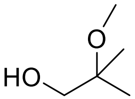
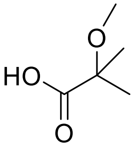
Compound	MW (g mol^{-1})	Sensitivity (ncps ppbv^{-1})	Product ion	m/z	Relative intensity
Isopropyl nitrate	105	≥7	$C_3H_3^+$	39	9
			$C_3H_5^+$	41	77
			$C_3H_7^+$	43	100
			NO_2^+	46	21
			$C_3H_7O^+$	59	4
			$M_m \cdot H^+$	106	0.2
Isobutyl nitrate	119	≥5.6	$C_3H_3^+$	39	2
			$C_3H_5^+$	41	19
			NO_2^+	46	12
			$C_4H_9^+$	57	100
			$C_4H_9O^+$	73	22
1-Pentyl nitrate	133	≥5	$C_3H_3^+$	39	12
			$C_3H_5^+$	41	100
			$C_3H_7^+$	43	95
			NO_2^+	46	20
			$C_5H_9^+$	69	45
			$C_5H_{11}^+$	71	37
Isopentyl nitrate	133	≥3.8	$C_3H_3^+$	39	12
			$C_3H_5^+$	41	100
			$C_3H_7^+$	43	92
			NO_2^+	46	15
			$C_5H_9^+$	69	43
			$C_5H_{11}^+$	71	35
			$C_5H_{11}O^+$	87	3
2-Ethylhexyl nitrate	175	≥3	$C_3H_5^+$	41	51
			$C_3H_7^+$	43	64
			$C_4H_9^+$	57	100
			$C_5H_9^+$	69	17
			$C_5H_{11}^+$	71	32
			$C_8H_{15}^+$	111	5
			$C_8H_{17}O^+$	129	5

Table S4

Database for the new extended SAR. Experimental values for organic nitrates (obtained in this work), and for ethers and cycloethers (from the literature) are compared to the simulated ones (obtained with the SAR parameters – Table 4).

Developed formula	$k_{OH, exp}$ / L mol^{-1} s^{-1}	Experimental error / L mol^{-1} s^{-1}	Reference	$k_{OH, sim}$ / L mol^{-1} s^{-1}
Organic nitrates				
	2.84 $\cdot 10^{8}$	5.59 $\cdot 10^{7}$	This work	3.04 $\cdot 10^{8}$
	1.74 $\cdot 10^{9}$	1.08 $\cdot 10^{9}$	This work	1.35 $\cdot 10^{9}$
	3.11 $\cdot 10^{9}$	4.59 $\cdot 10^{8}$	This work	3.18 $\cdot 10^{9}$
	2.22 $\cdot 10^{9}$	8.63 $\cdot 10^{8}$	This work	2.46 $\cdot 10^{9}$
	7.91 $\cdot 10^{7}$	4.23 $\cdot 10^{7}$	This work	1.33 $\cdot 10^{8}$
	8.72 $\cdot 10^{8}$	1.88 $\cdot 10^{8}$	This work	6.29 $\cdot 10^{8}$
	1.77 $\cdot 10^{9}$	4.81 $\cdot 10^{8}$	This work	1.42 $\cdot 10^{9}$
Ethers				

