Environmental Science & Technology

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Article

Effect of Inorganic Salts on N-Containing Organic Compounds Formed by Heterogeneous Reaction of NO_2 with Oleic Acid

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Cite This: *Environ. Sci. Technol.* 2021, 55, 7831−7840

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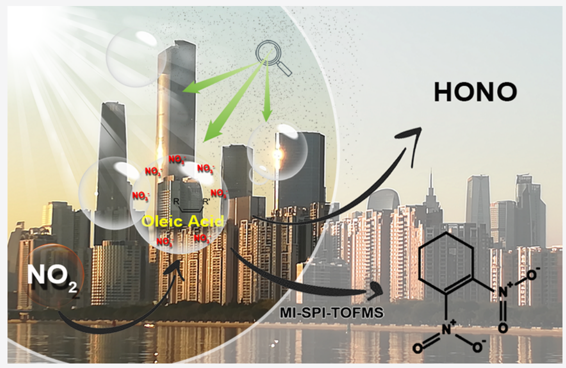
ABSTRACT: Fatty acids are ubiquitous constituents of grime on urban and indoor surfaces and they represent important surfactants on organic aerosol particles in the atmosphere. Here, we assess the heterogeneous processing of NO_2 on films consisting of pure oleic acid (OA) or a mixture of OA and representative salts for urban grime and aerosol particles, namely Na_2SO_4 and $NaNO_3$. The uptake coefficients of NO_2 on OA under light irradiation (300 nm < λ < 400 nm) decreased with increasing relative humidity (RH), from $(1.4 \pm 0.1) \times 10^{-6}$ at 0% RH to $(7.1 \pm 1.6) \times 10^{-7}$ at 90% RH. The uptake process of NO_2 on OA gives HONO as a reaction product, and the highest HONO production was observed upon the heterogeneous reaction of NO_2 with OA in the presence of nitrate (NO_3^-) ions. The formation of gaseous nitroaromatic compounds was also enhanced in the presence of NO_3^- ions upon light-induced heterogeneous processing of NO_2 with OA, as revealed by membrane inlet single-photon ionization time-of-flight mass spectrometry (MI-SPI-TOFMS). These results suggest that inorganic salts can affect the heterogeneous conversion of gaseous NO_2 on fatty acids and enhance the formation of HONO and other N-containing organic compounds in the atmosphere.



KEYWORDS: *oleic acid, heterogeneous reactions, nitrogen oxides, nitrous acid, nitroaromatic compounds, urban air pollution, indoor air*

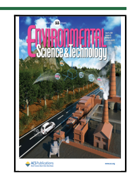
INTRODUCTION

Atmospheric aerosol particles are loaded with organic and inorganic compounds.[1] Organic compounds can affect the optical properties and hygroscopic growth of aerosol particles, and they can influence the heterogeneous reactions between oxidant species and inorganic constituents.[2] Among the organic compounds, fatty acids are emitted in the air by coal burning[3] and cooking.[4−6] Fatty acids represent one important portion of the organic compounds in aerosol and because of amphiphilic properties and poor solubility in the aqueous phase, they act as surfactants and have the ability to create a coating over the aerosol particle core.[7] The surface of aerosols that mainly contain sulfate (SO_4^{2-}) and nitrate (NO_3^-) can, for instance, be enriched with unsaturated fatty acids.[8] Oleic acid (OA, $C_{18}H_{34}O_2$) or 9-octadecenoic acid is an unsaturated fatty acid that is routinely detected in aerosol particles and can be used as a marker compound for cooking.[9,10] Recently, real-time measurements in indoor environments detected over 600 compounds among primary emitted cooking compounds and secondary products formed by reactions with hydroxyl radicals (OH).[11] Among all the detected compounds, 183 features were identified as unsaturated or saturated fatty acids, and OA was the most abundant unsaturated fatty acid.[11] The reaction of ozone with OA as a proxy for unsaturated fatty acids has been comprehensively evaluated in the past to better understand the oxidation processes affecting aerosol particles.[12−20] Studies have also been carried out on the oxidative processing of OA by other relevant atmospheric oxidants (radicals) such as hydroxyl (OH),[21] nitrate (NO_3),[14] and chlorine (Cl).[22]

The organic compounds adsorbed on urban grime can be oxidized by atmospheric oxidants and affect urban air quality.[23,24] In addition to the fatty acids and polycyclic aromatic hydrocarbons (PAHs), urban grime contains salts such as nitrate and sulfate that are major species in grime and are very stable within the organic film.[25,26] The average concentrations of SO_4^{2-} and NO_3^- were reported to be 7.6 and 1.5 μg cm^{-2}, respectively.[26]

Nitrate photolysis on grime, airborne particles, and other environmental surfaces has been suggested to produce nitrogen compounds such as NO, NO_2, and HONO.[23,27,28] It has also been suggested that light-induced heterogeneous processing of NO_2 on simulated urban grime represents a source of HONO

Received: February 12, 2021
Revised: May 20, 2021
Accepted: May 21, 2021
Published: June 4, 2021



https://doi.org/10.1021/acs.est.1c01043
Environ. Sci. Technol. 2021, 55, 7831−7840

in the metropolitan area.[23,29−32] Recently, it has been shown that light-enhanced NO_2 uptake on real urban grime gives high HONO yields, which are largely dependent on the relative humidity (RH%).[24] Indeed, light intensity, RH, temperature (T), and NO_2 concentrations all impact the NO_2 uptake and the HONO formation yields on various environmental surfaces.[24,33−41]

To date, there have been no studies reported on the kinetics or the formation of HONO upon the reaction of NO_2 with OA. In this study, for the first time, to our best knowledge, we investigate the influence of RH% and light intensity on the heterogeneous reaction of NO_2 with an organic film consisting of (i) oleic acid (OA), (ii) a mixture of OA and sodium sulfate (Na_2SO_4), and (iii) a mixture of OA and sodium nitrate ($NaNO_3$). The study was carried out in a well-established flow tube reactor, simultaneously coupled to a NO_x analyzer to follow the NO_2 decay and to a membrane inlet single-photon ionization time-of-flight mass spectrometer (MI-SPI-TOFMS) for online measurements of the secondarily formed volatile organic compounds (VOCs). The HONO yields were detected indirectly with a coated Na_2CO_3 denuder.

