Supplement to Yields of oxidized volatile organic compounds during the OH radical initiated oxidation of isoprene, methyl vinyl ketone, and methacrolein under high–NO_x conditions

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1 Lifetime detection method

The lifetime detection method speciates glyoxal and methylglyoxal by exploiting the difference in their time-dependent distribution of phosphorescence photons, an exponential decay, after excitation by a light source. This technique allows for differentiation with a single wavelength. The unique phosphorescent lifetimes of these molecules allow sample decays to be fit to a linear combination of these two decays as well as a constant background which accounts for PMT dark counts, laser scatter, and any ambient light which has reached the detector. The fitted prefactor of each ideal decay is proportional to its respective chemical. Limits of detection of 11 ppt and 270 ppt in 5 minutes (3σ) for glyoxal and methylglyoxal, respectively, are achieved with this method.

2 Measurement to model comparisons

Model performance was assessed by taking into account the slope, correlation coefficient (R^2), and relative residuals (resid) between measurement and model. Residuals are defined as the relative deviation between measurement and model:

$$resid = \left| \frac{[\mathrm{C}]_{model} - [\mathrm{C}]_{meas}}{[\mathrm{C}]_{meas}} \right| \tag{1}$$

The following equation was used to calculate a model-measurement fit parameter:

$$\mathrm{X} = (1 - R^2)(slope - 1)(\overline{resid}) \tag{2}$$

The mean of the relative residuals over the region of interest was used. Since a perfect fit between measurement and model would result in slope and R^2 values of 1, the difference between 1 and these values are taken. The smaller the residuals between measurement and model, the better the fit. Therefore, X would be zero for perfect model-measurement agreement. Negative values of X indicate that the model is predicting values lower than measurements. Model fits are shown in 2 . For the purposes of this assessment, first–generation production is defined as experiment start until the instantaneous production rate of a representative first–generation compound (e.g. MVK for an isoprene experiment, glycolaldehyde for MVK) is one–quarter of the initial instantaneous production rate. After this time, the experiment is considered to be in the higher generation production regime.

References

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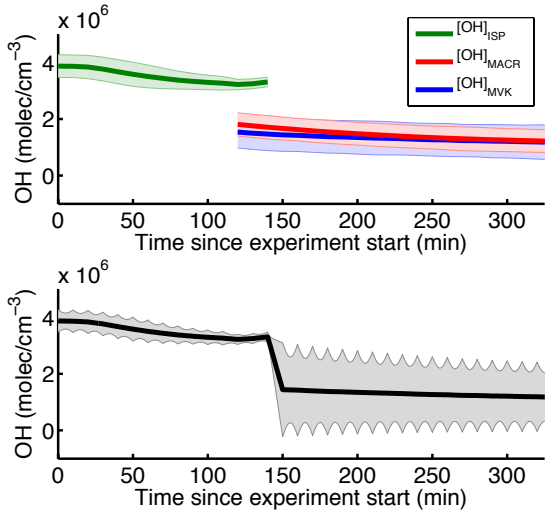


Fig. S1. OH calculated from isoprene, MVK, and MACR from Exp. 2 (see Sect. 3.2 for details). The uncertainty in OH is given as the 1σ error.

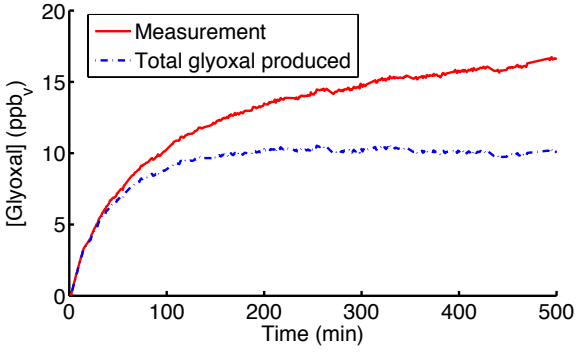


Fig. S2. Total produced glyoxal, corrected for loss to reaction with OH and photolysis from Exp. 3.