Developed formula	$k_{OH, exp}$ / L mol^{-1} s^{-1}	Experimental error / L mol^{-1} s^{-1}	Reference	$k_{OH, sim}$ / L mol^{-1} s^{-1}
	$1.02 \cdot 10^{9}$	–	Eibenberger J. 1980	$9.01 \cdot 10^{8}$
	$2.95 \cdot 10^{9}$	–	Eibenberger J. 1980	$2.37 \cdot 10^{9}$
	$4.47 \cdot 10^{9}$	–	Thomas 1965	$2.37 \cdot 10^{9}$
	$1.75 \cdot 10^{9}$	–	Eibenberger J. 1980	$8.58 \cdot 10^{8}$
	$2.96 \cdot 10^{9}$	–	Karpel Vel Leitner et al. 1994	$1.56 \cdot 10^{9}$
	$1.83 \cdot 10^{9}$	$1.70 \cdot 10^{9}$	Monod et al. 2005	$1.56 \cdot 10^{9}$
	$1.84 \cdot 10^{9}$	$3.36 \cdot 10^{8}$	Mezyk et al. 2001	$9.46 \cdot 10^{8}$
	$2.54 \cdot 10^{9}$	$4.61 \cdot 10^{8}$	Mezyk et al. 2001	$2.52 \cdot 10^{9}$
	$2.41 \cdot 10^{9}$	$4.41 \cdot 10^{8}$	Mezyk et al. 2001	$1.49 \cdot 10^{9}$
	$1.22 \cdot 10^{9}$	–	Eibenberger J. 1980	$1.92 \cdot 10^{9}$
	$1.68 \cdot 10^{9}$	–	Anbar et al. 1966	$1.51 \cdot 10^{9}$
	$2.24 \cdot 10^{9}$	–	Eibenberger J. 1980	$1.89 \cdot 10^{9}$
	$1.62 \cdot 10^{9}$	–	Anbar et al. 1966	$3.32 \cdot 10^{9}$

	$2.33 \cdot 10^{9}$	–	Anbar et al. 1966	$3.00 \cdot 10^{9}$
	$3.70 \cdot 10^{9}$	–	Janik et al. 2000	$3.25 \cdot 10^{9}$
	$5.10 \cdot 10^{9}$	$6.69 \cdot 10^{8}$	Stemmler and Von Gunten 2000	$4.08 \cdot 10^{9}$
	$2.13 \cdot 10^{9}$	–	Anbar et al. 1966	$2.11 \cdot 10^{9}$
	$1.72 \cdot 10^{9}$	–	Anbar et al. 1966	$2.24 \cdot 10^{9}$
	$1.32 \cdot 10^{9}$	–	Anbar et al. 1966	$1.50 \cdot 10^{9}$
	$6.22 \cdot 10^{8}$	–	Anbar et al. 1966	$6.24 \cdot 10^{8}$
	$4.73 \cdot 10^{8}$	–	Adams et al. 1965	$4.81 \cdot 10^{8}$
	$4.26 \cdot 10^{9}$	$8.08 \cdot 10^{8}$	Mezyk et al. 2009	$1.32 \cdot 10^{9}$
	$8.56 \cdot 10^{8}$	$1.60 \cdot 10^{8}$	Mezyk et al. 2009	$1.38 \cdot 10^{9}$
	$8.25 \cdot 10^{8}$	$1.53 \cdot 10^{8}$	Mezyk et al. 2009	$5.82 \cdot 10^{8}$