We show that the NO_2 uptake coefficients on solid OA films decrease as a function of RH. The presence of Na_2SO_4 and $NaNO_3$ suppresses NO_2 reactivity but, yet, the increase of RH leads to an increase in the NO_2 uptake on OA/Na_2SO_4 and OA/$NaNO_3$ mixtures. The reaction pathway of HONO and the nitroaromatic compound formation are discussed.

■ MATERIALS AND METHODS

The film preparation, ion analysis, and UV−vis absorption measurements are given in the Supporting Information (SI).

The flow tube reactor used to assess the reaction of NO_2 with the coated glass plates has been previously detailed,[24,42,43] and in the SI only a brief description is given.

NO_x and HONO Measurements. A saturated sodium carbonate (Na_2CO_3) solution was inserted into the denuder and allowed to stand for more than half an hour. Then, the denuder was wrapped in a tin foil and placed in an oven at about 106°C for drying. In this way, the denuder wall was coated with sodium carbonate crystals that are able to trap HONO (*vide infra*).

A NO_2 analyzer (Eco Physics, model CLD 88p) hyphenated with a photolytic (metal halide lamp) converter (Eco Physics, model PLC 860) was used to measure the NO_x signal at the end of the flow tube reactor. The limit of detection of the NO_x analyzer was 10 ppt with a time resolution of 1 s.[24]

The NO_x analyzer uses a chemiluminescence method to measure the NO_2 concentration by converting NO_2 into NO with a molybdenum converter. With this method, one can directly measure NO without using the converter and NO_x = NO + NO_2 when the converter is operational, thus obtaining NO_2 as the difference between the two signals. HONO will also be converted to NO, and thus, it has the same analytical response as NO_2. The same NO_x analyzer was used to simultaneously measure NO_2 (directly) and HONO[33,34,37,44−46] (indirectly as described in the SI).

Membrane Inlet Single-Photon Ionization Time-of-Flight Mass Spectrometry (MI-SPI-TOFMS). Membrane inlet single-photon ionization time-of-flight mass spectrometry (MI-SPI-TOFMS) is a promising technique for the online monitoring of VOCs. A commercial MI-SPI-TOF-MS device (SPIMS 3000, Guangzhou Hexin Instrument Co., Ltd., China) was used in this study for real-time monitoring of the gaseous product compounds generated by the reaction of NO_2 with OA, OA/$NaNO_3$, or OA/Na_2SO_4. The details of this instrument are given elsewhere[47−49] and here only a short description is given. Briefly, SPIMS 3000 consists of three parts: (1) a membrane inlet system, with porous membrane consisting of dimethylsiloxane (PDMS) with a thickness of 0.002 in. (Technical Production, Inc.) that serves to enrich the VOCs; (2) a single-photon ionization (SPI) source, which uses a commercial deuterium lamp (Hamamatsu, Japan), and (3) a reflectron TOF-MS, containing a double-pulsed acceleration region, a field-free drift tube, a reflector, and an ion detector.[47] The raw data were analyzed by software (SPIMS 3000 V1.0.1.2.0, Guangzhou Hexin Instrument Co., Ltd., China), whereas selected Gauss peaks above a predetermined threshold are rounded with an average value.[47−49]

Treatment of the Uptake Coefficients. The reactive uptakes of NO_2 (γ_{NO_2}) on the coated glass plates were estimated as follows:

$$\gamma_{NO_2} = \frac{4\, k_{1,NO_2} V}{\nu_{NO_2} S} \quad (1)$$

where k_{1,NO_2} is the determined pseudo-first-order rate constant for the reaction between NO_2 and the glass plate coated with either OA, OA/$NaNO_3$, or OA/Na_2SO_4, ν_{NO_2} is the relative mean speed of gaseous NO_2, S is the reactive surface of the glass plate, and V is the volume of the flow tube.[24] The estimation of k_{1,NO_2} is described in the SI.

We performed test experiments in the empty reactor to check for photodissociation of NO_2 and the formation of ozone.[50,51] Indeed, the lamps used in this study irradiate in the wavelength region between 300 and 400 nm, which can cause photolysis of NO_2. The photolysis rate of NO_2 ($J(NO_2)$) in the flow tube ranged from 9.5×10^{-5} to 3.2×10^{-4} s^{-1}, which implies only slight photodissociation of NO_2 (accounting for 0.1 to 0.4% of the total NO_2). The connected ozone analyzer at the exit of the reactor did not detect any ozone, which could eventually be formed by the photolysis of NO_2.

■ RESULTS AND DISCUSSION

Effect of RH. The uptake coefficients of NO_2 on oleic acid were assessed as a function of RH at 296 K (Figure 1). The NO_2 uptakes decreased linearly with the increase of RH, from $(1.4 \pm 0.1) \times 10^{-6}$ at 0% RH to $(7.1 \pm 1.6) \times 10^{-7}$ at 90% RH, under light irradiation (15.5 W m^{-2}, 5.3×10^{13} photons cm^{-2} s^{-1}; 300 nm < λ < 400 nm).

