Electronic Supplementary Information for

Secondary Organic Aerosol Formation from Gasoline and Diesel Vehicle Exhaust under Light and Dark Conditions

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S1. Normalized detection sensitivities of proton transfer reaction-mass spectrometry (PTR-MS) and PTR + selective reagent ionization-mass spectrometry (SRI-MS) in the NO⁺ mode

Gas-phase organic compounds were measured by using two commercial quadrupoletype PTR-MS instruments (PTR-QMS 500 and PTR-QMS-hs, Ionicon Analytik Gesellschaft m.b.H., Innsbruck, Austria) ¹⁻³. The air in the 6-m³ fluorinated ethylene propylene (FEP) film bag was pumped with a diaphragm pump equipped to a PTR-QMS 500 at a flow rate of ~500 standard cm³ min⁻¹ (sccm) through a 1/4-inch Teflon line (4 mm i.d., ~5 m length) with an estimated residence time of ~7 s. An in-line PTFE filter (PF020, ϕ 47, pore size 2 µm, ADVANTEC, Tokyo, Japan) was used to prevent particles from entering the instruments.

First, the PTR-QMS 500 instrument, which was modified so that it could be used to perform an NO⁺ mode of PTR+SRI-MS measurements, was operated under the same conditions as those described previously ⁴. Briefly, NO⁺ reagent ions were produced from pure air flowing at 5.0 sccm in a hollow cathode discharge ion source. The sample air was introduced into the drift tube from a port beneath the ion source (flow rate ~50 sccm). The pressure and the temperature of the drift tube were maintained at 2.1 mbar and 105 °C, respectively, and the field strength, *E/N*, of the drift tube, where *E* is the electric field strength (V cm⁻¹) and *N* is the buffer gas number density (molecule cm⁻³), was set to 67 Td (1 Td = 10^{-17} cm² V molecule⁻¹). An aliquot of reagent ions and product ions was extracted through a small orifice into a quadrupole mass spectrometer. The ions were detected using a secondary electron multiplier that counted ion pulses. The NO⁺ count rate, calculated from the *m/z* 31 ($^{15}N^{16}O^{+}$ and $^{14}N^{17}O^{+}$) count rate multiplied by 250, was typically 1.7×10^{7} counts per second (cps) at an *E/N* value of 67 Td. The ratio between the O₂⁺ count rate and the NO⁺ count rate was typically 0.015. However, NO₂⁺ was poorly suppressed, and the ratio between the NO₂⁺ count rate and the NO⁺ count rate was 0.08.

Mixing ratios of alkanes, alkenes, dienes, aromatic hydrocarbons, and ketones were measured with the NO^+ mode of the PTR + SRI-MS ⁵. In the case of alkane detection, alkanes (M) were ionized by the following reaction :

$$NO^+ + M \rightarrow [M-H]^+ + HNO$$
 (A1)

Alkenes, dienes, and aromatic hydrocarbons were ionized mainly by the following reaction:

$$NO^+ + M \rightarrow M^+ + NO$$
 (A2)

where M is a target molecule, because they have typically lower ionization energies than NO⁺. Ketones were ionized by the following reaction:

$$NO^{+} + M \rightarrow [M+NO]^{+}$$
(A3)

Normalized detection sensitivity for the PTR+SRI-MS system is defined as the normalized counts per second (ncps) relative to a reagent ion count rate of 10^6 cps, when 1 part per billion by volume (ppbv) of the volatile organic compound (VOC) of interest is present in the sample. The normalized detection sensitivities for C₄–C₁₃ normal alkanes and C₅–C₁₃ branched-chain alkanes, which have been reported previously ⁴, were used in this work (see Table S1). We assumed that ratios between the straight-chain and branched-chain alkane concentrations were the same as those of fuels, which were analyzed by GC/MS. The influence of O₂⁺ reactions was carefully excluded from the quantification process of alkanes. For C₁₄–C₁₈ alkanes, whose ion signals were observed in the diesel-vehicle experiments, the typical detection sensitivity was assumed to be 4 ncps ppbv⁻¹.

