Nitrogen Containing Organic Compounds and Oligomers in Isoprene Photooxidation Secondary Organic Aerosol

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Keywords: biogenic aerosol; SOA; 2-methylglyceric acid; monomer units; Orbitrap; tandem mass spectrometry; MS/MS; MS^n; organic nitrates

Supplementary Material

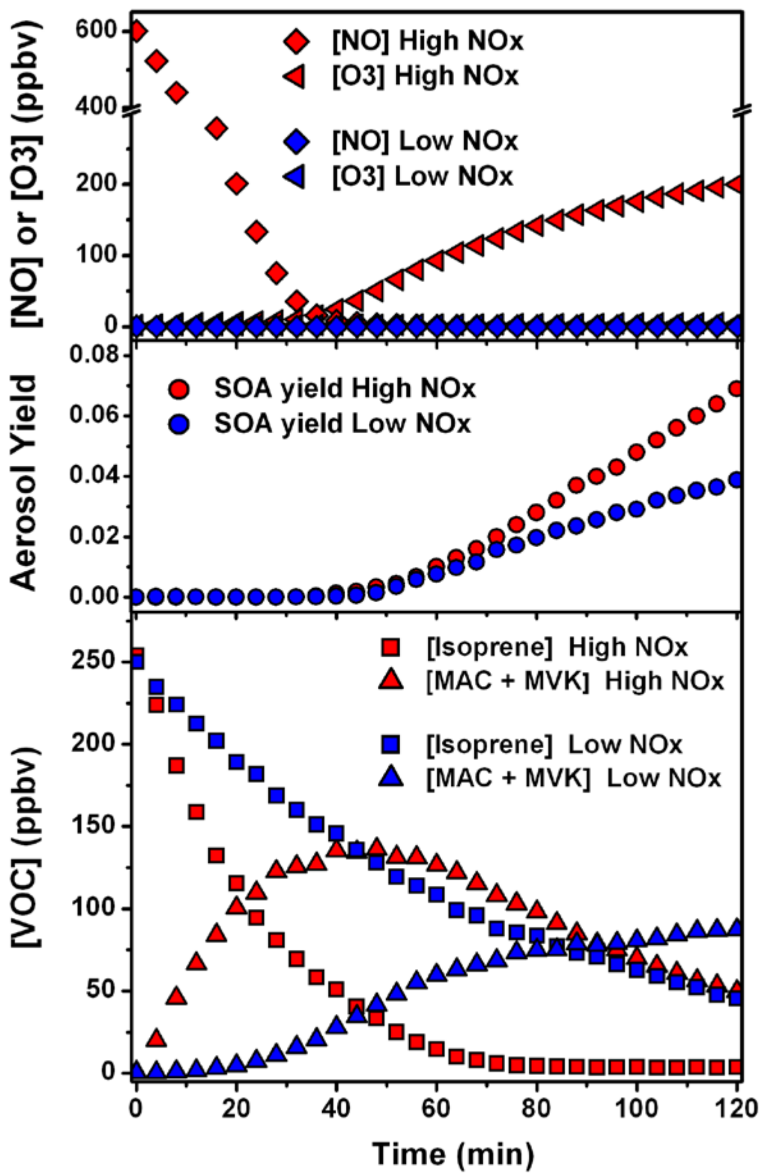


Figure S1: Representative time dependences of different species in the chamber under high- and low-NOx conditions. On the horizontal axis, t=0 corresponds to the photooxidation start time. (a) Nitric oxide and ozone; (b) the time-dependent SOA yield; (c) PTR-ToF-MS measurements of isoprene and its first-generation products methacrolein (MAC) and methylvinylketone (MVK), observed as isobaric species. The reaction rate is increased by a factor of ~ 2 under high-NOx conditions, and more SOA is formed from the oxidation of first-generation species.