The NO_2 uptake on OA at 0% RH was slightly higher than the reactive uptake reported for NO_2 on real urban grime ($\gamma(NO_2) = (1.1 \pm 0.2) \times 10^{-6}$ at 0% RH).[24] Although the NO_2 uptake values decreased with RH, the value $\gamma(NO_2) = (1.2 \pm 0.1) \times 10^{-6}$ observed at 30% RH was still about 2 times higher than the reactive uptake reported for NO_2 on fluoranthene/KNO_3 ($\gamma(NO_2) = 6.6 \times 10^{-7}$ at 35% RH) and phenanthrene/KNO_3 ($\gamma(NO_2) = 7.8 \times 10^{-7}$ at 35% RH).[33]

The decrease of NO_2 uptake values with increasing RH observed here is completely opposite to the dependence of the NO_2 uptake values on fluorene (FL) and FL/Na_2SO_4, where a nonlinear increase of NO_2 uptake was observed with increasing RH.[43]

Considering that OA is poorly soluble in water, when RH increases, the formation of a water layer may occur above OA that reduces the accessibility of NO_2 to the adsorption sites on

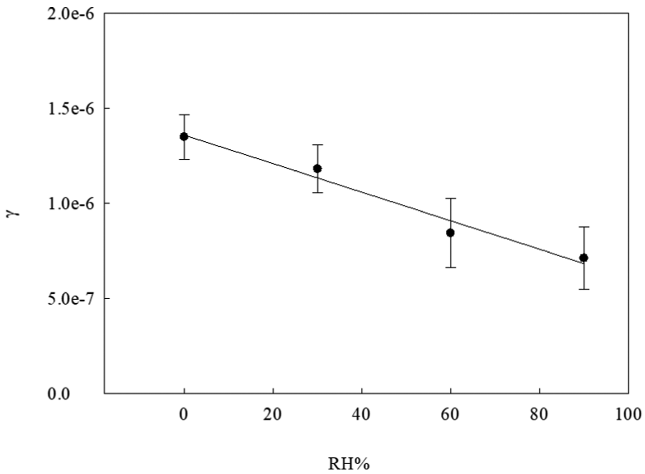


Figure 1. NO_2 uptake coefficients on (●) OA as a function of RH at a NO_2 mixing ratio of 40 ppb and under light irradiation (15.5 W m^{-2}, 5.3 × 10^{13} photons cm^{-2} s^{-1}; 300 nm < λ < 400 nm) at 296 K. The error bars are estimated from the uncertainties related to the calculation of the uptake coefficients.

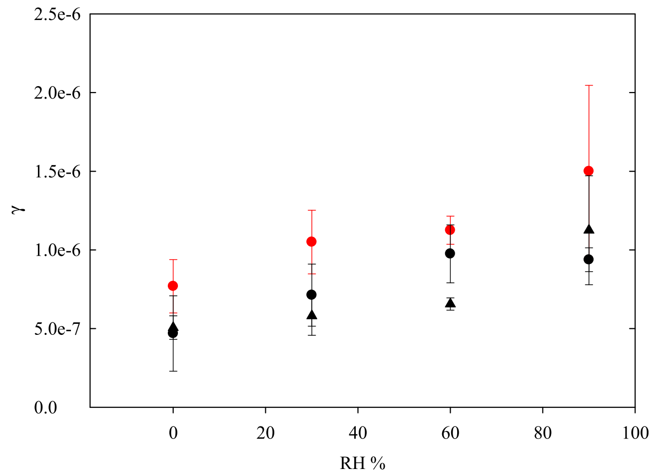


Figure 2. NO_2 uptake coefficients on (●) OA/$NaNO_3$ and (red solid circle) OA/Na_2SO_4, as a function of RH at a NO_2 mixing ratio of 40 ppb, and light irradiation (15.5 W m^{-2}, 5.3 × 10^{13} photons cm^{-2} s^{-1}; 300 nm < λ < 400 nm) at 296 K. NO_2 uptake coefficients on (▲) OA/$NaNO_3$ under dark conditions. The error bars are estimated from the uncertainties related to the calculation of the uptake coefficients.

OA. Considering that the melting point of OA is 288 K, the OA film is expected to be liquid at 296 K. Therefore, most likely, reversible adsorption of water occurs on liquid OA and leads to displacement or competition for adsorption with NO_2.

If this is the case, at 90% RH, the measured uptake coefficient of NO_2 on OA should correspond to the uptake coefficient of NO_2 on a water layer. To verify this hypothesis, we measured the NO_2 uptake coefficients on a clean glass plate at 90% RH in the absence of any organics. The uptake coefficient obtained in these conditions was (7.6 ± 0.5) × 10^{-7}, which is similar to the NO_2 uptake of (7.1 ± 1.6) × 10^{-7} measured on the OA film at 90% RH, and implies that OA is not accessible for NO_2 at 90% RH.

The addition to OA with Na_2SO_4 and $NaNO_3$ inhibited substantially the uptake of NO_2 at 0% RH: it passed from $\gamma(NO_2)$ = (1.4 ± 0.1) × 10^{-6} without salts to $\gamma(NO_2)$ = (7.7 ± 1.7) × 10^{-7} with Na_2SO_4, and $\gamma(NO_2)$ = (4.7 ± 2.4) × 10^{-7} with $NaNO_3$. Conversely, the uptake coefficient of NO_2 on a mixture OA/Na_2SO_4 was (1.5 ± 0.5) × 10^{-6} at 90% RH, which is similar to $\gamma(NO_2)$ = (1.4 ± 0.1) × 10^{-6} on OA at 0% RH. Indeed, increasing RH led to an increase of the NO_2 uptake values on both films, OA/Na_2SO_4 and OA/$NaNO_3$ (Figure 2).