Table S2 shows the normalized detection sensitivities for five hydrocarbons (isoprene, benzene, toluene, *p*-xylene, and 1,3,5-trimethylbenzene), one aldehyde (acetaldehyde), and two ketones (acetone and methyl vinyl ketone) using NO⁺ ionization. Detection sensitivities of 5.6 and 5.4 ncps ppbv⁻¹ were used as the typical detection sensitivities for the alkene and diene compounds for the analysis of the gasoline-vehicle (C4–C10) and the diesel-vehicle data (C4–C14), respectively. Similarly, detection sensitivities of 3.5 and 4.3 ncps ppbv⁻¹ were used as the typical detection sensitivities for aromatic hydrocarbons, except for C₆–C₉ benzenes in the analysis of the gasoline-vehicle (C₁₀–C₁₁-benzenes and naphthalene) and the diesel-vehicle data (C₁₀–C₁₄-benzenes, C₉–C₁₄-styrenes, and naphthalene), respectively. In addition, detection sensitivities of 4.0 and 3.8 ncps ppbv⁻¹ were used as the typical detection sensitivities for ketones in the analysis of the gasoline-vehicle (C₅–C₁₁) and the diesel-vehicle data (C₅–C₁₂), respectively. Aldehydes were also ionized by reaction (A1). A detection sensitivity of 2.7 ncps ppbv⁻¹ was used as the typical detection sensitivity of 2.7 ncps ppbv⁻¹ was used as the typical detection sensitivity of 2.7 ncps ppbv⁻¹ was used as the typical detection sensitivity for aldehydes (except for formaldehyde). Note that alkanes can be detectable as [M–H]⁺, the ion signals of which could overlap with those from saturated aldehydes. To determine mixing ratios of aldehydes, we used the sum of the isomeric aldehydes and ketones measured simultaneously by PTR-MS.

Second, the PTR-QMS-hs instrument, for which the reagent ion is H_3O^+ , was operated under the same conditions as those described previously ⁶. In brief, H_3O^+ ions were produced from a pure water vapor flow at 5.5 sccm in a hollow cathode discharge ion source. The sample air was introduced into the drift tube from a port beneath the ion source (flow rate ~50 sccm). Proton transfer from H_3O^+ enables soft ionization of chemical species (M) that have a proton affinity higher than that of water as follows:

$$H_{3}O^{+} + M \rightarrow [M+H]^{+} + H_{2}O \tag{A4}$$

The pressure and the temperature of the drift tube were maintained at 2.1 mbar and 105 °C, respectively, and the field strength was set to 108 Td. The count rate of H₃O⁺, calculated from the count rate at m/z 21 (H₃¹⁸O⁺) multiplied by 500, was typically 1 × 10⁷ counts per second (cps). The ratios of the count rates of O₂⁺ (m/z 32) and NO⁺ (m/z 30) to the count rate of H₃O⁺ were typically 0.02 and 0.004, respectively.

Table S3 shows the normalized detection sensitivities for five hydrocarbons (isoprene, benzene, toluene, *p*-xylene, and 1,3,5-trimethylbenzene), one aldehyde (acetaldehyde), and two ketones (acetone and methyl vinyl ketone) based on the H₃O⁺ ionization. Detection sensitivities of 8.3 and 10.0 ncps ppbv⁻¹ were used as the typical detection sensitivities for the sum of C₄-C₁₂ saturated aldehyde/ketone compounds in the analysis of the gasoline-vehicle and the diesel-vehicle data, respectively. The mixing ratios of saturated aldehydes were derived by subtracting the mixing ratios of saturated ketones determined by NO⁺ ionization-MS from those of the sum of saturated aldehyde/ketone compounds determined by H₃O⁺ ionization-MS. Then, the mixing ratios of alkanes could be obtained by subtracting the contribution of saturated aldehydes from the ion signals of $[M-H]^+$ obtained at NO⁺ ionization-MS. The detection sensitivity for formaldehyde was determined by the method described previously ⁷, using ion signals at *m/z* 31.