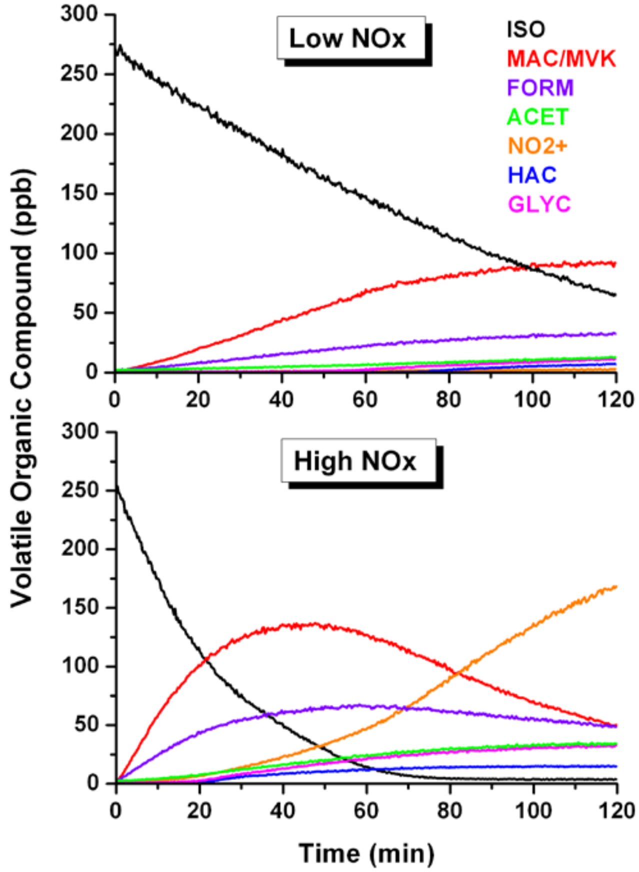


Figure S2: Time-dependent traces of VOC detected by PTR-ToF-MS in the low-NOx (top panel) and high-NOx photooxidation of isoprene. Note the faster disappearance of isoprene in the high NOx case. The signal at the mass corresponding to NO2+ does not come from NO2 itself , rather it is a product of decomposition of protonated organic nitrates and of nitric acid. The SOA collection started at 120 min, when the first generation products such as MVK and MAC were still present in significant concentrations.