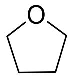
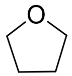
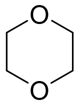
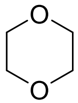
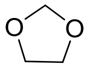
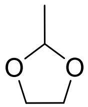
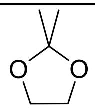
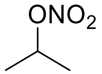
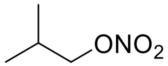
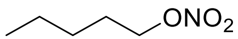
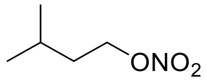
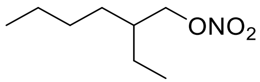
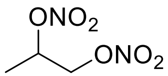
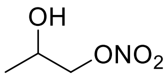
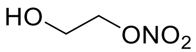
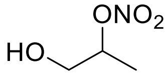
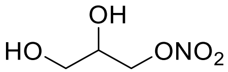
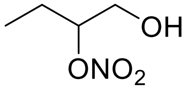
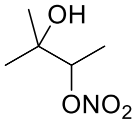
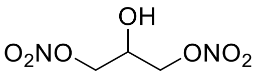
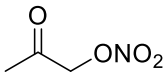
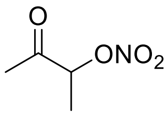
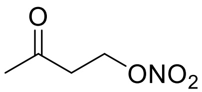
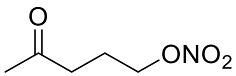
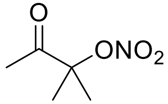
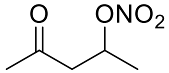
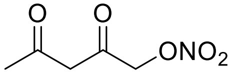
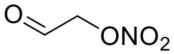
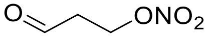
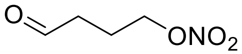
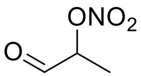
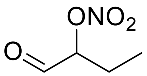
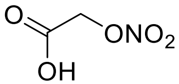
Cycloethers				
Developed formula	$\mathbf{k_{OH,\,exp}}$ **/ L mol^{-1} s^{-1}**	**Experimental error / L mol^{-1} s^{-1}**	**Reference**	$\mathbf{k_{OH,\,sim}}$ **/ L mol^{-1} s^{-1}**
	$3.30 \cdot 10^{9}$	$8.68 \cdot 10^{8}$	George et al. 2003	$3.98 \cdot 10^{9}$
	$4.07 \cdot 10^{9}$	–	Eibenberger J. 1980	$3.98 \cdot 10^{9}$
	$3.16 \cdot 10^{9}$	–	Eibenberger J. 1980	$2.24 \cdot 10^{9}$
	$2.69 \cdot 10^{9}$	–	Thomas 1965	$2.24 \cdot 10^{9}$
	$4.07 \cdot 10^{9}$	–	Eibenberger J. 1980	$2.25 \cdot 10^{9}$
	$3.56 \cdot 10^{9}$	–	Eibenberger J. 1980	$2.20 \cdot 10^{9}$
	$2.14 \cdot 10^{9}$	–	Eibenberger J. 1980	$9.02 \cdot 10^{8}$

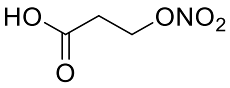
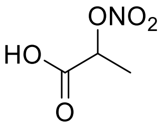
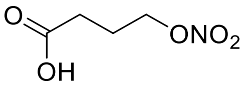
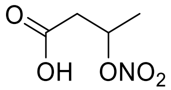
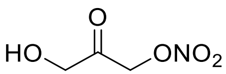
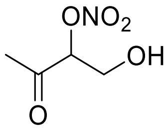
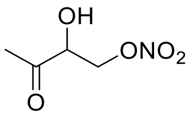
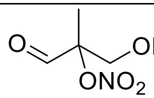
Table S5

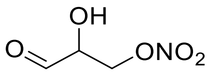
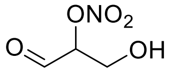
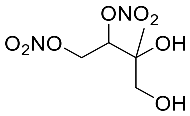
Atmospherically relevant organic nitrates properties: hydration, Henry's Law, and acidity constants, aqueous- and gas-phase rate constants, and OH-oxidation lifetimes.

			Alkyl nitrates				
Molecule structure	K_{hyd}[a]	K_H[b] / mol L^{-1} atm^{-1}	pK_a[c]	$k_{OH, aq}$[d] / L mol^{-1} s^{-1}	$k_{OH, gas}$[e] / cm^{-3} $molecules^{-1}$ s^{-1}	$\tau_{OH, multiphase}$[f] / days	$\tau_{OH, gas}$[g] / days
	–	0.75[i]	–	$2.84 \cdot 10^{8}$[j]	$3.48 \cdot 10^{-13}$	23.79	23.79
	–	0.6[i]	–	$1.74 \cdot 10^{9}$[j]	$1.43 \cdot 10^{-12}$	5.78	5.78
	–	0.74[i]	–	$3.11 \cdot 10^{9}$[j]	$3.09 \cdot 10^{-12}$	2.68	2.68
	–	0.4[i]	–	$2.22 \cdot 10^{9}$[j]	$2.81 \cdot 10^{-12}$	2.95	2.95
	–	0.52[i]	–	$5.88 \cdot 10^{9}$	$6.32 \cdot 10^{-12}$	1.31	1.31
	–	32.4	–	$1.19 \cdot 10^{8}$	$3.00 \cdot 10^{-13}$	27.54	27.56
			Hydroxy nitrates				
Molecule structure	K_{hyd}[a]	K_H[b] / mol L^{-1} atm^{-1}	pK_a[c]	$k_{OH, aq}$[d] / L mol^{-1} s^{-1}	$k_{OH, gas}$[e] / cm^{-3} $molecules^{-1}$ s^{-1}	$\tau_{OH, multiphase}$[f] / days	$\tau_{OH, gas}$[g] / days
	–	$6.7 \cdot 10^{3}$[i]	–	$8.72 \cdot 10^{8}$[j]	$5.10 \cdot 10^{-12}$	1.60	1.62
	–	$3.8 \cdot 10^{4}$[i]	–	$4.31 \cdot 10^{8}$	$1.41 \cdot 10^{-12}$	4.54	5.86