The gases and chemicals used for the calibration of the instruments are given below, including information on their suppliers and the stated purities of the chemicals. H₂CO/N₂ (0.910 ppmv; Takachiho, Tokyo, Japan). n-Butane/N₂ (9.98 ppmv; Japan Fine Products (JFP), Kawasaki, Japan). n-Pentane/N₂ (9.89 ppmv; JFP). Isopentane/N₂ (9.72 ppmv; JFP). A ten-VOC premixed standard gas containing toluene (4.98 ppmv), 1,3,5trimethylbenzene (1.01 ppmv), acetonitrile (4.95 ppmv), acetaldehyde (5.04 ppmv), methanol (5.05 ppmv), benzene (5.01 ppmv), acetone (4.99 ppmv), isoprene (4.99 ppmv), p-xylene (4.99 ppmv), and methyl vinyl ketone (5.00 ppmv) balanced with N₂ (JFP). n-Hexane (>96%; Wako Chemicals, Osaka, Japan). n-Heptane (>99.5%; Tokyo Chemical Industry (TCI), Tokyo, Japan). n-Octane (>99.5%; TCI). n-Nonane (>99.5%; TCI). n-Decane (>99.5%; TCI). n-Undecane (>99.5%; TCI). n-Dodecane (>99.5%; TCI). n-Tridecane (>98%; Kanto Chemicals, Tokyo, Japan). 2-Methylpentane (>99%; Sigma-Aldrich, St Louis, MO, USA). 2-Methylhexane (>99.0%; TCI). 2-Methylheptane (>98.0%; TCI). 2-Methyloctane (>99.0%; TCI). 2-Methylnonane (>99.0%; Sigma-Aldrich).

S2. SOA yields from alkenes and dienes

SOA formation from anthropogenic alkenes (including dienes) has not been considered in most recent air quality models ⁸⁻¹⁰ with some exception ¹¹. As summarized in Figure S1, SOA has been reported to be produced from \geq C8 terminal alkenes, \geq C14 internal alkenes, \geq C5 cycloalkenes, and \geq C4 dienes ¹¹⁻¹⁶. Experimental studies of SOA formation from anthropogenic dienes are limited ¹⁴, whereas SOA from biogenic dienes (e.g., isoprene, monoterpene, and sesquiterpene) have been extensively examined in previous studies ^{14, 17}. Sato, *et al.* ¹⁴ have indicated that the SOA yields of butadiene (4–18% with SOA 10–100 µg m⁻³) are similar to those of isoprene. In this study, we assumed that the SOA yields of anthropogenic dienes were similar to those of biogenic dienes.

Figure S2 summarizes the fraction of oxidized alkenes measured by the PTR-MS. This figure indicates the oxidized amounts of alkenes over the first two hours of the experiments. Only internal alkenes can be measured by the PTR-MS¹⁸. Emission rates of C6–C11 1-alkenes from gasoline and diesel vehicles are summarized ¹⁹, and contributions of compounds with \geq C8 terminal alkenes are negligible. Yang, *et al.* ²⁰ have indicated that low-carbon number alkenes could contribute to gasoline-vehicle SOA through aldol condensation. However, their contributions are not yet quantified, and SOA formation from terminal alkenes (OLE1) was thus not included in this study. We could not separate dienes and cycloalkenes with PTR-MS measurements. However, both of these types of

compounds have similar SOA formation yields, as shown in Figure S1. Based on consideration of SOA formation yields (Figure S1) and composition of anthropogenic alkenes/dienes, SOA yields from alkenes/dienes were estimated to be 2.8–6.4% for gasoline exhaust and 5.5–11.6% for diesel exhaust, as summarized in Table S8. It is thus likely that alkenes/dienes from vehicle exhaust may have contributed to SOA production during our experiments. The SOA yields for diesel vehicles of OLE2 compounds were close to those estimated with VBS parameters in Murphy and Pandis ¹¹ (6.5–9.2%), but those for gasoline vehicles were about half the yields estimated from VBS parameters. Thus, we used the SOA yields of OLE2 for diesel-exhaust SOA, and we halved the SOA yields for gasoline-exhaust SOA (Table S7). We used the same SOA yields from alkanes for all the oxidants (OH, O₃, and NO₃ in our simulation), because the differences of the SOA yields for the different oxidants were not systematically quantified.

