Table SI-1. k_{OH}, a, F, and SOA yield values for VOCs. Not all VOCs are listed. Yields are for M_o = 5 μg/m3. "(E)" indicates that the values are estimated.

Species	**k_{OH} (× 10^{12} cm^3 $molecules^{-1}$ s^{-1})**	**a**	**F**	**Y (%)**
CO	0.24	1.0	1	0
methane	0.0063	2.0	1	0
ethane	0.3	2.0	0.98	0
propane	1.1	2.0	0.96	0
n-butane	2.4	2.85	0.92	0
n-pentane	4.0	2.85 (E)	0.90	0
n-hexane	5.5	2.85 (E)	0.86	0
n-heptane	7.0	2.85 (E)	0.82	0
n-octane	8.7	2.85 (E)	0.77	0
n-nonane	10	2.85 (E)	0.75 (E)	0.3
n-decane	11.2	2.85 (E)	0.7 (E)	0.7
n-undecane	12.0	2.85 (E)	0.7 (E)	1.6
n-dodecane	13.0	2.85 (E)	0.7 (E)	2.8
isobutane	2.2	2.85 (E)	0.93	0
isopentane	3.7	2.85 (E)	0.93 (E)	0
2-methylpentane	5.4	2.85 (E)	0.86 (E)	0
2,2,4-trimethylpentane	9.0	2.85 (E)	0.86 (E)	0.1
cyclopentane	5.0	2.85 (E)	0.9 (E)	0
methylcyclopentane	5.7	2.85 (E)	0.85 (E)	0
cyclohexane	7.2	2.85 (E)	0.83 (E)	0
methylcyclohexane	10.0	2.85 (E)	0.83 (E)	0
ethene	9	2.0	0.99	0
propene	26	2.0	0.99	0
1-butene	31	2.0	0.98	0
trans-2-butene	64	2.0	0.97 (E)	0
cis-2-butene	56	2.0	0.96 (E)	0
1-pentene	31	2.0	0.95 (E)	0
trans-2-pentene	67	2.0	0.95 (E)	0
cis-2-pentene	65	2.0	0.95 (E)	0

1-hexene	37	2.0	0.93 (E)	0
trans-2-hexene	62	2.0	0.93 (E)	0
1-heptene	42	2.0	0.93 (E)	0
1,3-butadiene	67	2.0	0.93	0
benzene	1.2	2.0	0.9 (E)	10.6
toluene	6	2.0	0.9 (E)	6.1
o-xylene	13.7	2.0	0.9 (E)	3.6
m- and p-xylene	19	2.0	0.9 (E)	3.6
ethylbenzene	7.1	2.0	0.9 (E)	2.9
m- and p-ethyltoluene	15.6	2.0	0.9 (E)	1.4
o ethyltoluene	12.3	2.0	0.9 (E)	1.4
1,2,3 trimethylbenzene	58	2.0	0.9 (E)	1.4
1,2,4 trimethylbenzene	58	2.0	0.9 (E)	1.4
1,3,5 trimethylbenzene	33	2.0	0.9 (E)	1.4
isoprene	101	2.0	0.96	0.2 (Carlton)
limonene	171	2.0	0.9	6.1 (Griffin)
a-pinene	53.7	2.85	0.82	2.4
Formaldehyde	8	1.0	1	0
Acetaldehyde	16	3.0	1	0
Acetone	0.2	2.85 (E)	1	0

All species listed above were measured in both La Porte and Mexico City, with the exception of n-undecane and n-dodecane, which were only measured in Mexico City. Additional compounds that were measured but not included in Table SI-1 are listed below. (M) means the compound was only measured in Mexico City and (T) means the compound was only measured in La Porte.

2,2-dimethylbutane
2,3-dimethylbutane
ethylpentane (M)
3-methylpentane
2,4-dimethylpentane
2-methylhexane (T)
3-methylhexane (T)
2,2,4-trymethylpentane

2,5-dimethylhexane (M)
2,4-dimethylhexane (M)
2,3,4-trimethylpentane (M)
2,3-dimethylhexane (M)
2,3-methylheptane (M)
3-ethylhexane (M)
1-octene (M)
trans-4-octene (M)
cis-2-hexene (M)
1-decene (M)
3-methyl-1-butene
2-methyl-1-butene
2-methyl-2butene
butyne
ethyne
propyne
cyclooctene
cumene (T)
1,2,3,4 tetramethylbenzene (M)
3-methyl 2-butanone (T)
propanal (T)
methylethylketone (T)

Table SI-2. P(SOA)/P(O_x) calculations for VOCs measured at 06:30, 29 March 2006 at the T0 supersite in Mexico City. For the sake of producing atmospherically realistic absolute values for P(O_x) and P(SOA), OH concentrations of 10^6 and 6×10^6 molecules/cm^3 were used for the Mexico City (T0) and La Porte calculations, respectively, though the calculated ratio from eq. 9 is not affected by the choice of [OH]. SOA yields are based on M_o = 5 μg/m^3. Not all VOCs are listed. Aerosol yields are rounded to the nearest 0.1%.