The obtained NO_2 uptake coefficients on OA/$NaNO_3$ in the dark (Figure 2) are very similar to those observed under irradiation, which could be ascribed to the light-absorbing properties of OA/$NaNO_3$ and to the spectral irradiance emitted by the lamps. Namely, Figure S1 shows that the absorption spectrum of OA/$NaNO_3$ only slightly overlaps with the emission spectrum of the lamps in the near-UV region (300 nm < λ < 400 nm).

Considering that the deliquescent RH for $NaNO_3$ particles is 74.5 %,[52] the binary system OA/NO_3^- is in a relatively dry state. In the presence of NO_3^- ions, at RH higher than 74.5%, the liquid film becomes deliquesced. Therefore, it is most likely that at RH > 74.5%, the salting-out effect makes OA more accessible for the reaction with NO_2. A salting-out effect has been previously observed for the reactions of ozone (O_3) with acetosyringone[53] and pyruvic acid[54] in the presence of SO_4^{2-} and Br^-, respectively.

Effect of Light Intensity. The effect of light intensity on the NO_2 uptake coefficients measured on OA, OA/Na_2SO_4, and OA/$NaNO_3$ was also evaluated. The uptake coefficients of NO_2 on OA were almost independent of light intensity and ranged between (5.6 ± 0.9) × 10^{-7} at 4.1 W m^{-2} and (6.9 ± 0.6) × 10^{-7} at 15.5 W m^{-2} (Figure 3).

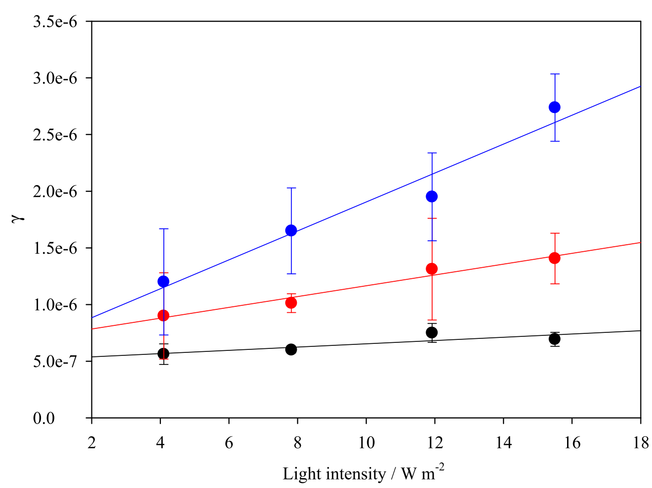


Figure 3. NO_2 uptake coefficients on (●) OA, (red solid circle) OA/Na_2SO_4, and (blue solid circle) OA/$NaNO_3$ as a function of the photon flux, at a NO_2 mixing ratio of 40 ppb with 40% RH at 296 K. The error bars are estimated from the uncertainties related to the calculation of the uptake coefficients. The black, red, and blue lines represent the regression lines for the dependence of NO_2 uptake coefficients on OA, OA/Na_2SO_4, and OA/$NaNO_3$, respectively.

When OA was mixed with Na_2SO_4, the NO_2 uptake coefficients slightly increased from (9.0 ± 3.8) × 10^{-7} at 4.1 W m^{-2} to (1.4 ± 0.2) × 10^{-6} at 15.5 W m^{-2}. In contrast, in the case of OA + $NaNO_3$ simultaneously exposed to NO_2 and light, there was a significant increase in the NO_2 uptake coefficients by a factor of about 2 (Figure 3), from (1.2 ± 0.5) × 10^{-6} at 4.1 W m^{-2} to (2.7 ± 0.3) × 10^{-6} at 15.5 W m^{-2}. This latter finding could be ascribed to the increased overlap of the

https://doi.org/10.1021/acs.est.1c01043
Environ. Sci. Technol. 2021, 55, 7831−7840

Table 1. Formation Yields of HONO and NO in Dark and under Light Irradiation (15.5 W m^{-2}) with Different RH Values, at 40 ppb of NO_2 and 293 K

	oleic acid				oleic acid + Na_2SO_4				oleic acid + $NaNO_3$			
	dark		light		dark		light		dark		light	
RH %	HONO yield%	NO yield%	HONO yield%	NO yield%	HONO yield%	NO yield%	HONO yield%	NO yield%	HONO yield%	NO yield%	HONO yield%	NO yield%
0	11.8	4.8	17.2	9.2	18.5	7.7	28.7	8.4	62.2	15.2	44.5	10.6
30	15.9	0.5	31.9	22.5	15.6	7.7	19.7	6.4	25.5	3.8	30.4	10.4
60	25.9	5.1	28.1	9.2	13.9	6.0	25.7	4.0	47.4	9.5	49.0	5.6
90	26.0	3.3	30.8	8.8	30.6	2.0	27.8	4.1	36.5	4.5	40.3	24.6

emission spectrum of 3 and 4 UV lamps with the absorption spectrum of OA/$NaNO_3$ (Figure S1).