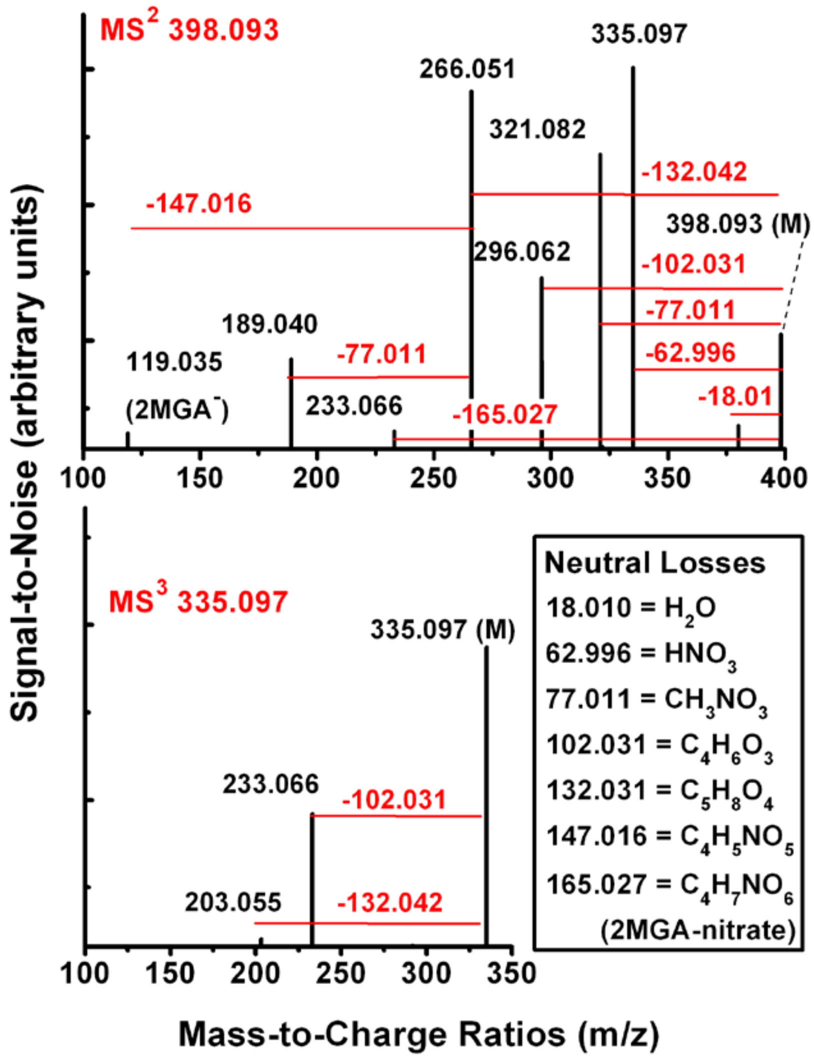


Figure S3: Representative MS^2 spectrum of m/z 398.093 ($C_{13}H_{20}NO_{13}^-$) and MS^3 spectrum of its largest ionic fragment m/z 335.097 ($C_{13}H_{19}O_{10}^-$). Neutral loss masses are shown in red. The corresponding neutral fragment formulas shown in the legend are the most abundant neutral losses observed in CID of all oligomeric NOC studied in this work. These data are also shown in a tabular form in table S2.

Table S1: Abundant monomer units in isoprene photooxidation SOA ranked by the total frequency of their occurrence in high-NOx mass spectra. Literature references refer to observation of these monomers amongst products of isoprene photooxidation.

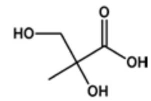
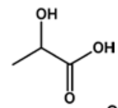
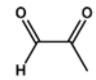
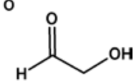
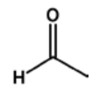
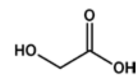
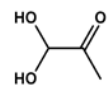
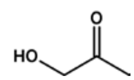
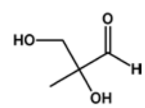
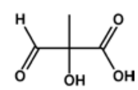
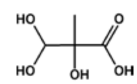
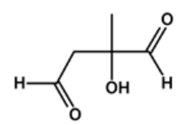
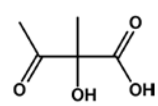
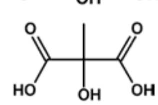
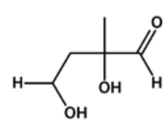
Repeating Units	Repetition Frequency	Corresponding Monomer	Monomer Name	Proposed Structure	Literature References
$C_4H_6O_3$ and $C_4H_8O_4$	571	$C_4H_8O_4$	2-methylglyceric acid (2MGA)		[6, 20, 57]
$C_3H_4O_2$	546	$C_3H_6O_3$ or $C_3H_4O_2$	lactic acid or methylglyoxal	 	[63, 80-82]
C_2H_2O and $C_2H_4O_2$	523	$C_2H_4O_2$	glycolaldehyde		[75, 77, 82]
C_2H_4O	510	$C_2H_6O_2$ or C_2H_4O	acetaldehyde or ethylene glycol	 	[this work]
$C_2H_2O_2$	506	$C_2H_4O_3$	hydroxyacetic acid		[this work]
$C_3H_4O_3$and $C_3H_6O_3$	495	$C_3H_6O_3$	hydrolyzed methylglyoxal		[64, 80]
$C_3H_6O_2$	462	$C_3H_6O_2$	hydroxyacetone		[20, 80, 82]
$C_4H_6O_2$ & $C_4H_8O_3$	462	$C_4H_8O_3$	2-methyl-glyceraldehyde		[this work]
$C_4H_6O_4$ & $C_4H_4O_3$	459	$C_4H_6O_4$ or $C_4H_8O_5$	oxo-acid of 2MGA or 3-hydroxy, 2MGA	 	[this work]
$C_5H_8O_3$	449	$C_5H_8O_3$	2-hydroxy-2-methylbutanedial		[this work]
$C_5H_6O_3$	396	$C_5H_8O_4$	2-hydroxy-2-methyl-3-oxobutanoic acid		[this work]
$C_4H_4O_4$ & $C_4H_2O_3$	344	$C_4H_6O_5$	hydroxy(methyl) propanedioic acid		[this work]
$C_5H_{10}O_3$	309	$C_5H_{10}O_3$	2,4-dihydroxy-2-methylbutanal		[this work]

Table S2: MS^2 and MS^3 tables of select ON oligomers. MS^2 product ions (a,b,c, etc.) are observed after CID of the parent ion (M). MS^3 ions (I, II, III, etc.) are the CID products of selected high-abundance MS^2 ions. Relative abundances are normalized to the most abundant ion observed within a certain level of CID. Losses are observed as neutral molecules. HNO_3 and CH_3NO_3 losses are characteristic of organic nitrates.