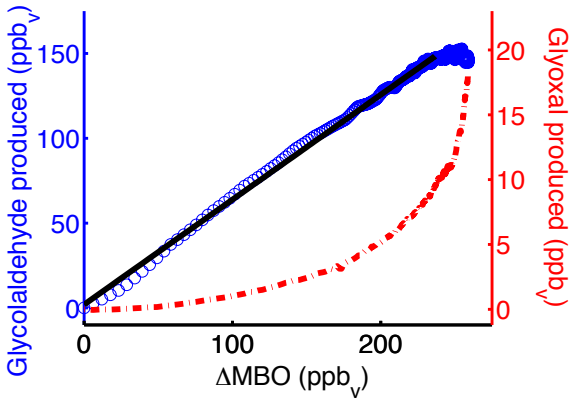


Fig. S3. Glycolaldehyde and glyoxal production as a function of MBO reacted (Exp. Chan 3). Formation of glycolaldehyde, a first generation oxidation product, has a linear relationship with reacted MBO. Glyoxal, a second generation oxidation product, produced primarily via oxidation of glycolaldehyde, has a nonlinear relationship and appears with a lag with respect to reacted MBO. The slope of the line observed for loss-corrected glycolaldehyde production versus reacted-MBO corresponds to the first generation yield.

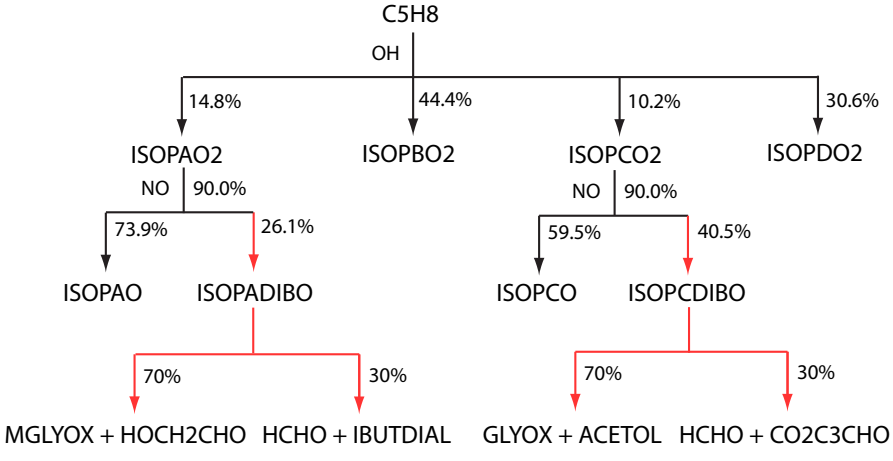


Fig. S4. Details of modifications of the MCM to incorporate first generation production of glyoxal, methylglyoxal, hydroxyacetone and glycolaldehyde from isoprene. Pathways highlighted in red are added reactions. Yields of competing pathways (ISOCO/IOSPCDIBO and ISOPAO/ISOPADIBO) were adjusted to match observed first generation production of glyoxal and methylglyoxal and to assure carbon balance. The branching ratios/yields for ISOPAO2, ISOPBO2, ISOPCO2 and ISOPDO2 from isoprene pathways are from the MCM v. 3.2 and the branching ratio of the ISOPADIBO and ISOPCDIBO products (70/30%) are taken from Paulot et al. (2009). Structures can be found in Table 3.

Table S1. MBO experiments, previously published by Chan et al. (2009) and low NO_x isoprene, MVK, and MACR experiments.

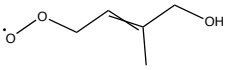
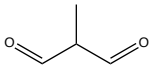
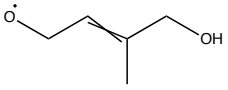
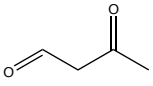
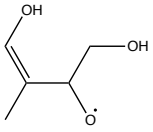
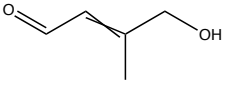
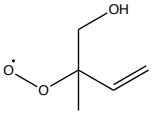
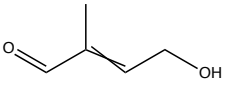
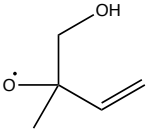
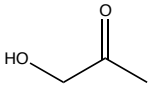
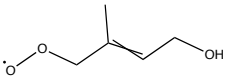
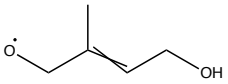
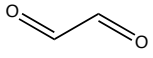
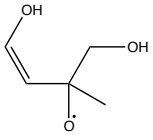
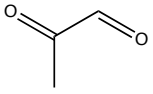
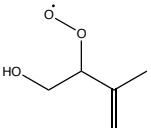
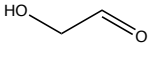
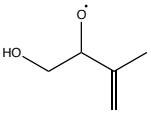
Exp. #	Date (mm/dd/yy)	Compound	Initial conc. (ppb)	Initial NO (ppb)	Initial NO_2 (ppb)	RH (%)	T (K)	Lights	OH source
C3		MBO	288	304	<1	4	295	10%	HONO
C4		MBO	255	422	640	4	295	10%	HONO
C5		MBO	239	539	522	66	293	10%	HONO
C6		MBO	299	<2	<1	6	298	50%	H_2O_2
C7		MBO	289	<2	<1	6	298	50%	H_2O_2
S1	10/18/09	Isoprene	22.22	1	<1	10	294	50%	H_2O_2
S2	10/20/09	MVK	25.59	1	2	10	293	50%	H_2O_2
S3	10/22/09	MACR	40.40	1	3	10	293	50%	H_2O_2
S4	10/24/09	Blank	None	1	<1	8	294	50%	H_2O_2