From the regression line of the plot of γ versus light intensity, eq 2 is obtained that can be used to predict the reactive uptake of NO_2 on OA/$NaNO_3$ under realistic light intensity, which is here expressed in W m^{-2} in the near-UV region of the solar spectrum (300 nm < λ < 400 nm) at different solar zenith angles (SZA).

$$\gamma = (6.3 \pm 2.2) \times 10^{-7} + (1.3 \pm 0.2) \times 10^{-7} \cdot \text{light intensity/W m}^{-2}$$
$$r^2 = 0.99 \qquad (2)$$

It is interesting to compare, with previous studies, the extrapolated NO_2 uptake coefficient on a film consisting of OA/$NaNO_3$, at a UV radiation intensity of 46 W m^{-2} for the wavelength range 300−400 nm corresponding to a solar zenith angle of 48° (National Renewable Energy Laboratory (NREL)[55]), which would be $\gamma = 6.6 \times 10^{-6}$. This value is of the same order of magnitude as the uptake of NO_2 on pyrene[29] ($\gamma = 8.8 \times 10^{-6}$ at 50 ppb of NO_2), and is about 4 times higher than the uptake of NO_2 on simulated soot made up of gentisic acid ($\gamma = 1.6 \times 10^{-6}$, obtained at a NO_2 mixing ratio of 20 ppb and 20% RH, under UV−vis light irradiation at 40° solar zenith angle).[32] The uptake of NO_2 (20 ppb) on fluoranthene, $\gamma = 1 \times 10^{-6}$,[33] was about 7 times lower than the uptake of NO_2 on OA/$NaNO_3$ as determined in this study ($\gamma = 6.6 \times 10^{-6}$). Moreover, our latter value (6.6×10^{-6}) is 1.5 times lower than the NO_2 uptake on a solid film of fluorene, obtained at a NO_2 mixing ratio of 40 ppb and 60% RH, under a light intensity of 46 W m^{-2} for λ = 300−400 nm.[43] Our value is also 1.5 times lower than the uptake coefficient of NO_2 measured on a simulated soil surface consisting of humic acid ($\gamma = 1 \times 10^{-5}$) under an irradiation intensity of 400 W m^{-2}, in the visible range of wavelengths (λ = 400−700nm) at 48° solar zenith angle, with a NO_2 mixing ratio of 30 ppb, T = 298 K, and 30% RH.[34]

The extrapolated NO_2 uptake coefficient (eq 3) on an OA/Na_2SO_4 film under the same irradiation conditions would be $\gamma = 2.9 \times 10^{-6}$, which is about 2 times lower than the value of γ on OA/$NaNO_3$, but still ca. 3 times higher than the NO_2 uptakes on gentisic acid, $\gamma = 1.6 \times 10^{-6}$, and on fluoranthene, $\gamma = 1 \times 10^{-6}$.[32,33] With OA/$Na_2SO_4$ one gets the following equation

$$\gamma = (6.9 \pm 0.7) \times 10^{-7} + (4.8 \pm 0.6) \times 10^{-8} \cdot \text{light intensity/W m}^{-2}$$
$$r^2 = 0.96 \qquad (3)$$

Finally, the extrapolated NO_2 uptake coefficient on a film containing only pure OA (eq 4) under the same irradiation conditions would be 1.2×10^{-6}, which falls in the range of the NO_2 uptakes on gentisic acid, $\gamma = 1.6 \times 10^{-6}$,[32] and fluoranthene, $\gamma = 1 \times 10^{-6}$.[33]

$$\gamma = (5.1 \pm 0.7) \times 10^{-7} + (1.4 \pm 0.7) \times 10^{-8} \cdot \text{light intensity/W m}^{-2}$$
$$r^2 = 0.7 \qquad (4)$$

Considering that in the UV range of wavelengths, the light flux in the indoor environment is 9 W m^{-2},[56] the interpolated NO_2 uptake coefficients would be 1.8×10^{-6}, 1.1×10^{-6}, and 6.4×10^{-7} in the cases of OA/$NaNO_3$, OA/Na_2SO_4, and OA, respectively. Although these uptakes are relatively low when compared to the corresponding values obtained for urban grime under a UV light intensity of 46 W m^{-2} (see above), the observed HONO yields generated by NO_2 conversion on OA/$NaNO_3$, OA/Na_2SO_4, and OA (*vide infra*) can have health implications for the inhabitants who inhale HONO.[57,58] Moreover, HONO photolysis and the associated production of hydroxyl radicals (OH) may play a key role in the formation of toxic secondary compounds in urban and indoor air.[11,48,59−62]

Comparison between Spectral Irradiance and UV Absorption Spectra. To understand the dependence of the uptake coefficients on the light intensity (Figure 3), we measured the spectral irradiance of the four UV lamps used to irradiate the glass plates in our flow tube reactor and compared it with the UV−vis absorption spectra of the coated (OA, OA/Na_2SO_4, OA/$NaNO_3$) glass plates (Figure S1).

Figure S1 shows only a slight overlap of spectral irradiance with UV absorption spectra when one or two UV lamps were used. This is the most likely reason for the very similar values of the NO_2 uptake coefficients measured on OA/$NaNO_3$, in the dark and under irradiation with two lamps (Figure 2). By increasing the number of lamps, one has a stronger overlap between the film absorption spectra and the lamp spectral irradiance, which may explain the increase of the uptake coefficients with the light intensity shown in Figure 3, especially in the case of OA/$NaNO_3$.

It is known that nitrates can absorb UVB as well as short-wavelength UVA radiation and produce HONO after the photodissociation process.[27,28] The photolysis rate of HNO_3 adsorbed on borosilicate glass (the same material as the glass plates used in this study) has been reported as 1.2×10^{-5} s^{-1} at 50% RH, which is two orders of magnitude higher compared to liquid-phase and gas-phase HNO_3 under comparable irradiation conditions.[27] Moreover, solid nitrate near the surface does not undergo the solvent-cage effect that is experienced in aqueous solutions, where photogenerated OH + NO_2 are