MS^2	**m/z = 266.051 (M)**		**Ionic Product**		**Abundance**	**Neutral Fragment**	
	$C_8H_{12}NO_9^-$		**m/z**	**Formula**	**(%)**	**Mass**	**Formula**
		a	189.040	$C_7H_9O_6$	100.0	M - 77.011	CH_3NO_3
		b	119.035	$C_4H_7O_4$	2.9	M - 147.016	$C_4H_5NO_5$
		c	164.020	$C_4H_6NO_6$	1.2	M - 102.031	$C_4H_6O_3$
		d	203.056	$C_8H_{11}O_6$	1.0	M - 62.995	HNO_3
MS^3	**m/z = 189.040 (a)**	**I**	87.009	$C_3H_3O_3$	100.0	102.031	$C_4H_6O_3$

MS^2	**m/z = 368.083 (M)**		**Ionic Product**		**Abundance**	**Neutral Product**	
	$C_{12}H_{18}NO_{12}^-$		**m/z**	**Formula**	**(%)**	**Mass**	**Formula**
		a	291.072	$C_{11}H_{15}O_9$	100.0	M-77.012	CH_3NO_3
		b	305.088	$C_{12}H_{17}O_9$	99.6	M-62.996	HNO_3
		c	266.051	$C_8H_{12}NO_9$	55.2	M-102.032	$C_4H_6O_3$
		d	292.079	$C_{11}H_{16}O_9$	14.2	M-76.004	CH_2NO_3
MS^3	**m/z = 291.072 (a)**	**I**	159.066	$C_7H_{11}O_4$	100.0	a - 132.006	$C_4H_4O_5$
	$C_{11}H_{15}O_9^-$	**II**	119.035	$C_4H_7O_4$	97.0	a - 172.037	$C_7H_8O_5$
		III	189.040	$C_7H_9O_6$	39.6	a - 102.032	$C_4H_6O_3$
		IV	203.056	$C_8H_{11}O_6$	35.2	a - 88.016	$C_3H_4O_3$
		V	192.027	$C_6H_8O_7$	20.1	a - 99.045	$C_5H_7O_2$
MS^3	**m/z = 305.088 (b)**	**I**	203.056	$C_8H_{11}O_6$	100.0	b - 102.032	$C_4H_6O_3$
	$C_{12}H_{17}O_9^-$	**II**	101.024	$C_4H_5O_3$	12.6	I - 102.032	$C_4H_6O_3$
MS^4	**m/z = 189.040 (aIII) $C_7H_9O_6^-$**	**a**	87.009	$C_3H_3O_3$	100.0	c - 102.032	$C_4H_6O_3$

MS^2	**m/z = 384.114 (M)**		**Ionic Product**		**Abundance**	**Neutral Product**	
A	**$C_{13}H_{22}NO_{12}^-$**		**m/z**	**Formula**	**(%)**	**Mass**	**Formula**
		a	321.119	$C_{13}H_{21}O_9$	100.0	M - 62.996	HNO_3
		b	282.082	$C_9H_{16}NO_9$	10.7	M - 102.032	$C_4H_6O_3$
		c	119.035	$C_4H_7O_4$	4.3	b - 163.047	$C_5H_9NO_5$
MS^3	**m/z = 321.119 (a)**	**I**	219.087	$C_9H_{15}O_6$	100.0	a - 102.031	$C_4H_6O_3$
	$C_{13}H_{21}O_9^-$	**II**	189.076	$C_8H_{13}O_5$	9.8	I - 30.011	CH_2O

MS^2 B	m/z = 384.114 (M) $C_{13}H_{22}NO_{12}^-$		Ionic m/z	Product Formula	Abundance (%)	Neutral Mass	Product Formula
		a	307.066	$C_{11}H_{15}O_{10}$	100.0	M - 77.048	$C_2H_7NO_2$
		b	263.077	$C_{10}H_{15}O_8$	83.1	a - 43.990	CO_2