Table S2. Assessment of model to measurement agreement for all experiments.

Exp. #	Init cmpd	MBO		C5H8		MVK		MACR		HOCH2CHO		ACETOL		GLYOX		MGLYOX	
		Early	Late	Early	Late	Early	Late	Early	Late	Early	Late	Early	Late	Early	Late	Early	Late
Chan 3	MBO	4.6E-09	1.5E-09							1.5E-03	3.9E-04			5.4E-05	2.0E-05		
Chan 4	MBO	6.7E-09	6.5E-09											0.080	0.31		
Chan 6	MBO	7.8E-13	1.1E-12							-0.26	-0.030			-1.9E-03	-5.3E-03		
Chan 7	MBO	4.7E-10	4.8E-10							-0.43	-0.26			0.035	0.063		
S1	Isoprene			6.9E-10	7.9E-10	-0.17	-0.05	-0.09	-0.03	0.015	0.017	1.8E-03	6.7E-04	-2.1	-0.43	-0.019	-0.020
S2	MVK					2.6E-11	1.7E-11			-0.17	-0.16	10	10	-0.024	-0.068	-0.076	-0.023
S3	MACR							7.5E-10	7.3E-10			-5.0E-03	-2.8E-03			-0.038	-0.13
2	Isoprene	8.8E-08	2.4E-07			ND	ND	ND	ND	ND	ND	ND	ND	-0.018	-0.046	ND	ND
3	Isoprene	8.6E-08	5.6E-08			ND	ND	ND	ND	ND	ND	ND	ND	-6.3E-03	-0.015	ND	ND
4	Isoprene	-3.1E-03	-0.017			0.07	0.039	0.01	0.0049	-0.072	-0.040	-0.034	-0.045	ND	ND	ND	ND
5	Isoprene	3.8E-05	1.5E-04			-0.011	-3.5E-03	-3.3E-04	-1.0E-03	5.8E-03	1.7E-03	-1.5E-03	-8.3E-04	1.6E-03	5.9E-03	-0.032	-0.020
6	Isoprene																
7	Isoprene	-8.6E-07	-1.77E-06			6.4E-04	4.4E-04	4.7E-03	4.5E-03	2.9E-03	0.015	-0.016	-0.018	-0.016	-0.041	0.057	0.048
8	MVK					2.8E-10	2.1E-10			-0.072	-0.17	-88	-45	2.3E-05	2.8E-05	7.2E-03	0.017
9	MVK					2.7E-09	2.4E-09			-0.13	-1.1	-4.0	-18	4.5E-03	0.025	0.56	1.4
10	MACR							2.8E-09	20.E-09			-0.037	-0.085			-0.18	-0.86

ND=No data

Table S3. Molecular structures for compounds referenced in Fig. 6 and S4. All structures are from MCM v. 3.2 unless otherwise noted.

Compound	Structure	Compound	Structure
ISOPAO2		IBUTDIAL	
ISOPAO		CO2C3CHO	
ISOPADIBO[a,b]		HC4ACHO	
ISOPBO2		HC4CCHO	
ISOPBO		ACETOL	
ISOPCO2		HCHO	
ISOPCO		GLYOX	
ISOPCDIBO[a,b]		MGLYOX	
ISOPDO2		HOCH2CHO	
ISOPDO			

[a] Dibble (2004a,b)

[b] Paulot et al. (2009)