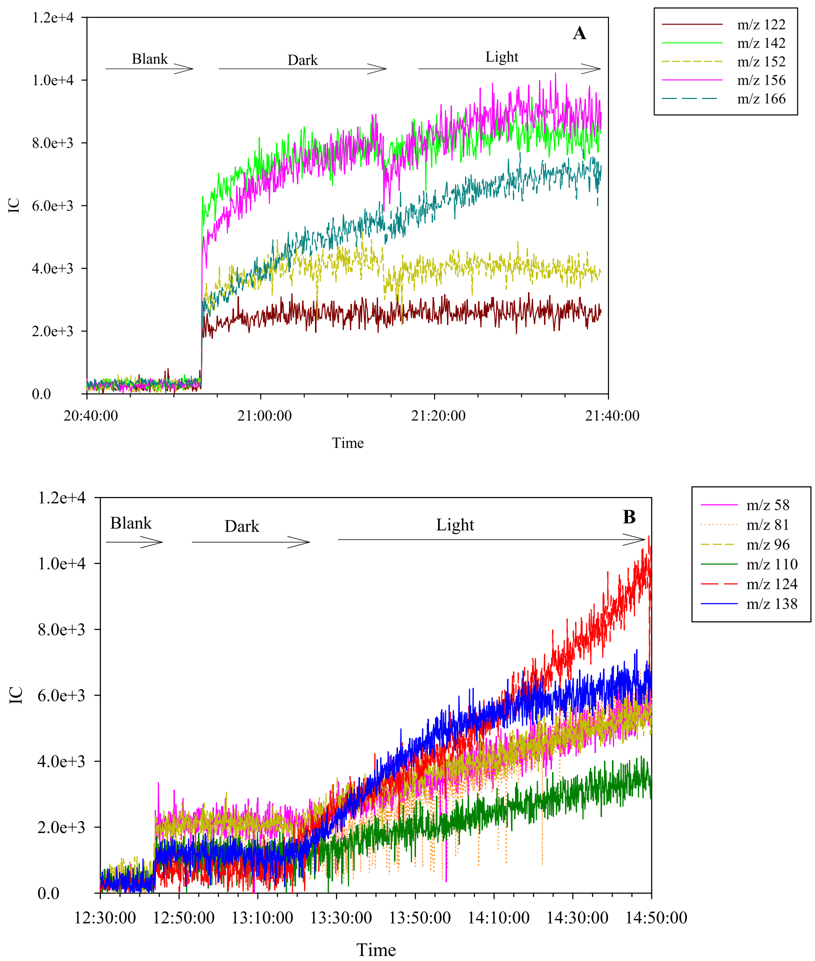


Figure 4. Typical profiles of gas-phase compounds formed upon heterogeneous reactions of NO_2 with (A) OA and (B) OA/$NaNO_3$.

initially surrounded by a cage of water molecules that favor the recombination to NO_3^- + H^+ at the expense of diffusion of OH and NO_2 into the solution bulk. Indeed, the solvent-cage effect decreases the net rate of NO_3^-/HNO_3 photolysis in the solution (*vide infra*).[63]

HONO and NO Yields. When the NO_x analyzer was directly hyphenated to the flow tube reactor, a decrease of the NO_2 signal was observed due to the uptake of NO_2 by the OA film. When the Na_2CO_3 denuder was connected between the flow tube reactor and the NO_x analyzer, an additional decrease of the NO_2 signal was observed that corresponds to the HONO trapped by the denuder. The HONO mixing ratio was obtained as the difference between the NO_2 signals without and with the Na_2CO_3 denuder.

The HONO and NO yields produced by light-induced heterogeneous reaction of NO_2 with films containing OA, OA/Na_2SO_4, and OA/$NaNO_3$ were calculated as the ratios ΔHONO/ΔNO_2 and ΔNO/ΔNO_2, respectively (Table 1). Table 1 shows that the HONO and NO yields only slightly varied with the RH. The most efficient conversion of NO_2 to HONO was observed with OA/$NaNO_3$ in the dark, with HONO yields ranging from 26% at 30% RH to 62% in the absence of RH. Under light irradiation, the most efficient HONO formation was also observed with OA/$NaNO_3$, with HONO yields ranging from 30% at 30% RH to 49% at 60% RH. This finding suggests that nitrate promotes the conversion process of NO_2 to HONO on the fatty acid surface (Table 1).

Table S7 shows the effect of nitrate ions on HONO formation, in the dark and under light irradiation. It can be seen from Table S7 that the quantity of HONO (ΔHONO) formed upon reaction of NO_2 with OA/$NaNO_3$ under light irradiation is higher than that in dark, especially at high RH. At the same time, however, NO_2 uptake increased as well and the overall HONO yield was almost unchanged. It can also be seen that the formed amount of HONO, during the light-induced reaction of NO_2 with OA/$NaNO_3$, increases with increasing RH. The ion chromatography analysis revealed that the quantity of NO_3^- at 60% RH increased from 9 ppm before the reaction to, respectively, 24 and 22 ppm after 1 h of heterogeneous reaction of NO_2 with OA/$NaNO_3$, in the dark and under irradiation. These results suggest that at 60% RH, 49% of NO_2 was converted into gaseous HONO but the remaining ≈50% was converted into nitric acid (HNO_3), which remained on the flow tube surface. The quantity of NO_2^- only slightly increased, from 0 ppm before the reaction to 0.067 and 0.008 ppm following the reaction of NO_2 with OA/$NaNO_3$, respectively, in the dark and under irradiation. The amounts of NO_3^- and NO_2^- ions also increased from 2 to 5 ppm and from 0.017 to 0.027 ppm, respectively, after 1 h light-induced heterogeneous reaction of NO_2 with the OA film. Intriguingly, the quantity of NO_3^- and NO_2^- ions decreased from 0.003 to 0 ppm and from 0.04 to 0.006 ppm, respectively, after 1 h reaction of NO_2 with the film consisting of OA/Na_2SO_4 in the presence of light.

https://doi.org/10.1021/acs.est.1c01043
Environ. Sci. Technol. 2021, 55, 7831−7840

Gas-Phase Product Compounds Detected by MI-SPI-TOFMS Analysis. The formation of gaseous compounds released upon heterogeneous reactions of NO_2 with OA, OA/$NaNO_3$, and OA/Na_2SO_4 at 30% RH, in the dark and under irradiation was monitored online by MI-SPI-TOF-MS. The increase of RH to 90% substantially reduced the total ion counts of the gas-phase compounds observed with NO_2 + OA (Figure S2), thereby confirming our hypothesis that at higher RH, OA is covered with a water layer that both inhibits the reaction and leads to lower NO_2 uptake values (Figure 1).