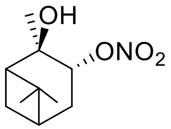
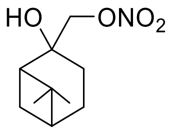
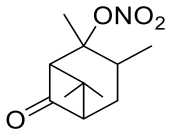
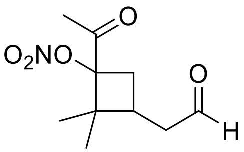
	–	$4.5 \cdot 10^{3, i}$	–	$5.18 \cdot 10^{8}$	$6.70 \cdot 10^{-12}$	1.25	1.23
	–	$6.31 \cdot 10^{6}$	–	$1.08 \cdot 10^{9}$	$1.30 \cdot 10^{-11}$	1.06	0.64
	–	$6.03 \cdot 10^{3}$	–	$1.06 \cdot 10^{9}$	$7.40 \cdot 10^{-12}$	1.12	1.12
	–	$2.00 \cdot 10^{3}$	–	$6.08 \cdot 10^{8}$	$1.53 \cdot 10^{-12}$	5.24	5.40
	–	$2.88 \cdot 10^{5}$	–	$2.53 \cdot 10^{8}$	$1.42 \cdot 10^{-12}$	4.87	5.82
Ketonitrates							
Molecule structure	**K_{hyd}[a]**	**K_H[b] /** mol L^{-1} atm^{-1}	**pK_a[c]**	**$k_{OH, aq}$[d] /** L mol^{-1} s^{-1}	**$k_{OH, gas}$[e] /** cm^{-3} $molecules^{-1}$ s^{-1}	**$\tau_{OH, multiphase}$[f] /** days	**$\tau_{OH, gas}$[g] /** days
 [h]	0.05	$1.00 \cdot 10^{3,i}$	–	$7.91 \cdot 10^{7,j}$	$4.33 \cdot 10^{-13}$	19.03	19.08
	0.21	$1.45 \cdot 10^{3}$	–	$2.37 \cdot 10^{8}$	$1.00 \cdot 10^{-12}$	8.20	8.27
	$1.89 \cdot 10^{-2}$	$2.24 \cdot 10^{3}$	–	$2.47 \cdot 10^{8}$	$2.90 \cdot 10^{-12}$	2.87	2.85
	$7.20 \cdot 10^{-3}$	$2.14 \cdot 10^{3}$	–	$6.03 \cdot 10^{8}$	$3.30 \cdot 10^{-12}$	2.49	2.51