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Table S1. Product ion(s) and the normalized detection sensitivities (ncps $ppbv^{-1}$) for normal and branched alkanes (C_nH_{2n+2}) based the detection via PTR+SRI-MS (NO⁺ mode)

C_nH_{2n+2}	NO^+ reaction			C_nH_{2n+2}			
n	<i>m/z</i> ,	normal	branched	п	m/z	normal	branched
3	43	0.02 ± 0.01^{a}	_	11	155	2.74 ± 0.61^{a}	3.8 ^b
4	57	0.04 ± 0.01^{a}	2.4 ± 0.1^{a}		113	0.04 ± 0.01^{a}	
5	71	0.08 ± 0.01^{a}	3.2 ± 0.1^{a}		99	0.07 ± 0.02^{a}	
6	85	0.23 ± 0.05^{a}	4.1 ± 0.9^{a}		85	0.11 ± 0.03^{a}	
7	99	0.27 ± 0.06^{a}	3.24 ± 0.72^{a}		71	0.08 ± 0.02^{a}	
	57	0.27 ± 0.07^{a}	1.65 ± 0.37^{a}		57	0.07 ± 0.03^{a}	
8	113	0.93 ± 0.21^{a}	2.84 ± 0.64^{a}	12	169	4.69 ± 1.05^{a}	3.9 ^b
	71	0.31 ± 0.08^{a}	0.71 ± 0.16^{a}		127	0.04 ± 0.01^{a}	
	57	0.22 ± 0.05^{a}	0.49 ± 0.12^{a}		113	0.07 ± 0.02^{a}	
9	127	1.72 ± 0.38^{a}	3.74 ± 0.84^{a}		99	0.08 ± 0.02^{a}	
	85	0.16 ± 0.05^{a}	0.30 ± 0.07^{a}		85	0.09 ± 0.03^{a}	
	71	0.26 ± 0.06^{a}	0.51 ± 0.12^{a}		71	0.08 ± 0.03^{a}	
	57	0.13 ± 0.04^{a}	0.23 ± 0.06^{a}		57	0.08 ± 0.03^{a}	
10	141	2.21 ± 0.49^{a}	2.35 ± 0.53^{a}	13	183	3.25 ± 0.73^{a}	4.0 ^b
	99	0.06 ± 0.02^{a}	0.06 ± 0.02^{a}		169	0.02 ± 0.01^{a}	
	85	0.15 ± 0.04^{a}	0.17 ± 0.04^{a}		127	0.03 ± 0.01^{a}	
	71	0.14 ± 0.04^{a}	0.25 ± 0.06^{a}		113	0.04 ± 0.01^{a}	
	57	0.08 ± 0.03^{a}	0.12 ± 0.03^{a}		99	0.02 ± 0.01^{a}	
	43	_	0.17 ± 0.06^{a}		85	0.04 ± 0.01^{a}	
					71	0.04 ± 0.02^{a}	
					57	0.05 ± 0.02^{a}	

^aCalibrated at an E/N of 67 Td in the drift tube. The error limits represent the 95% confidence interval calculated using the *t*-test.; ^bEstimated from the rate constants for the reactions of NO⁺ with these alkanes.

 Table S2. Normalized detection sensitivity^a (ncps ppbv⁻¹) for some hydrocarbons and

 oxygenated compounds based on their detection via PTR+SRI-MS (NO⁺ mode)

Compound (M)	mpound (M) m/z $[M-H]^+$		\mathbf{M}^+	$[M+NO]^+$
	Alk	enes and dienes		
Isoprene	68		5.6 ± 1.0	
	Arom	atic hydrocarboi	ıs	
Benzene	78		4.3 ± 0.7	
	108			1.3 ± 0.2
Toluene	92		5.5 ± 1.0	
<i>p</i> -Xylene	106		4.5 ± 0.9	
1,3,5-	120		3.5 ± 0.7	
Trimethylbenzene				
		Aldehydes		
Acetaldehyde	43	2.7 ± 0.5		
		Ketones		
Acetone	88			2.9 ± 0.5
Methyl vinyl ketone	100			4.0 ± 0.8

(A) For GDI and GPI data analysis

(B) For Diesel-P and Diesel-T data analysis

Compound (M)	m/z	$[M-H]^+$	\mathbf{M}^+	$[M+NO]^+$
	Alk	enes and dienes		
Isoprene	68		5.4 ± 0.1	
	Arome	atic hydrocarbor	ıs	
Benzene	78		3.9 ± 0.1	
	108			1.2 ± 0.1
Toluene	92		5.2 ± 0.3	
<i>p</i> -Xylene	106		4.8 ± 0.7	
1,3,5-	120		4.3 ± 0.9	
Trimethylbenzene				
		Aldehydes		
Acetaldehyde	43	2.7 ± 0.1		
		Ketones		
Acetone	88			2.6 ± 0.1
Methyl vinyl ketone	100			3.8 ± 0.2

^aError limits represent the 95 % confidence interval calculated using the *t*-test.

