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Performance and selectivity of the terephthalic acid probe for $\bullet\text{OH}$ as a function of temperature, pH and composition of atmospherically relevant aqueous media

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Keywords

Hydroxyl radical; chemical probe; fluorescence; atmospheric oxidant.

Abstract

In the present study, we investigate the performance and selectivity of terephthalic acid (TA) as a trapping molecule for the laboratory quantification of photogenerated $\bullet\text{OH}$ in synthetic water (where the organic and inorganic concentration is perfectly controlled), adopted as a proxy of natural atmospheric water (*i.e.* cloud droplets). TA reacts with $\bullet\text{OH}$ to yield 2-hydroxyterephthalic acid (TAOH). First, we focused our investigation on the reactivity of TA as a function of pH and temperature of laboratory-made solutions, by using nitrate and hydrogen peroxide as photochemical $\bullet\text{OH}$ sources. For the pH dependence of the TAOH formation yield (Y_{TAOH}), by fitting data using linear regression we obtained the relationship

$Y_{\text{TAOH}} = (0.0248 \pm 0.0059) \text{ pH} + (0.046 \pm 0.035)$ at $T = 288 \text{ K}$, in the pH range 3.9-7.5. For the temperature dependence we got $Y_{\text{TAOH}} = (0.0059 \pm 0.0011) T - (1.50 \pm 0.31)$, between 278 and 303 K at pH 5.4. Furthermore, the performance and selectivity of TA were assessed in the presence of different photochemical $\bullet\text{OH}$ sources (nitrate and H_2O_2) and scavengers (alcohols and carboxylic acids) at variable concentrations. These species are naturally present in the atmospheric aqueous phase. From these experiments we obtained the second-order reaction rate constant between TA and $\bullet\text{OH}$, $k_{\text{TA},\bullet\text{OH}} = (4.0 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in aerated solution, at pH 6.0 and $293 \pm 2 \text{ K}$.

1. Introduction

The quantification of the hydroxyl radical in aquatic systems and more particularly in atmospheric water is of great interest, because $\bullet\text{OH}$ is a major oxidant. In the atmosphere, the relevant impact of $\bullet\text{OH}$ (also called the “cleaning agent” of the atmosphere) on the chemical composition of the gas phase, of aerosols and of cloud droplets is well established [1-3]. In particular, aerosols and cloud droplets could modify the ground radiation budget and play the double role of cooling (reflecting the incident solar light) and reheating the Earth (greenhouse effect) [4-6]. This opposing role strongly depends on the chemical aerosol composition and, as a consequence, also on the photochemical fate of its constituents.

A large number of recent studies allows for a proper characterization of the main physico-chemical and chemical properties of the particles in the atmosphere [7]. However, as far as the reactive species (*e.g.* $\bullet\text{OH}$) are concerned, the most important mechanisms of their photochemical generation and the relevant quantification techniques are still not completely understood or have not been characterized. The quantification of the possible sources and sinks of photogenerated radical species is a key step in assessing the transformation of organic and inorganic molecules in the atmosphere, including the formation of Humic-Like substances (HULIS) that may play an important role in photosensitized reactions [8].

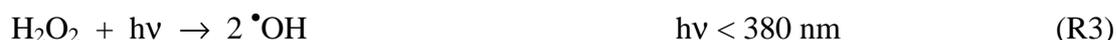
Moreover, the current atmospheric models are able to predict the physico-chemical processes of the atmosphere, to prevent pollution episodes and help a policy targeted at the improvement of air quality. However, to predict the atmospheric fate of organic compounds, the models require more precise estimates of the radical reactions that take place in the gas, liquid and on the solid phases. The exact quantification of $\bullet\text{OH}$ photogeneration in cloud water is, therefore, of paramount importance.

The radical $\bullet\text{OH}$ in cloud water could be generated via ozone (O_3) photolysis to electronically excited oxygen atoms $\text{O}({}^1\text{D})$, followed by reaction with water. It could also reach the aqueous phase by dissolution from the gas phase [1]. Moreover, atmospheric hydrogen peroxide is currently considered as an important photochemical source of hydroxyl ($\bullet\text{OH}$) and hydroperoxyl ($\text{HO}_2\bullet$) radicals [1]. In addition, inorganic species and organic pollutants present in the atmospheric aqueous phase such as NO_3^- , NO_2^- , Fe complexes and more recently nitro-PAHs, are known sources of $\bullet\text{OH}$ via photochemical and photosensitized reactions [9-12]. The relative importance of the cited $\bullet\text{OH}$ sources is highly variable, depending on the composition of the aqueous phase.

