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FORMATE (MARKER OF CONTINENTAL PARTICULATE MATTER) UNDERGOES FASTER PHOTOTRANSFORMATION THAN THE BIOGENIC MARINE MARKER METHANESULPHONATE UNDER CONDITIONS RELEVANT TO ATMOSPHERIC AEROSOLS

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Abstract

Organic markers play an important role in the apportionment of the sources of atmospheric particulate matter, a component having important effects on human health and climate. Formate and methanesulphonate can be used as tracers of continental and biogenic marine aerosols, respectively, but transformation processes during transport could modify the concentration values of these compounds in particulate and introduce a bias in the assessment of particle sources. Unfortunately, very little is known about transformation of these compounds in the aerosol phase. To overcome this knowledge gap, we carried out irradiation of formate and methasulphonate in the presence of nitrate and hematite, important photosensitisers in aerosols that can produce reactive species and cause degradation of organic compounds. The time evolution of formate and methasulphonate was monitored by ion chromatography. Under the adopted conditions formate is transformed from 1.6±0.9 (µ±σ) to 4.1±0.7 times faster than methanesulphonate, partly due to higher reactivity with the hydroxyl radical, and partly due to reaction with other transients such as nitrogen dioxide. Such results strongly suggest faster formate transformation during particle transport. Therefore, when formate and methanesulphonate as used as particle tracers, an overestimation is expected of marine biogenic vs. continental particle sources. This has potentially important consequences for climate prediction models, because marine biogenic particles have a cooling effect on climate.

Keywords. Airborne particulate matter; source apportionment; atmospheric photochemistry; sensitised transformation; deliquesced particles; nitrite.
1. Introduction

Formate (HCOO\(^{-}\)) and methanesulphonate (CH\(_3\)SO\(_3\)^{-}\)) are important constituents of atmospheric particles and can be useful for source apportionment (Fattori et al. 2005; Raman and Hopke 2006). The atmospheric occurrence of HCOO\(^{-}\) is mainly linked to primary and secondary sources located in continental areas, such as combustion of fossil fuels and biomass, emission by microorganisms, soil and vegetation, and secondary formation from atmospheric oxidation of hydrocarbons (Khare et al. 1999). CH\(_3\)SO\(_3\)^{-}\) arises by atmospheric oxidation of dimethylsulphide, emitted by marine algae (Jourdain and Legrand 2001).

A major issue in the use of HCOO\(^{-}\) and CH\(_3\)SO\(_3\)^{-}\) as particle markers is that they could undergo transformation upon long-range transport, and HCOO\(^{-}\) could also be partitioned to the gas phase under acidic conditions (Anderson et al. 2008). A difference in reaction kinetics would significantly modify the concentration ratios, biasing source apportionment. For instance, HCOO\(^{-}\) is more reactive than CH\(_3\)SO\(_3\)^{-}\) toward \(^{\cdot}\)OH, which is an important oxidising agent in the atmospheric condensed phase (Buxton et al. 1988).

The goal of this paper is the study of the transformation kinetics of HCOO\(^{-}\) and CH\(_3\)SO\(_3\)^{-}\) with irradiated nitrate and hematite (\(\alpha\)-Fe\(_2\)O\(_3\)), two important photoactive compounds in atmospheric aerosols (Borghesi et al. 2005). For the first time to our knowledge, we assessed the role of \(^{\cdot}\)OH vs. other photogenerated transients in the transformation of HCOO\(^{-}\) and CH\(_3\)SO\(_3\)^{-}\). Experiments were carried out in aqueous systems, which are representative of the photoreactivity of deliquesced particles (George and Anastasio 2007).