Table S3. Normalized detection sensitivity^a (ncps ppbv-1) for some hydrocarbons and oxygenated compounds based on their detection by PTR-MS

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Compound (M)	m/z	$[M+H]^+$					
Alkenes c	and dienes						
Isoprene	69	4.4 ± 0.1					
Aromatic hydrocarbons							
Benzene	79	4.2 ± 0.2					
Toluene	93	4.2 ± 0.4					
<i>p</i> -Xylene	107	3.6 ± 0.4					
1,3,5-	121	7.5 ± 0.4					
Trimethylbenzene							
Alde	hydes						
Acetaldehyde	45	13.5 ± 0.2					
Ketones							
Acetone	59	11.2 ± 0.2					
Methyl vinyl ketone	71	8.3 ± 0.2					

(B) For DieselP and DieselT data analysis

Compound (M)	<i>m/z</i> ,	$[M+H]^+$				
Alkenes	and dienes					
Isoprene	69	5.4 ± 0.1				
Aromatic h	ydrocarbo	ons				
Benzene	79	6.2 ± 0.1				
Toluene	93	6.8 ± 0.4				
<i>p</i> -Xylene	107	6.8 ± 0.8				
1,3,5-	121	6.0 ± 1.2				
Trimethylbenzene						
Alde	ehydes					
Acetaldehyde	45	12.5 ± 0.3				
Ketones						
Acetone	59	11.8 ± 0.6				
Methyl vinyl ketone	71	10.0 ± 0.5				

^aError limits represent the 95 % confidence interval calculated using the t-test.

Vehicle	Condition	Decay rate (h ⁻¹)	Estimation
GDI	Light	-0.19	EC
	Dark	-1.41	SMPS (Number)
GPI	Light	-0.19	EC
	Dark	-0.19	EC
Diesel-P	Light	-0.36	SMPS (Volume)
	Dark	-0.34	SMPS (Volume)
Diesel-T	Light	-0.21	SMPS (Volume)
	Dark	-0.45	SMPS (Volume)

Table S4. Estimated decay rate of OA due to particle wall loss and the estimation methods.

Abbreviations: EC: Elemental carbon, SMPS: Scanning mobility particle sizer

Table S5. The organic compounds measured by PTR-MS in this study mapped to surrogate VOCspecies based on SAPRC99.

Species in SAPRC99	Components measured by PTR-MS	SOA precursors
ALK4	C ₅ -C ₇ Alkanes	Yes
ALK5	C ₇ -C ₁₁ Alkanes	Yes
ARO1	C7-C9 Monoalkyl Benzenes	Yes
ARO2	C8-C9 Polyalkyl Benzenes	Yes
OLE1	C ₃ -C ₁₁ Terminal Alkenes	No
OLE2	C ₄ -C ₁₁ Internal Alkenes	Yes
ISOP	Isoprene	Yes
ACET	C ₃ Ketone	No
MEK	C ₄ -C ₅ Ketones	No
PROD2	C ₇ -C ₁₁ Ketones	No
НСНО	C ₁ Aldehyde	No
ССНО	C ₂ Aldehyde	No
RCHO	C ₃ -C ₁₁ Aldehydes	No
НСООН	Formic Acid	No
CCO_OH	Acetic Acid	No

Table S6. Initial concentrations of the eight experiments mapped to aggregated VOC species in SAPRC99. The unit for SVOC and IVOC is $\mu g m^{-3}$; for other species, it is ppm. The concentrations of alkane IVOCs are reported for compounds with saturation concentrations (C^*) of 10⁴, 10⁵, or 10⁶ $\mu g m^{-3}$; those of aromatic IVOCs are reported for compounds with C^* of 10⁵ and 10⁶ $\mu g m^{-3}$; those of SVOCs are reported for compounds with C^* of 0.1, 1, 10, or 100 $\mu g m^{-3}$.