Due to its high reactivity with the organic and inorganic constituents of atmospheric waters, the quantification of $\bullet\text{OH}$ is extremely difficult. Moreover, reactive species such as triplet states, singlet oxygen and NO_x radicals could react with the $\bullet\text{OH}$ probe molecules and perturb as a consequence the $\bullet\text{OH}$ measurement. In order to determine its photochemical formation and to quantify $\bullet\text{OH}$ in natural systems, different techniques are employed and different reactive molecules are used as probes: benzene, benzoic acid, salicylate, hydroxymethanesulfonate (HMSA) and more recently phthalhydrazide [13-16].

Fang and coworkers [17] investigated the possible reaction of $\bullet\text{OH}$ with TA upon addition to the aromatic ring. The authors reported that the main reaction was the attack of $\bullet\text{OH}$ to produce 2-hydroxyterephthalic acid (TAOH) (see Figure 1), quantifiable via fluorescence. The yield was estimated to be at least 84 % in oxygen-free solution. However, the presence of oxygen enables ring-fragmentation reactions that reduce the hydroxylation yield to 35 %. Unfortunately no literature data are available, to our knowledge, on the dependence of the TAOH formation yield as a function of pH, temperature and the presence of inorganic or organic compounds that could modify the chemical composition and the ionic strength of the solution [18-21]. These knowledge gaps could considerably hinder the applicability of TA as a molecular probe for $\bullet\text{OH}$ quantification in laboratory studies.

Therefore, the aim of this work is to assess the suitability of terephthalic acid (TA) as a probe for photogenerated hydroxyl radical in water, using nitrate and hydrogen peroxide (both naturally present in atmospheric water [22]) as photochemical $\bullet\text{OH}$ precursors:



In the first part of the work, we assessed the performance and selectivity of terephthalic acid as $\bullet\text{OH}$ probe, studying the TAOH yield as a function of the pH and temperature of the aqueous solution. In the second part, we investigated on the reactivity of TA towards $\bullet\text{OH}$, photogenerated by nitrate and hydrogen peroxide, and on the impact that inorganic and organic compounds present in cloud water can have on the reaction.

2. Materials and methods

2.1. Chemicals. Terephthalic acid (Benzene-1,4-dicarboxylic acid) (Aldrich) and 2-hydroxyterephthalic acid (TAOH) (Atlantic Research Chemical), with a purity of 98 and 97 % respectively, were used without additional purification. NaOH, HClO_4 , 2-propanol (HPLC grade) and other solvents were purchased from Aldrich.

The water used to prepare the solutions was purified with a Millipore water system (Millipore αQ , resistivity $18\text{ M}\Omega\text{ cm}$, $\text{DOC} < 0.1\text{ mg L}^{-1}$). All synthetic solutions were stored in the dark at 277 K and their stability was checked regularly by ion chromatography. Fresh solutions doped with nitrate or H_2O_2 were prepared before each experiment. The concentration of the stock solution of H_2O_2 in milli-Q water was determined using a molar absorption coefficient of $38.1 \pm 1.4\text{ M}^{-1}\text{ cm}^{-1}$ at 240 nm [23].

2.2. Quantification of TAOH in aqueous solution. Two different setups were used to explore and understand the sensitivity and suitability of TA as probe for the quantification of $\bullet\text{OH}$ in irradiated aqueous solutions.

Polychromatic irradiation followed by quantification of TA and TAOH concentration via HPLC analysis was used to explore the effect of pH and temperature on the phototransformation yield of TA into TAOH. The adopted procedure was the following: 40 mL of TA solution with nitrate (or H_2O_2) were irradiated in a thermostated cylindrical reactor under polychromatic radiation ($\lambda > 300\text{ nm}$), generated by a 1000 W Xenon lamp equipped with a Pyrex filter. At fixed time intervals an aliquot of the solution ($200\text{ }\mu\text{L}$) was withdrawn and analyzed by HPLC (Waters Alliance instrument) equipped with UV-visible and fluorescence detectors. The column used was a Hypersil BDS C18 ($5\text{ }\mu\text{m}$, $125\text{ mm} \times 4\text{ mm}$). The samples were eluted with a gradient of CH_3CN (A) and H_2O (B), the latter containing 5 mM tetrabutylammonium bromide at pH 2.8, adjusted with H_3PO_4 . The gradient used was: 80 % (B) at $t = 0$, to 70 % (B) at $t = 15\text{ min}$ and keep for 1 min, back to the initial conditions in 1