2. Experimental

2.1. Reagents and materials

NaNO\(_3\) (purity grade 99%), NaNO\(_2\) (> 97%), CH\(_3\)SO\(_3\)Na (98%), HClO\(_4\) (70%), NaHCO\(_3\) (> 99%) and K\(_2\)CO\(_3\) (> 99%) were purchased from Aldrich, 2-propanol (Chromasolv) from Riedel de Haën, HCOONa from VWR Int., and used as received. \(\alpha\)-Fe\(_2\)O\(_3\) nanocubes were synthesised according to Pu et al. (2006).

2.2. Procedures

Nitrate was irradiated under a UVB lamp (Philips TL 01) with maximum emission at 313 nm, relatively near the 305-nm absorption maximum of NO\(_3\)^{-}. The photon flux of the lamp in solution was \(6.7 \times 10^{-7}\) Einstein L\(^{-1}\) s\(^{-1}\), actinometrically determined (Kuhn et al. 2004). Irradiation of \(\alpha\)-Fe\(_2\)O\(_3\) and of \(\alpha\)-Fe\(_2\)O\(_3\) + nitrite took place under a UV (Philips TL K 40W/05, emission maximum at 365 nm, \(8.3 \times 10^{-6}\) Einstein L\(^{-1}\) s\(^{-1}\)) and a blue lamp (Philips TL K 40W/03, emission maximum at 420 nm, \(3.6 \times 10^{-6}\) Einstein L\(^{-1}\) s\(^{-1}\)), respectively. For the lamp spectra see Maddigapu et al. (2011). When needed, initial pH was adjusted to 6 with HClO\(_4\).

After irradiation, HCOO\(^{-}\) and CH\(_3\)SO\(_3\)^{-}\) were monitored with a Dionex LC 30 ion chromatograph equipped with 20 \(\mu\)L Rheodyne injector, Dionex GP40 gradient pump, AG9-HC guard column, AS9-HC anion-exchange column, ASRS ultra 4-mm conductivity suppression unit and ED40 conductometric detector. The eluent was 0.5 mM NaHCO\(_3\) + 1.2 mM K\(_2\)CO\(_3\) at a flow rate of 0.9 mL min\(^{-1}\). The retention times were (min): HCOO\(^{-}\) (9.2), CH\(_3\)SO\(_3\)^{-}\) (10.1), NO\(_3\)^{-} (23.0), column dead time 2.3 min. In the runs with NO\(_3\)^{-}, after 8
min the eluent composition was modified to 5 mM NaHCO₃ + 12 mM K₂CO₃, kept for 5 min (NO₃⁻ retention time was 12.4 min), then back to the initial conditions in 1 min, kept for 10 min.

2.3. Kinetic data treatment
The time evolution data of HCOO⁻ and CH₃SO₃⁻ were fitted with pseudo-first order equations of the form \( C_t = C_o e^{-kt} \), where \( C_t \) is the concentration at the time \( t \), \( C_o \) the initial concentration and \( k \) the pseudo-first order transformation rate constant. The initial transformation rates were calculated as \( \text{Rate} = k C_o \). The errors on the rates were derived at ±σ level from data scattering around the fit curve.

3. Results and discussion
The transformation of HCOO⁻ and CH₃SO₃⁻ was studied upon UVB irradiation of nitrate, which is an important \(^{•}\)OH source in atmospheric aerosols, and in the presence of α-Fe₂O₃ that is a quite common photoactive compound on particles (Borghesi et al. 2005; Cwiertny et al. 2008). Irradiation experiments were carried out at pH 6. Lower pH values would be representative of acidified atmospheric phases, and the main issue would be the protonation of HCOO⁻ to HCOOH at pH < 4. HCOOH is for instance less reactive than HCOO⁻ toward \(^{•}\)OH (Buxton et al., 1988), but in the atmosphere it would also undergo important partitioning to the gas phase (Anderson et al., 2008). Therefore, under acidic conditions photochemistry would not be the main factor affecting the concentration ratio of (HCOOH+HCOO⁻) to CH₃SO₃⁻ in particles.