Species	GDI	GPI D		Diesel-P		Diesel-T		
	Light	Dark	Light	Dark	Light	Dark	Light	Dark
ALK4	184.2	182.0	133.4	213.2	43.2	51.1	48.9	32.9
ALK5	94.0	116.2	63.0	97.1	88.0	98.0	123.1	96.1
ARO1	123.3	190.1	86.3	108.5	6.3	7.7	6.1	3.9
ARO2	122.9	424.1	180.4	208.9	18.3	20.6	32.0	29.9
OLE1	49.1	60.9	61.5	59.2	176.8	193.8	110.9	96.5
OLE2	88.6	111.1	80.8	77.3	100.2	110.2	77.5	65.4
ISOP	6.8	7.2	5.7	4.7	10.7	13.7	7.6	7.7
ACET	6.9	8.5	3.6	13.1	100.9	104.9	63.9	53.6
MEK	3.2	5.9	3.1	12.5	32.4	34.1	25.6	19.5
PROD2	0.7	0.9	0.5	0.6	16.1	19.9	15.5	9.9
НСНО	5.0	9.8	2.7	3.6	105.0	128.2	111.3	91.1
ССНО	18.5	20.9	19.5	24.8	162.2	198.2	146.3	104.0
RCHO	3.2	2.9	3.7	2.6	9.4	16.6	16.4	6.8
НСООН	2.6	11.5	3.8	6.3	13.7	12.4	32.2	15.2
CCO_OH	0.9	2.0	0.8	1.5	140.2	147.6	104.2	87.3
IVOC-ALK ($C^* = 10^6$)	12.2	22.9	12.5	14.7	388.3	409.3	376.4	316.8
IVOC-ALK ($C^* = 10^5$)	4.1	7.6	4.2	4.9	456.7	481.4	442.7	372.6
IVOC-ALK ($C^* = 10^4$)	6.1	11.5	6.2	7.4	363.9	383.6	352.8	296.9
IVOC-ARO ($C^* = 10^6$)	50.7	95.5	52.0	61.4	4.9	5.1	4.7	4.0
IVOC-ARO ($C^* = 10^5$)	12.2	22.9	12.5	14.7	9.8	10.3	9.5	8.0
SVOC ($C^* = 10^{-1}$)	1.4	1.2	0.5	0.4	0.1	0.1	8.1	3.6
SVOC ($C^* = 10^0$)	5.1	4.4	1.7	1.6	0.2	0.2	10.4	4.7
SVOC ($C^* = 10^1$)	27.7	23.7	9.1	8.8	11.7	12.9	30.0	13.5
SVOC ($C^* = 10^2$)	19.2	16.5	6.3	6.1	6.0	6.6	28.8	13.0

Table S7. NO_x-dependent stoichiometric mass-based product yields used in simulations. The yields from surrogate VOC species in SAPRC07 are with saturation concentrations (C^*) of 1, 10, 100, and 1000 µg m^{-3 11}.

Precursors	SOA yields in high NO _x			SOA yields in low NO _x				
	<i>C</i> *=1	C*=10	C*=100	C*=1000	<i>C</i> *=1	C*=10	C*=100	C*=1000
ALK5	0	0.15	0	0	0	0.30	0	0
ARO1	0.003	0.165	0.3	0.435	0.075	0.225	0.375	0.525
ARO2	0.002	0.195	0.3	0.435	0.075	0.3	0.375	0.525
OLE2 (gasoline)	0.0015	0.01275	0.04125	0.135	0.01125	0.02175	0.0645	0.1875
OLE2 (diesel)	0.003	0.0255	0.0825	0.27	0.0225	0.0435	0.129	0.375
ISOP	0.0003	0.0225	0.015	0	0.009	0.030	0.015	0

 Table S8. SOA yields of OLE2 estimated from individual compounds (Section S2) and volatility

 basis set (VBS) parameters.

Case	Settings	SOA yield
From individual compounds ^a	Gasoline, high	$6.4\%\pm0.9\%$
	Gasoline, low	$2.8\%\pm0.6\%$
	Diesel, high	$11.6\%\pm0.4\%$
	Diesel, low	$5.5\%\pm0.4\%$
From VBS parameters ^b	$(OA=50 \ \mu g \ m^{-3})$	6.5%
	$(OA=100 \ \mu g \ m^{-3})$	9.2%

^a SOA yields of individual compounds (high and low cases) are referred to Figure S1. ^b SOA yield parameters of OLE2 in high NOx conditions under the VBS framework are taken from Murphy and Pandis ¹¹.