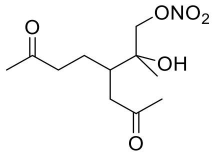
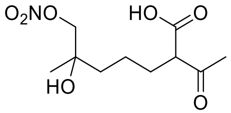
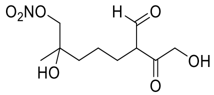
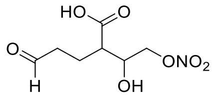
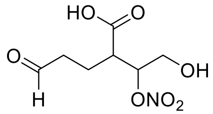
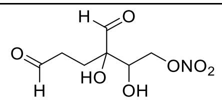
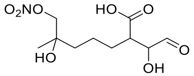
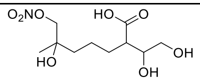
	0.21	$1.10 \cdot 10^{3}$	–	$2.70 \cdot 10^{8}$	$2.60 \cdot 10^{-12}$	3.19	3.18
	$1.89 \cdot 10^{-2}$	$1.66 \cdot 10^{3}$	–	$3.18 \cdot 10^{8}$	$1.25 \cdot 10^{-12}$	6.54	6.61
	1.86	$6.76 \cdot 10^{5}$	–	$6.68 \cdot 10^{8}$	$1.00 \cdot 10^{-12}$	1.96	8.27
Aldehyde nitrates							
Molecule structure	**K_{hyd}[a]**	**K_H[b] /** mol L^{-1} atm^{-1}	**pK_a[c]**	**$k_{OH, aq}$[d] /** L mol^{-1} s^{-1}	**$k_{OH, gas}$[e] /** cm^{-3} $molecules^{-1}$ s^{-1}	**$\tau_{OH, multiphase}$[f] /** days	**$\tau_{OH, gas}$[g] /** days
 [h]	67.5	$6.17 \cdot 10^{3}$	–	$5.53 \cdot 10^{8}$	$7.44 \cdot 10^{-12}$	1.14	1.11
	6.04	$5.13 \cdot 10^{3}$	–	$1.59 \cdot 10^{9}$	$2.15 \cdot 10^{-11}$	0.39	0.38
	2.30	$2.40 \cdot 10^{3}$	–	$2.12 \cdot 10^{9}$	$2.29 \cdot 10^{-11}$	0.36	0.36
	67.5	$2.57 \cdot 10^{3}$	–	$6.13 \cdot 10^{8}$	$1.31 \cdot 10^{-11}$	0.72	0.63
	67.5	$1.95 \cdot 10^{4}$	–	$1.15 \cdot 10^{9}$	$1.40 \cdot 10^{-11}$	0.63	0.59
Nitrooxy carboxylic acids							
Molecule structure	**K_{hyd}[a]**	**K_H[b] /** mol L^{-1} atm^{-1}	**pK_a[c]**	**$k_{OH, aq}$[d] /** L mol^{-1} s^{-1}	**$k_{OH, gas}$[e] /** cm^{-3} $molecules^{-1}$ s^{-1}	**$\tau_{OH, multiphase}$[f] /** days	**$\tau_{OH, gas}$[g] /** days
	–	$1.62 \cdot 10^{5}$	2.47	$2.65 \cdot 10^{7}$	$5.99 \cdot 10^{-13}$	22.91	13.80

	–	$2.34 \cdot 10^{5}$	3.18	$1.95 \cdot 10^{8}$	$9.87 \cdot 10^{-13}$	6.57	8.38
	–	$1.20 \cdot 10^{5}$	2.72	$1.06 \cdot 10^{8}$	$7.70 \cdot 10^{-13}$	10.80	10.74
	–	$2.29 \cdot 10^{5}$	3.44	$5.48 \cdot 10^{8}$	$1.84 \cdot 10^{-12}$	2.57	4.49
	–	$1.78 \cdot 10^{5}$	3.41	$2.63 \cdot 10^{8}$	$1.34 \cdot 10^{-12}$	4.96	6.17
More Polyfunctionalized Organic Nitrates							
Molecule structure	**K_{hyd}[a]**	**K_H[b] /** mol L^{-1} atm^{-1}	**pK_a[c]**	**$k_{OH, aq}$[d] /** L mol^{-1} s^{-1}	**$k_{OH, gas}$[e] /** cm^{-3} $molecules^{-1}$ s^{-1}	**$\tau_{OH, multiphase}$[f] /** days	**$\tau_{OH, gas}$[g] /** days
	1.29	$7.59 \cdot 10^{4}$	–	$6.36 \cdot 10^{8}$	$3.03 \cdot 10^{-12}$	2.28	2.73
 [h]	0.44	$1.86 \cdot 10^{5}$	–	$5.38 \cdot 10^{8}$	$3.89 \cdot 10^{-12}$	2.14	2.13
 [h]	0.12	$9.55 \cdot 10^{4}$	–	$2.99 \cdot 10^{8}$	$2.47 \cdot 10^{-12}$	3.57	3.35
 [h]	139	$4.17 \cdot 10^{6}$	–	$9.40 \cdot 10^{8}$	$1.60 \cdot 10^{-11}$	1.19	0.52