3.1. Transformation of HCOO⁻ and CH₃SO₃⁻ by nitrate under UVB irradiation
Figure 1 reports the initial transformation rates of HCOO⁻ and of CH₃SO₃⁻ (10 µM initial concentration in both cases), irradiated separately in the presence of variable concentration values of nitrate. The Figure shows a linear increase of the rates, which is consistent with the fact that the absorbed photon flux by NO₃⁻ increases with increasing concentration, in the absence of absorption saturation (Nissenson et al. 2010). It is also shown that the transformation of HCOO⁻ is faster compared to CH₃SO₃⁻. The linear equations that fit the experimental data are \( \text{Rate}_{\text{HCOO}^-} = (1.89 \pm 0.11) \times 10^{-7} [\text{NO}_3^-] \) and \( \text{Rate}_{\text{CH}_3\text{SO}_3^-} = (6.92 \pm 0.52) \times 10^{-8} [\text{NO}_3^-] \). Therefore, the transformation of HCOO⁻ with irradiated nitrate was 2.73±0.36 times faster on average than that of CH₃SO₃⁻.
Figure 1. Initial transformation rates of 10 µM HCOONa and of 10 µM CH$_3$SO$_3$Na upon UVB irradiation of NaNO$_3$ at variable concentration values. Irradiation was carried out at pH 6 in air-equilibrated solutions. The transformation rate of HCOO$^-$ was 2.73±0.36 times faster than that of CH$_3$SO$_3^-$ . Such a difference cannot be accounted for by higher reactivity of HCOO$^-$ vs. CH$_3$SO$_3^-$ toward *OH, and the most likely explanation is that HCOO$^-$ reacts with additional photogenerated transients (e.g. HOONO, O and *NO$_2$).

Literature rate constant values (Buxton et al. 1988) suggest that the reaction HCOO$^- + \cdot$OH is 2.3 times faster than CH$_3$SO$_3^- + \cdot$OH. However, this issue is not a likely explanation of the reaction rate difference in the present case. Indeed, HCOO$^-$ and CH$_3$SO$_3^-$ have been irradiated separately and in both systems the organic substrate would be the only important *OH scavenger. If transformation only takes place upon reaction with *OH, the disappearance rates of both HCOO$^-$ and CH$_3$SO$_3^-$ should be equal to the *OH generation rate by nitrate, which is expected to be the same in the two systems at equal nitrate concentration.

Moreover, the adopted 10 µM substrate concentration is too low to cause significant perturbation of nitrate photolysis due to solvent-cage effects (Nissenson et al. 2010; Vione et al. 2011). Therefore, nitrate photolysis is expected to occur to a similar extent with both HCOO$^-$ and CH$_3$SO$_3^-$ . A possible explanation of the difference in the observed transformation rates is the involvement of additional reactive species formed upon nitrate photolysis, such as *NO$_2$ (reaction 1), HOONO and O (reactions 2, 3; Mack and Bolton 1999), provided that HCOO$^-$ is more reactive than CH$_3$SO$_3^-$ toward these species.

\[
\text{NO}_3^- + h\nu + H^+ \rightarrow \cdot \text{OH} + \cdot \text{NO}_2
\]  
\[
\text{NO}_3^- + h\nu + H^+ \rightarrow \text{HOONO}
\]  
\[
\text{NO}_3^- + h\nu \rightarrow \text{NO}_2^- + O
\]  