Figures S4−S6 show the signal intensities obtained from scans of mass-to-charge ratios (m/z) ranging between 50 and 250 amu, which are relevant to the observed gas-phase compounds formed upon reaction of NO_2 with OA, OA/$NaNO_3$, and OA/Na_2SO_4, in the dark and under irradiation with simulated sunlight, at 30% RH. The main differences that can be observed are related to the presence of either $NaNO_3$ or Na_2SO_4 on the film consisting of OA. Namely, the presence of NO_3^- promotes the formation of N-containing organic compounds (see the Reaction Mechanism section), and the presence of SO_4^{2-} increases substantially the number of the formed compounds. Tables S1−S3 summarize all the detected m/z values under different conditions, showing that the highest abundances occurred with OA/Na_2SO_4, both in the dark and under irradiation.

It can be seen from Figures S4−S6 that certain product peaks are separated by $\Delta m/z$ = 16, which corresponds to multiple additions of O atoms that suggest the formation of carbonyl compounds and alcohols.[21] The oxidation of the saturated alkyl groups is in fact associated with an addition of 14 Da (carbonyl) and then by the 16 Da (hydroxyl) pattern (Figures S4−S6).[64]

Figure 4 shows typical profiles for the formation of gas-phase compounds upon the reaction of NO_2 with OA and OA/$NaNO_3$, in the dark and under irradiation. The variation trend of five compounds (m/z 122, 142, 152, 156, and 166) formed upon heterogeneous reactions of NO_2 with OA is shown in Figure 4A. The profiles of these five products were very similar in the dark and in the presence of light. However, the presence of nitrate ions in the OA film suppressed the formation of VOCs in the dark (Table S2) but induced the formation of several new compounds (m/z 58, 81, 96, 110, 124, and 138) under irradiation (Figure 4B). The MS data suggest that the latter compounds likely bear nitro groups. This finding indicates that the NO_3^- ions favor the formation of secondary nitro-organics as well as HONO, which would be released upon light-induced NO_2 reactions with OA. Figure S3 shows that the total ion current (TIC) at different m/z values slightly decreased with increasing RH (from 30 to 90% in the dark) but then increased again to the initial level upon light irradiation of OA/$NaNO_3$ at 90% RH. When sulfate ions were present in the OA film, most of the gas-phase compounds were formed in the dark (Figure S4). Compared to the gas-phase compounds formed by the reaction of NO_2 with OA and the OA/$NaNO_3$ surface, there were three distinct compounds (m/z 100, 188, 216) formed upon the dark heterogeneous reaction of NO_2 with OA/Na_2SO_4 (Figure S7 and Table S3). In addition, there are some compounds, the intensities of which increase under light irradiation (m/z 57, 81, 124, 138) (Figure S7).

Reaction Mechanism. Unsaturated fatty acids such as OA contain double bonds, which are susceptible to NO_2 attack *via* either homolytic or heterolytic (ionic) reactions. Hydrogen (H) atom abstraction might also occur at the bis-allylic methylene center of OA, which leads to the formation of pentadienyl radicals.[65] The initial product compounds of H-abstraction by NO_2 from OA would be HONO and a resonance-stabilized allylic radical,[66] but H-abstraction is too slow to compete with NO_2 addition to the double bond.[67] Nevertheless, in the presence of O_2, alkoxy radicals could be formed through dissociation of peroxynitrates, as follows.[68]

$$RO - ONO_2 \rightarrow RO^{\bullet} + NO_3 \qquad \text{(R-1)}$$

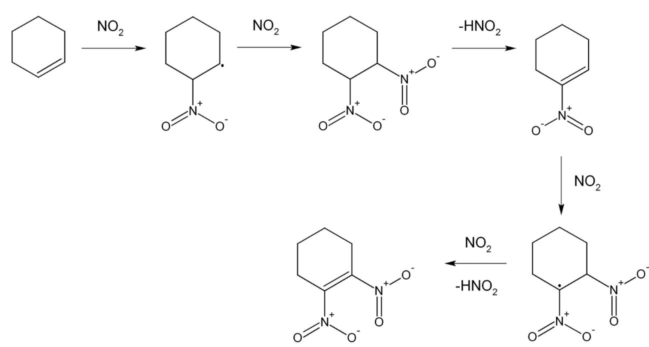
The formed alkoxy radicals could abstract the H-atom from cyclohexene (m/z 82) to produce 2-cyclohexenol (m/z 98) (Tables S1−S3).[67]

The reaction of NO_2 with OA proceeds through fast and reversible addition of NO_2 to alkene double bonds to initially form β-nitroalkyl radicals.[67] The reaction of the β-nitroalkyl radical with another NO_2 molecule might then proceed through H-abstraction, which would yield nitro-OA and HONO. This process, which can also take place in the dark, would produce HONO with 50% yield and might significantly contribute to HONO production, especially at low RH (Table 1). At the same time, nonvolatile nitro-OA would remain attached to the film and would not contribute to the observed nitrated VOCs. In contrast, the formation of 50% HONO + 50% HNO_3 that was observed at 60% RH is consistent with the well-known hydrolysis pathway of NO_2 in the presence of a liquid phase

$$2\,NO_2 \leftrightarrows N_2O_4 \xrightarrow{H_2O} HONO + H^+ + NO_3^- \qquad \text{(R-2)}$$