Species	**Mixing ratio (ppbv)**	**P(O_x)** pptv/s	**%**	**P(SOA)** 10^{-6} μg m^{-3}/s	**%**
CO	3500	**0.8**	**8.0**	**0**	**0**
ethane	27.3	0.02	0.1	0	0
propane	205	0.44	4.1	0	0
n-butane	20.8	0.55	5.3	0	0
n-pentane	12.7	0.13	1.2	0	0
n-hexane	10.0	0.14	1.3	0	0
n-decane	0.34	0	0	0.2	0.1
n-undecane	0.44	0.04	0.4	2.4	1.2
n-dodecane	0.78	0.02	0.2	2.2	1.1
Alkanes Total		**2.9**	**27.3**	**10.5**	**5.3**
ethene	40.3	0.7	6.8	0	0
propene	9.40	0.5	4.5	0	0
Alkenes total		**4.0**	**38.1**	**0.5**	**0.2**
benzene	16	0.04	0.3	7.1	3.5
toluene	40	0.43	4.1	60.2	30.3
C2 benzenes	23.2	0.71	6.8	66.3	33.3
C3-benzenes	13.2	0.55	5.2	23.9	12.0
Aromatics total		**1.9**	**18.2**	**167**	**84.2**
Formaldehyde	8	0.06	0.6	0	0
Acetaldehyde	8.4	0.40	3.8	0	0
Acetone	16	0.01	0.1	0	0
OVOC total		**0.5**	**4.5**	**0**	**0**

isoprene	0.33	0.06	0.6	0.2	0
limonene	0	0	0	0	0
α-pinene	2.6	0.3	3.1	20.4	10.3
Biogenics total		**0.4**	**3.7**	**20.6**	**10.3**
Total		**10.5**	**100**	**197**	**100**
P(SOA)/P(O_x)		**19**			
(ug m^{-3}/ppmv)					

Table SI-3. P(SOA)/P(O_x) calculations for selected VOCs (not all) measured at La Porte at 14:00, 30 August 2000. An [OH] value of 6×10^6 molecules/cm^3 and an M_o value of 5 $\mu g/m^3$ was used for the calculations.

Species	**Mixing ratio (ppbv)**	**P(O_x)** pptv/s	**%**	**P(SOA)** 10^{-6} µg m^{-3}/s	**%**
CO	**210**	**0.30**	**2.6**	**0**	**0**
ethane	13.1	0.05	0.4	0	0
propane	5.2	0.07	0.6	0	0
n-butane	2.6	0.10	0.8	0	0
n-pentane	4.3	0.27	2.2	0.01	0
n-hexane	1.0	0.08	0.7	0.02	0
n-decane	0.1	0.01	0.1	0.4	1.5
Alkanes Total		**1.4**	**12.1**	**0.64**	**2.6**
ethene	25.7	2.75	23.2	0	0
propene	6.2	1.91	16.1	0	0
Alkenes total		**5.8**	**48.4**	**0.04**	**0.1**
benzene	1.2	0.02	0.1	3.1	12.5
toluene	1.0	0.06	0.5	8.6	34.9
xylenes	0.34	0.06	0.5	5.9	24.0
ethyl-benzenes	0.14	0.01	0	0.8	3.2
isopropyl-benzene	0.25	0.02	0.1	1.5	6.1
trimethyl-benzenes	0.05	0.02	0.1	0.9	3.7
Aromatics total		**0.19**	**1.6**	**20.8**	**84.6**
formaldehyde	28	1.34	11.3	0	0
acetaldehyde	7.1	2.04	17.1	0	0
acetone	12.3	0.05	0.4	0	0
OVOC total		**3.9**	**33.1**	**0.04**	**0.2**

isoprene	0.19	0.22	2.1	0.53	2.2
limonene	0.003	0	0	1.13	4.6
α-pinene	0.03	0.02	0.2	1.41	5.7
Biogenic VOCs		**0.25**	**2.1**	**3.1**	**12.5**
Total		**11.9**	**100**	**24.6**	**100**
P(SOA)/P(O_x)		**2.1**			
(ug m^{-3}/ppmv)					