Evidence supporting this hypothesis was obtained upon UVB irradiation of HCOO$^-$ / CH$_3$SO$_3^-$ mixtures with 4 mM nitrate. In the presence of 5 µM HCOO$^-$ + 5 µM CH$_3$SO$_3^-$, the ratio of the respective initial transformation rates was \( \text{Rate}_{HCOO^-} / \text{Rate}_{CH_3SO_3^-} \) = 4.1±0.7, and with 10 µM HCOO$^-$ + 10 µM CH$_3$SO$_3^-$ it was \( \text{Rate}_{HCOO^-} / \text{Rate}_{CH_3SO_3^-} \) = 2.8±0.4. If a compound \( i \) only reacts with *OH, its initial transformation rate would be \( \text{Rate}_i = k_i \cdot [\cdot \text{OH}] \cdot C_i \), where \( C_i \) is the initial concentration of \( i \). In the presence of HCOO$^-$ and...
CH$_3$SO$_3^-$ at equal concentration, one would expect $Rate_{HCOO^-} (Rate_{CH_3SO_3^-})^{-1} = k_{HCOO^- \cdot \cdot OH} (k_{CH_3SO_3^- \cdot \cdot OH})^{-1} = 2.3$. The fact that the experimental ratio of the initial rates was higher than expected for a reaction merely involving $^\circ$OH, suggests that additional species formed by nitrate photolysis would be involved in transformation. It also implies that HCOO$^-$ would be more reactive than CH$_3$SO$_3^-$ toward these species.

Nitrogen dioxide is one of the reactive transients formed upon nitrate photolysis that could be involved in the process. A rather straightforward way of producing $^\circ$NO$_2$ is irradiation of $\alpha$-Fe$_2$O$_3$ and nitrite (Chiron et al. 2009), which was adopted here to assess the possible reaction of HCOO$^-$ and CH$_3$SO$_3^-$ with $^\circ$NO$_2$.

### 3.2. Assessment of the reactivity of HCOO$^-$ and CH$_3$SO$_3^-$ with $^\circ$NO$_2$

Figure 2 reports the transformation rates of 10 µM HCOO$^-$ and 10 µM CH$_3$SO$_3^-$ (irradiated separately under blue light) with 100 mg L$^{-1}$ $\alpha$-Fe$_2$O$_3$, 0.01 M nitrite, and 100 mg L$^{-1}$ $\alpha$-Fe$_2$O$_3$ + 0.01 M nitrite. Transformation was negligible with $\alpha$-Fe$_2$O$_3$, significant with NO$_2^-$, and considerably enhanced with $\alpha$-Fe$_2$O$_3$ + NO$_2^-$, which also caused significantly faster transformation of HCOO$^-$ compared to CH$_3$SO$_3^-$.

**Figure 2.** Initial transformation rates of 10 µM HCOONa and 10 µM CH$_3$SO$_3$Na, irradiated separately in the presence of 100 mg L$^{-1}$ $\alpha$-Fe$_2$O$_3$, of 0.01 M nitrite, and of 100 mg L$^{-1}$ $\alpha$-Fe$_2$O$_3$ + 0.01 M nitrite. Irradiation was carried out at pH 6, under blue light and in air-equilibrated solutions or suspensions. The considerable enhancement of substrate (HCOO$^-$ and CH$_3$SO$_3^-$) degradation in the mixture of $\alpha$-Fe$_2$O$_3$ + nitrite is evidence of significant reactivity with $^\circ$NO$_2$. Furthermore, the data suggest that HCOO$^-$ is considerably more reactive than CH$_3$SO$_3^-$ toward $^\circ$NO$_2$.

Irradiation of the semiconductor oxide $\alpha$-Fe$_2$O$_3$ below 530 nm induces the production of electron-hole couples ($e^-_{CB}/h^+_{VB}$), because of light-induced $e^-$ promotion from the valence (VB) to the conduction band (CB) (Siffert and Sulzberger, 1991). The $e^-_{CB}$ would react with Fe(III) and O$_2$ to yield O$_2^-$, while h$^+_{VB}$ could react with dissolved substrates. Nitrite irradiation yields $^\circ$OH, $^\circ$NO and $^\circ$NO$_2$ (Mack and Bolton 1999), but $\alpha$-Fe$_2$O$_3$ would somewhat inhibit the photolysis of NO$_2^-$ by absorption and scattering of radiation. A major process with $\alpha$-Fe$_2$O$_3$ + NO$_2^-$ would be the oxidation of NO$_2^-$ to $^\circ$NO$_2$ by h$^+_{VB}$ (Chiron et al. 2009).