	36.8	$9.77 \cdot 10^{5}$	–	$9.09 \cdot 10^{8}$	$1.51 \cdot 10^{-11}$	1.10	0.55
	139	$5.50 \cdot 10^{6}$	–	$9.94 \cdot 10^{8}$	$1.65 \cdot 10^{-11}$	1.27	0.50
 [h]	–	$8.71 \cdot 10^{7}$	–	$5.03 \cdot 10^{9}$	$8.36 \cdot 10^{-12}$	1.03	0.99

Terpene Nitrates

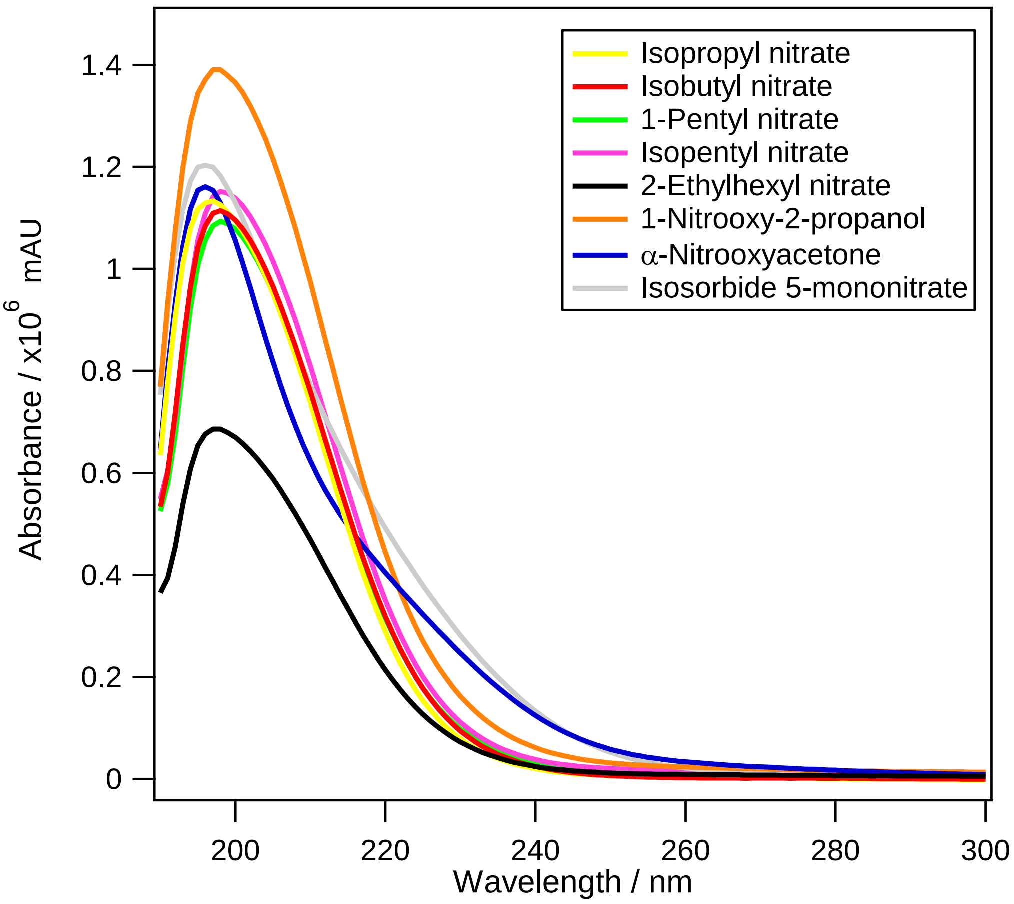
Molecule structure	**K_{hyd}**[a]	**K_H**[b] / mol L^{-1} atm^{-1}	**pK_a**[c]	**$k_{OH, aq}$**[d] / L mol^{-1} s^{-1}	**$k_{OH, gas}$**[e] / cm^{-3} $molecules^{-1}$ s^{-1}	**$\tau_{OH, multiphase}$ (LWC = 0.35 g m^{-3})** / days	**$\tau_{OH, multiphase}$ (LWC = $3 \cdot 10^{-5}$ g m^{-3})** / days	**$\tau_{OH, gas}$**[g] / days
	–	$8.32 \cdot 10^{3}$	–	$2.83 \cdot 10^{9}$	$6.56 \cdot 10^{-12}$	1.11	1.26	1.26
	–	$8.71 \cdot 10^{3}$	–	$3.91 \cdot 10^{9}$	$9.23 \cdot 10^{-12}$	0.79	0.90	0.90
	$5.65 \cdot 10^{-2}$	$2.34 \cdot 10^{7}$	–	$1.78 \cdot 10^{9}$	$6.21 \cdot 10^{-12}$	0.65	1.31	1.33
	2.66	$4.57 \cdot 10^{6}$	–	$3.56 \cdot 10^{9}$	$2.66 \cdot 10^{-11}$	0.32	0.31	0.31