Justification of assumptions used for eq. 9

$$P(O_X) = \sum_i k_i [OH][VOC_i](a_i F_i)$$

One approximation needed to quantify $P(O_x)$ using eq. 9 (above) is that HO_2 reacts solely with NO. This is a reasonable approximation for most periods of the day in both Mexico City and La Porte. Two example time periods are examined quantitatively. Typical NO and HO_2 concentrations at T0 in Mexico City at 09:00 are 100 ppbv and 2×10^7 molecules/cm^3, respectively (Dusanter et al., 2009). Using the rate constants from Sander et al. (Sander et al., 2006) and a water vapor mixing ratio 0.7%, we calculate that the ratio $(k_{HO2+HO2}[HO_2][HO_2])/(k_{HO2+NO}[HO_2][NO])$ is $5x10^{-6}$. At La Porte, a typical NO mixing ratio at 15:00 was 0.7 ppbv. For a water vapor mixing ratio of 2% and an estimated HO_2 mixing ratio of 30 pptv, the ratio is 0.03, indicating that this approximation is valid.

Constraints on the product of the SOA yield and the molecular weight of "missing" organic compounds based on OH reactivity measurements and calculations

We use the $P(SOA)/P(O_x)$ calculations from the morning of 29 March 2006 (table SI-2) as an example. Using a value of 10^6 molecules cm^{-3} for [OH] (this does not affect the results but is useful for creating "meaningful" values) we calculate that $P(SOA) = 2 \times 10^{-4}$ μg m^{-3}/s, $P(O_x)$ = 10.5 pptv/s, and $P(SOA)/P(Ox)$ = 19 μg m^{-3}/ppmv. If we assume that the $P(O_x)$ value is accurate (as described in section 4.3), then we must increase P(SOA) by a factor of ~6 to have $P(SOA)/P(O_x)$ reflect an $\Delta[OOA]/\Delta[O_x]$ value of 120 μg m^{-3}/ppmv. We add an additional term (with subscript "m") to the numerator of eq. 11 and set the sum equal to 1.2 μg m^{-3}/s:

$$\sum_i k_i[OH][VOC_i]y_i + k_m[OH][VOC_m]y_m = 1.2 \times 10^{-3} \text{ μg m}^{-3}\text{/s} \quad \text{(SI-1)}$$

$$k_m[VOC_m]y_m = 10^{-3} \text{ μg m}^{-3}\text{/s} \quad \text{(SI-2)}$$

With unit conversions added, the equation is

$$k_m[VOC_m][OH]Y_m MW_m N_A^{-1}(10^6 \text{ μg/g})\,(10^6 \text{cm}^3/\text{m}^3) = 10^{-3} \text{ μg m}^{-3}\text{ s}^{-1} \quad \text{(SI-3)}$$

where the units for the first five terms are (cm^3 $molecule^{-1}$ s^{-1}), (molecules cm^{-3}), (molecules cm^{-3}), (unitless), and (g mol^{-1}), respectively, and N_A is Avogadro's number (g/mol). The value of $k_m[VOC_m]$ is constrained by the agreement (within ~20% to 30%) between direct measurements of the total OH reactivity (Shirley et al., 2006) and those calculated using individual VOC measurements. Using the VOC measurements from 28 March at 06:30, we calculate the OH reactivity ($\sum k_{OH+VOC}[VOC]$) as 155 s^{-1} - well within the range of values measured in Mexico City during the early morning in 2003 (Shirley et al., 2006). If we assume that the missing SOA precursor organic compounds account for 30 s^{-1} (19% of the total OH reactivity), then we can solve for the product of $Y_m MW_m$ in

eq. SI-3 to obtain $Y_m MW_m$ = 20 g/mol. For example, if the average molecular weight of the missing SOA precursors is 378, then the SOA yield would be 5.3%.

References

DUSANTER, S., VIMAL, D., STEVENS, P. S., VOLKAMER, R. & MOLINA, L. T. (2009) Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign Part 1: Deployment of the Indiana University laser-induced fluorescence instrument. *Atmos. Chem. Phys.,* 9**,** 1665-1685.

SANDER, S. P., FRIEDL, R. R., GOLDEN, D. M., KURYLO, M. J., MOORTGAT, G. K., WINE, P. H., RAVISHANKARA, A. R., KOLB, C. E., MOLINA, M. J., FINLAYSON-PITTS, B. J., HUIE, R. E. & ORKIN, V. L. (2006) Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies: Evaluation Number 15. Jet Propulsion Laboratory.

SHIRLEY, T. R., BRUNE, W. H., REN, X., MAO, J., LESHER, R., CARDENAS, B., VOLKAMER, R., MOLINA, L. T., MOLINA, M. J., LAMB, B., VELASCO, E., JOBSON, T. & ALEXANDER, M. (2006) Atmospheric oxidation in the Mexico City Metropolitan Area (MCMA) during April 2003. *Atmos. Chem. Phys.,* 6**,** 2753-2765.