\[
\begin{align*}
\alpha\text{-Fe}_2\text{O}_3 + h\nu &\rightarrow e^-_{CB} + h^+_{VB} \quad (4) \\
e^-_{CB} + \text{Fe(III)} &\rightarrow \text{Fe(II)} \rightarrow (+ \text{O}_2) \rightarrow \text{Fe(III)} + \text{O}_2^- \quad (5)
\end{align*}
\]
\[ \text{NO}_2^- + \text{hv} + \text{H}^+ \rightarrow \cdot \text{OH} + \cdot \text{NO} \]  
\[ \text{NO}_2^- + \cdot \text{OH} \rightarrow \cdot \text{NO}_2 + \text{OH}^- \]  
\[ \text{h}^*_{\text{VB}} + \text{NO}_2^- \rightarrow \cdot \text{NO}_2 \]  

Photogenerated \( \cdot \text{NO}_2 \) could react with dissolved species (HCOO\(^-\) or CH\(_3\)SO\(_3^-\)) in the present case, undergo dimerisation/hydrolysis or react with O\(_2^-\) (Mack and Bolton 1999; Vione et al. 2011). Because of competition between these processes, the transformation rates of organic compounds with \( \alpha\)-Fe\(_2\)O\(_3\) + NO\(_2^-\) under irradiation would be proportional to their reactivity with \( \cdot \text{NO}_2 \) (Chiron et al., 2009).

The significant transformation of both HCOO\(^-\) and CH\(_3\)SO\(_3^-\) with \( \alpha\)-Fe\(_2\)O\(_3\) + NO\(_2^-\), compared with insignificant transformation with \( \alpha\)-Fe\(_2\)O\(_3\) alone, indicates that nitrite would be considerably more reactive than either HCOO\(^-\) or CH\(_3\)SO\(_3^-\) toward h\(^*\)\(_{\text{VB}}\). Reaction (8) would in fact transform h\(^*\)\(_{\text{VB}}\) into \( \cdot \text{NO}_2 \) that reacts with organic substrates. Moreover, the faster transformation of HCOO\(^-\) compared to CH\(_3\)SO\(_3^-\) in the presence of \( \alpha\)-Fe\(_2\)O\(_3\) + NO\(_2^-\) suggests higher reactivity of formate with \( \cdot \text{NO}_2 \). This result is consistent with our previous findings (section 3.1) on transformation of the two substrates with irradiated nitrate. Figure 2 suggests that, depending on the importance of reactions (6,7) (nitrite photolysis) in the presence of \( \alpha\)-Fe\(_2\)O\(_3\) + NO\(_2^-\), the radical \( \cdot \text{NO}_2 \) would react from 1.52±0.22 to 2.27±1.13 times faster with HCOO\(^-\) than with CH\(_3\)SO\(_3^-\).

When \( \alpha\)-Fe\(_2\)O\(_3\) is irradiated in the UV region, in addition to reactions (4, 5), excitation of surface Fe\(^{3+}\)-OH groups produces \( \cdot \text{OH} \) (reaction 9; Siffert and Sulzberger, 1991). Because of \( \alpha\)-Fe\(_2\)O\(_3\) atmospheric significance, the transformation of HCOO\(^-\) and CH\(_3\)SO\(_3^-\) was also studied under UV irradiation.

\[ = \text{Fe}^{3+}\text{-OH} + \text{hv} \rightarrow =\text{Fe}^{2+} + \cdot \text{OH} \]  