Table S9. Stoichiometric mass-based product yields from IVOC with saturation concentrations (C^*) of 0.1, 1, 10, and 100 µg m⁻³.²¹ Yields from alkane (ALK) and aromatic (ARO) VOC with $C^* = 10^4 - 10^6 \mu \text{g m}^{-3}$ are shown.

Precursors	SOA yield			
	C*=0.1	<i>C</i> *=1	C*=10	C*=100
IVOC-ALK ($C^* = 10^6 \mu \text{g m}^{-3}$)	0.009	0.045	0.118	0.47
IVOC-ALK ($C^* = 10^5 \mu \text{g m}^{-3}$)	0.051	0.061	0.394	0.494
IVOC-ALK ($C^* = 10^4 \mu g m^{-3}$)	0.068	0.083	0.523	0.239
IVOC-ARO ($C^* = 10^6 \mu g m^{-3}$)	0.022	0.109	0.251	0.005
IVOC-ARO ($C^* = 10^5 \mu g m^{-3}$)	0.143	0.021	0.329	0.358

$C^* (\mu g \mathrm{m}^{-3})$	0.1	1	10	100	1000
Aromatic SOA		0.8	0.7	0.6	0.5
Alkane/alkene SOA		0.6	0.4	0.3	0.25
Aromatic IVOC	0.7	0.6	0.5	0.45	
Alkane IVOC	0.35	0.3	0.25	0.2	

Table S10. Distributions of O:C ratios for first-generation SOA products with saturation concentrations of 0.1, 1, 10, 100, and 1000 μ g m⁻³.

Table S11. Emission factors for NO_x, NMHC, EC, and POA and production factor of SOA from four vehicles.

		NOx	NMHC	EC			SOA
				EC	FUA	(light)	(dark)
GDI	(mg kg-fuel ⁻¹)	253.9	1658.1	55.33	18.98	21.27	131.85
	$(mg \ km^{-1})$	11.1	72.5	2.42	0.83	0.93	5.76
GPI	(mg kg-fuel ⁻¹)	171.0	1031.7	0.65	3.82	40.32	60.46
	$(mg \ km^{-1})$	7.9	47.6	0.03	0.17	1.82	2.73
Diesel-P	(mg kg-fuel ⁻¹)	2566.0	897.3	0	1.75	35.07	287.97
	$(mg \ km^{-1})$	132.0	47.1	0	0.09	1.84	15.11
Diesel-T	(mg kg-fuel ⁻¹)	14945.7	914.1	153.42	18.39	7.45	235.31
	$(mg \ km^{-1})$	1524.6	93.2	15.65	1.88	0.76	24.04

Table S12. Comparison of emission factors of EC and POA or production factors of SOA between this study and previous studies. Units of emission and production factors are mg kg-fuel⁻¹, though data reported in a unit of mg km⁻¹ are also shown in parentheses.

References	Vehicle type	EC	POA	SOA	OH exposure
		mg kg-fuel ⁻¹	mg kg-fuel ⁻¹	mg kg-fuel ⁻¹	10 ⁶ molec. cm ⁻³ h
This study (light)	GDI	55	19	21	2
		(2.4 mg km^{-1})	(0.8 mg km^{-1})		
	GPI	0.7	3.8	40	2
	011	$(0.03 \text{ mg km}^{-1})$	(0.2 mg km^{-1})		
Du, <i>et al</i> . ²²	GDI	11	42	55	5
	GPI	2.4	25	21	5
Saliba, <i>et al.</i> ²³	GDI	(3 mg km ⁻¹)	(0.4 mg km^{-1})	_	
	GPI	(0.6 mg km^{-1})	(0.6 mg km^{-1})	-	
Platt, et al. ²⁴	GDI	15–29	2.4–7.2	5.7–28	10
	GPI	9.5	7.8	45	10
Gordon, <i>et al.</i> ²⁵	GDI	33	2.4	17	5
	GPI	0–122	0–136	0–108	5
Zhang, et al. ²⁶	GPI?	-	0.32–1.5	9.1–23	1.4–4.7
Pieber, et al. ²⁷	GDI	5–70	3–8	16–500	39–160
Roth, <i>et al</i> . ²⁸	GDI	$(1.5-1.9 \text{ mg km}^{-1})$	$(0.5-0.6 \text{ mg km}^{-1})$	(1.4–3.9 mg km ⁻¹)	
Nordin, et al. ²⁹	GPI	_	0.1–2.9	5–480	5