One of the gaseous products formed by NO_2 addition to the C=C bond is 1,2-dinitrocyclohexene (m/z 174),[67] which was also tentatively identified in this study (Tables S1 and S3). A tentative reaction pathway leading to the formation of this compound, assuming cyclohexene as the precursor, is provided in Scheme 1. Interestingly, the proposed addition−elimination

Scheme 1. Proposed Reaction Pathway for the Formation of the Tentatively Detected Compound 1,2-Dinitrocyclohexene[a]



[a]Here, we assume that cyclohexene derives from OA fragmentation.

pathway is exactly the opposite as the nitration of phenolic compounds by NO_2, which first proceeds via H-abstraction to produce HONO and a phenoxyl radical, followed by NO_2 addition to finally produce the nitrophenol.[69]

The relatively high HONO values formed at high RH in the presence of OA/$NaNO_3$ under irradiation (Table S7) could be accounted for by an additional process, yielding HONO from the photochemistry of nitrate. Indeed, liquid-phase NO_3^- is a significant photochemical source of NO_2^- and of the gas-phase

https://doi.org/10.1021/acs.est.1c01043
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HONO as a consequence (see the reaction sequence from reaction R-3 to R-9).[70]

$$NO_3^- \xrightarrow{h\nu, H^+} [NO_2 + OH]_{cage} \quad (R\text{-}3)$$

$$[NO_2 + OH]_{cage} \rightarrow NO_3^- + H^+ \quad (R\text{-}4)$$

$$[NO_2 + OH]_{cage} \rightarrow NO_2 + OH \quad (R\text{-}5)$$

$$[NO_2 + OH]_{cage} + OA \rightarrow OA_{ox} + NO_2 \quad (R\text{-}6)$$

$$NO_3^- \xrightarrow{h\nu} NO_2^- + O \quad (R\text{-}7)$$

$$2NO_2 \leftrightarrows N_2O_4 \xrightarrow{H_2O} HONO + H^+ + NO_3^- \quad (R\text{-}8)$$

$$NO_2^- + H^+ \leftrightarrows HONO \quad (R\text{-}9)$$

$$NO_2^- \xrightarrow{h\nu, H^+} OH + NO \quad (R\text{-}10)$$

$$HONO \xrightarrow{h\nu} OH + NO \quad (R\text{-}11)$$

where OA_{ox} is a radical species arising from the OH addition to OA. The formation of OA as an OH scavenger could enhance the photoproduction of HONO by inhibiting the recombination between the geminate species produced by nitrate photolysis inside the solvent cage.[63] The photogeneration of OH by photolysis of nitrate and possibly of photogenerated NO_2^- and HONO (reactions R-10 and R-11)[69] could significantly contribute to the occurrence of oxidized/hydroxylated compounds.

At the same time, however, the hydroxyl radicals produced under irradiation could cause NO_2 oxidation and enhance its conversion (reaction R-12). Indeed, although a significant part of OH would be scavenged by OA, reaction R-12 cannot occur in the dark as no OH is generated in such conditions. Therefore, it is reasonable for NO_2 conversion to be faster under irradiation than in the dark.

$$NO_2 + OH \rightarrow NO_3^- + H^+ \quad (R\text{-}12)$$

The increase in both HONO production and NO_2 processing might explain why the HONO yield changed very little with $NaNO_3$ in the dark or under irradiation (Table 1), despite the increased production of HONO under irradiation (Table S7).

Interestingly, the photolysis of the formed N-containing compounds such as 1,2-dinitrocyclohexene (Scheme 1) can be plausibly linked with HONO formation, as shown by reaction R-13, which can be an additional photochemical source of HONO in the metropolitan area.[71−73]

$$R - NO_2 \xrightarrow{h\nu} R' + HONO \quad (R\text{-}13)$$

Considering that fatty acids are ubiquitous surfactants in the atmospheric particles and on urban and indoor grime, the obtained results suggest that fatty acids can contribute to urban- and indoor air pollution through heterogeneous conversion of NO_2 into N-containing organic compounds. The detailed knowledge of HONO formation processes is paramount with respect to the urban and indoor air chemistry because HONO is the main source of OH radicals through its photolysis in the urban environment[60−62] and in sunlit areas of the indoor environment.[48,59] Especially, the formation of N-containing organic compounds by the reaction of NO_2 with the OA in the presence of nitrate ions can exhibit health problems. The presence of NO_3^- ions during the heterogeneous NO_2 processing of OA stimulates the formation of nitroaromatic compounds, which are potential light-absorbing (brown carbon) compounds that could affect the climate through positive radiative forcing (warming).[74]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c01043.

Film preparation; ion analysis; description of the flow tube reactor; estimation of the pseudo-first-order rate constant; indirect detection of HONO; comparison of the spectral irradiance of the UV lamps with the absorption spectra of OA, $OA/NaNO_3$, and OA/Na_2SO_4; total ion count of the monitored gaseous compounds; the relative intensity of the observed m/z; typical profiles of gas-phase compounds formed upon heterogeneous reactions of NO_2 with OA/Na_2SO_4; HONO and NO values and yields (PDF)

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https://doi.org/10.1021/acs.est.1c01043
Environ. Sci. Technol. 2021, 55, 7831−7840

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Notes

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■ ACKNOWLEDGMENTS

This study was financially supported by the National Natural Science Foundation of China (Nos. 41773131 and 41977187), Chinese Academy of Science, International Cooperation Grant (No. 132744KYSB20190007), State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry (SKLOG2020-5, and KTZ_17101), and Guangdong Foundation for Program of Science and Technology Research (No. 2017B030314057).

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https://doi.org/10.1021/acs.est.1c01043
Environ. Sci. Technol. 2021, 55, 7831−7840