3.3. Transformation of HCOO\(^-\) and CH\(_3\)SO\(_3^-\) by hematite under UV irradiation

Figure 3 reports the initial transformation rates of HCOO\(^-\) and CH\(_3\)SO\(_3^-\) in mixture upon UV irradiation of hematite in aqueous suspension at different loadings. The Figure shows that HCOO\(^-\) rates are higher than those of CH\(_3\)SO\(_3^-\). Moreover, the rates are maximum for 50-100 mg L\(^{-1}\) \( \alpha\)-Fe\(_2\)O\(_3\). The decrease of the rates at high \( \alpha\)-Fe\(_2\)O\(_3\) is probably accounted for by radiation scattering of \( \alpha\)-Fe\(_2\)O\(_3\) particles (Hoffmann et al. 1995). The ratio Rate\(_{\text{HCOO}}\) (Rate\(_{\text{CH}_3\text{SO}_3}\))\(^{-1}\) varied in the range of 1.6±0.9 to 2.9±1.0 at different loadings of \( \alpha\)-Fe\(_2\)O\(_3\). Such values of the ratio could be consistent with the involvement of photogenerated \( \cdot \text{OH} \) in the transformation of the two substrates, which would give Rate\(_{\text{HCOO}}\) (Rate\(_{\text{CH}_3\text{SO}_3}\))\(^{-1}\) = 2.3. In fact, irradiation of HCOO\(^-\) and CH\(_3\)SO\(_3^-\) in mixture means that the two anions would compete for reaction with the hydroxyl radical, and transformation rates are expected to be proportional to the respective rate constants with \( \cdot \text{OH} \). Note that insignificant adsorption of either HCOO\(^-\) or CH\(_3\)SO\(_3^-\) on hematite was observed in dark experiments, which implies that measured transformation rates were genuine and not biased by adsorption.

An important role of \( \cdot \text{OH} \) in phototransformation by \( \alpha\)-Fe\(_2\)O\(_3\) would be consistent with the limited reactivity observed between HCOO\(^-\) / CH\(_3\)SO\(_3^-\) and h\(^*\)\(_{\text{VB}}\) under blue light. h\(^*\)\(_{\text{VB}}\) is in fact the most important
alternative reactant to *OH in the presence of irradiated α-Fe₂O₃ (Siffert and Sulzberger, 1991). Additional evidence of *OH playing an important role in the system is the significant inhibition of photodegradation upon addition of 2-propanol (data not shown), which is a known *OH scavenger (Buxton et al. 1988).

Figure 3. Initial transformation rates of 10 µM HCOONa and 10 µM CH₃SO₃Na in mixture upon UV irradiation of α-Fe₂O₃ at variable loading. The dashed lines are just a guide for the eye. Irradiation at pH 6, air-equilibrated suspensions. The transformation of HCOO⁻ is about twice as fast compared to CH₃SO₃⁻. Considering the poor reactivity between the two substrates and the valence-band holes of α-Fe₂O₃, transformation would be accounted for mainly by *OH.

4. Conclusions

The phototransformation of formate was considerably faster than that of methanesulphonate in the presence of both nitrate and α-Fe₂O₃ under irradiation. The ratio \( \frac{Rate_{HCOO^-}}{Rate_{CH₃SO₃^-}} \) varied depending on the conditions, from 1.6±0.9 (α-Fe₂O₃ at low loading) to 4.1±0.7 (4 mM nitrate). Formate, in addition to reacting faster than CH₃SO₃⁻ toward *OH, would also undergo reaction with additional transients such as *NO₂.

Considering the significance of both nitrate and α-Fe₂O₃ as photoactive species in atmospheric aerosols, it is suggested that formate (marker of continental particles) would undergo faster transformation than methanesulphonate (biogenic marine marker) during particle transport. Transport would thus reduce the HCOO⁻/CH₃SO₃⁻ concentration ratio and cause an under-estimate of the continental particle sources, with a corresponding over-estimate of the marine biogenic ones. Because marine biogenic particles have a cooling potential (Fattori et al. 2005; Anderson et al. 2008), faster HCOO⁻ phototransformation may finally lead to over-estimating the cooling effect of aerosols on the global climate.

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References


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