	2.10	$1.12 \cdot 10^{10}$	–	$3.68 \cdot 10^{9}$	$4.58 \cdot 10^{-11}$	0.31	0.29	0.18
	$4.28 \cdot 10^{-2}$	$7.59 \cdot 10^{10}$	3.74	$3.02 \cdot 10^{9}$	$9.66 \cdot 10^{-12}$	0.38	0.39	0.86
	15.2	$2.34 \cdot 10^{11}$	–	$4.43 \cdot 10^{9}$	$4.05 \cdot 10^{-11}$	0.26	0.26	0.20
	2.00	$4.37 \cdot 10^{10}$	3.28	$3.49 \cdot 10^{9}$	$3.70 \cdot 10^{-11}$	0.33	0.33	0.22
	2.30	$1.51 \cdot 10^{12}$	3.35	$3.38 \cdot 10^{9}$	$3.25 \cdot 10^{-11}$	0.34	0.34	0.25
	144	$7.41 \cdot 10^{10}$	–	$2.85 \cdot 10^{9}$	$4.86 \cdot 10^{-11}$	0.41	0.40	0.17
	19.4	$9.12 \cdot 10^{12}$	3.71	$4.24 \cdot 10^{9}$	$3.82 \cdot 10^{-11}$	0.27	0.27	0.22
	–	$2.63 \cdot 10^{14}$	3.82	$4.77 \cdot 10^{9}$	$2.55 \cdot 10^{-11}$	0.24	0.24	0.32

[a]Calculated following Raventos-Duran et al., (2010) except for α-nitrooxyacetone. [b]Calculated following Raventos-Duran et al., (2010) when there were no experimental values. [c]Calculated values with MarvinSketch. [d]Simulated k_{OH} rate constants using the extended SAR (pH was set to 5 for carboxylic acids). [e]Calculated following Jenkin et al., (2018) [f]Calculated ·OH-oxidation lifetime in air parcel with a LWC = 0.35 g m^{-3}. [g]Calculated ·OH-oxidation lifetime in air parcel with no LWC (i.e. gas phas only). [h]Products of isoprene photooxidation. [i]Sander, (2015). [j]Experimental value from this work.

Figure S1

UV-VIS spectra of the studied organic nitrates reported from the UHPLC-UV detector. All compounds were injected at 10^{-3} mol L^{-1}.



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