(A) Gasoline

(B) Diesel

References	Vehicle type	EC	РОА	SOA	OH exposure
		mg kg-fuel ⁻¹	mg kg-fuel ⁻¹	mg kg-fuel ⁻¹	10^{6} molec. cm ⁻³ h
This study (light)	DOC + DPF	0.0	1.8	35	2
	DOC	153.4	18.4	7	2
Platt, et al. ²⁴	DOC + DPF	0.1–1	1.1–2	_	10
Gordon, <i>et al.</i> ³⁰	DOC + DPF	0–5.5	0–8.8	0–10	10–20
	DOC	216–546	47–124	67–85	
	None	53-792	77–545	57–166	
Jathar, et al. ³¹	DOC + DPF		43–70	9.5–85	27
Chirico, <i>et al.</i> ³²	DOC + DPF	0	0	12	(5 h)
	DOC	466–763	136–143	19–47	
	None	490	81	254	

Abbreviations: GDI: gasoline direct injection, GPI: gasoline port-fuel injection, DOC: diesel oxidation catalyst, DPF: diesel particle filter.

Table S13. Normalized mean error (NME, $\frac{\sum_{i=1}^{n} |M_i - O_i|}{\sum_{i=1}^{n} (O_i)}$) and normalized mean bias (NMB, $\frac{\sum_{i=1}^{n} (M_i - O_i)}{\sum_{i=1}^{n} (O_i)}$) of the OA concentrations and O:C ratios during the first 2 h of the individual experiments (Table 1) based on the standard simulation. M_i and O_i represent simulated and observed values, respectively.

Vehicle	Condition	OA concentr	ration	O:C ratio	
		NME (%)	NMB (%)	NME (%)	NMB (%)
GDI	Light	35.0	-28.9	9.6	-9.3
	Dark	7.7	7.2	4.6	-4.1
GPI	Light	43.4	-36.5	13.6	-13.6
	Dark	14.7	-8.5	9.0	9.0
Diesel-P	Light	97.3	-96.0	11.4	11.4
	Dark	11.0	-9.3	16.1	15.7
Diesel-T	Light	18.0	10.9	45.9	-45.9
	Dark	6.9	-5.4	8.0	8.0



Figure S1. SOA yields of alkenes and dienes with different carbon numbers. Data with OA concentrations of ~100 (or \geq 50) µg m–3 were selected if the OA concentrations were reported. References: Ma09: Matsunaga, *et al.* ¹², G05: Gong, *et al.* ¹³, N17: Nakayama, *et al.* ¹⁵, Mu09: Murphy and Pandis ¹¹, S11: Sato, *et al.* ¹⁴, K04: Keywood, *et al.* ¹⁶. Sensitivity calculations are those used for the model calculation.



Figure S2. Mass fraction of oxidized alkenes/dienes during the first 2 h after t = 0 during the individual experiments.



Figure S3. Budget of production and loss rates of the OH, HO₂, and RO₂ radicals (left axis) and branching ratio, β , estimated with Equation (3) (right axis) in the simulation on a linear timescale.



Figure S4. Simulated OH concentrations in the eight experiments on a logarithmic timescale.



Figure S5. (a) Time-series of observed concentrations of organic aerosol (OA) and (b) O:C ratios, (c) and scatterplots of O:C ratios and secondary organic aerosol (SOA)/OA ratios under light and dark conditions. SOA/OA ratios were determined only for the experiments with a gasoline-direct injection (GDI) vehicle and a diesel-fueled truck (Diesel-T). The left and right axes show the scales for OA concentrations under light and dark conditions, respectively.



Figure S6. Observed and simulated concentrations of sum of aromatic VOCs in the eight experiments.



Figure S7. Observed concentrations of SOA and NO, and branching ratio (β) estimated with Equation (3).



Figure S8. Contributions of oxidants to the reactions with OLE2 during the first 2 h of the individual experiments.