MS^2	m/z = 398.093 (M) $C_{13}H_{20}NO_{13}^-$		Ionic m/z	Product Formula	Abundance (%)	Neutral Mass	Product Formula
		a	335.097	$C_{13}H_{19}O_{10}$	100.0	M-62.996	HNO_3
		b	266.051	$C_8H_{12}NO_9$	95.5	M-132.042	$C_5H_8O_4$
		c	321.082	$C_{12}H_{17}O_{10}$	78.7	M-77.011	CH_3NO_3
		d	296.062	$C_9H_{14}NO_{10}$	48.4	M-102.031	$C_4H_6O_3$
		e	189.040	$C_7H_9O_6$	28.5	b - 77.011	CH_3NO_3
		f	380.083	$C_9H_{18}NO_{12}$	12.3	M-18.010	H_2O
		g	233.066	$C_9H_{13}O_7$	10.9	M-165.027	$C_4H_7NO_6$
		h	119.035	$C_4H_7O_4$	9.6	b - 147.016	$C_4H_5NO_5$
MS^3	m/z = 335.097 (a)	I	233.066	$C_9H_{13}O_7$	100.0	a - 102.031	$C_4H_6O_3$
	$C_{13}H_{19}O_{10}^-$	II	203.055	$C_7H_9O_6$	22.2	a - 132.042	$C_5H_8O_4$
MS^3	m/z = 266.051 (b) $C_8H_{12}NO_9^-$	I	189.040	$C_7H_9O_6$	100.0	b - 77.011	CH_3NO_3

MS^2	m/z = 400.109 (M) $C_{13}H_{22}NO_{13}^-$		Ionic m/z	Product Formula	Abundance (%)	Neutral Mass	Product Formula
		a	298.077	$C_9H_{16}NO_{10}$	100.0	M - 102.032	$C_4H_6O_3$
		b	337.113	$C_{13}H_{21}O_{10}$	94.9	M - 62.996	HNO_3
		c	263.077	$C_{10}H_{15}O_8$	73.5	M – 137.032	$C_3H_6O_2$
		d	161.045	$C_6H_9O_5$	28.3	c - 102.032	$C_4H_6O_3$
		e	323.098	$C_{12}H_{19}O_{10}$	15.2	M - 77.011	CH_3NO_3
		g	119.035	$C_4H_7O_4$	13.7	c - 144.042	$C_6H_8O_4$
MS^3	m/z = 298.077 (a) $C_9H_{16}NO_{10}^-$	I	235.082	$C_9H_{15}O_7$	100.0	a - 62.996	HNO_3

MS^2	m/z = 410.0935 (M) $C_{14}H_{20}NO_{13}^-$		Ionic m/z	Product Formula	Abundance (%)	Neutral Mass	Product Formula
		a	308.062	$C_{10}H_{14}NO_{10}$	100.0	M - 102.032	$C_4H_6O_3$
		b	347.098	$C_{14}H_{19}O_{10}$	31.2	M - 62.996	HNO_3
		c	307.067	$C_{11}H_{15}O_{10}$	14.8	M - 103.027	$C_3H_5NO_3$
		d	333.082	$C_{13}H_{17}O_{10}$	11.0	M - 77.011	CH_3NO_3

MS^2	m/z = 470.115 (M) $C_{16}H_{24}NO_{15}^-$		Ionic Product m/z	Formula	Abundance (%)	Neutral Product Mass	Formula
		a	393.104	$C_{15}H_{21}O_{12}$	100.0	M - 77.011	CH_3NO_3
		b	368.083	$C_{12}H_{16}NO_{12}$	9.7	M - 102.032	$C_4H_6O_3$
		c	407.119	$C_{16}H_{23}O_{12}$	8.3	M - 62.996	HNO_3
MS^3	m/z = 393.104 (a)	I	291.072	$C_{11}H_{15}O_9$	100.0	a - 102.032	$C_4H_6O_3$
	$C_{15}H_{21}O_{12}^-$	II	221.067	$C_8H_{13}O_7$	50.0	a - 172.037	$C_7H_8O_5$
		III	189.041	$C_7H_9O_6$	35.3	II- 32.026	CH_3OH
		IV	273.061	$C_{11}H_{13}O_8$	8.7	I - 18.011	H_2O
		V	305.088	$C_{12}H_{17}O_9$	7.0	a - 88.016	$C_3H_4O_3$
		VI	261.098	$C_{11}H_{17}O_7$	5.8	V - 43.990	CO_2