min and keep for 2 min. TAOH was detected by fluorescence ($\lambda_{\text{exc}} = 320$ nm and $\lambda_{\text{em}} = 420$ nm), TA by UV-vis absorption at 240 nm. The flow rate was 1 mL min^{-1} , the injection volume $50 \text{ }\mu\text{L}$. The column was thermostated at 293 K and, under such conditions, the retention times were (min): TA (4.9) and TAOH (11.8).

The time evolution of TA was fitted with pseudo-first order decay equations of the form $C_t = C_o \exp(-k_{TA}^d t)$, where C_t is the concentration of TA at the time t , C_o its initial concentration, and k_{TA}^d the pseudo-first order degradation rate constant of TA. The initial degradation rate of TA is $k_{TA}^d C_o$. The time evolution of TAOH was fitted with $C'_t = k_{TAOH}^f C_o (k_{TAOH}^d - k_{TA}^d)^{-1} [\exp(-k_{TA}^d t) - \exp(-k_{TAOH}^d t)]$, where k_{TAOH}^f and k_{TAOH}^d are the pseudo-first order rate constants for the formation and the degradation of TAOH, respectively. The initial formation rate of TAOH is $k_{TAOH}^f C_o$. The error bounds associated to the rate data represent $\mu \pm \sigma$, derived from the scattering of the experimental data around the fitting curves (intra-series variability).

To check the reactivity of TA toward different $\bullet\text{OH}$ sources at variable concentrations, we proceeded as follows: 3 mL of TA solution ($50 \text{ }\mu\text{M}$ if not otherwise specified) were irradiated in a stirred quartz cuvette (Hellma QS) under monochromatic light (313 nm) by means of a Hg 200 W lamp (ORIEL) equipped with a monochromator. The incident photon flux at 313 nm was measured as 12 W m^{-2} using ferrioxalate actinometry [24]. At fixed time intervals during irradiation, the cuvette was transferred into a Perkin-Elmer MPF 3 L spectrofluorimeter. The formation of $\bullet\text{OH}$ was monitored from the fluorescence of TAOH ($\lambda_{\text{exc}} = 320$ nm, $\lambda_{\text{em}} = 420$ nm), quantifiable using standard solutions. TAOH derives from the $\bullet\text{OH}$ -mediated oxidation of TA. Monochromatic irradiation experiments were carried out at ambient temperature (293 ± 2 K). It should be noted that the direct determination of TAOH by fluorescence spectroscopy is much easier and faster than the HPLC analysis.

Figure 2 reports the emission spectrum of the 1000 W xenon lamp, measured with an Ocean Optics SD 2000 CCD spectrophotometer (calibrated by using a DH-2000-CAL Deuterium Tungsten Halogen reference lamp), and the absorption spectra of TA, nitrate and H_2O_2 , measured with a Varian Cary 300 UV-Vis spectrophotometer.

2.3. Hydroxylation yield of TA into TAOH. The hydroxylation yield of TA into TAOH (Y_{TAOH}) in the presence of $\bullet\text{OH}$ was determined as the ratio between the initial formation rate of TAOH (R_{TAOH}^f) and the initial degradation rate of TA (R_{TA}^d). For each experiment, a control was carried out to evaluate the possible formation of TAOH in the dark. The initial formation

rate of TAOH was then calculated as $R_{TAOH}^f = R_{TAOH}^{irradiation} - R_{TAOH}^{dark}$, where $R_{TAOH}^{irradiation}$ and R_{TAOH}^{dark} are the formation rates of TAOH with and without irradiation, respectively. No dark formation of TAOH was appreciated with nitrate as the $\bullet\text{OH}$ source, while in the presence of H_2O_2 the dark formation of TAOH had to be taken into account to calculate R_{TAOH}^f . In order to evaluate the possible formation of TAOH and the degradation of TA under the adopted photochemical conditions, both molecules were irradiated in ultra-pure water for 20 min under polychromatic and monochromatic wavelengths. No variations of the UV-vis spectrum and fluorescence signal were noticed.

3. Results and discussion

The goal of this work is to assess the performance and sensitivity of TA as a probe for $\bullet\text{OH}$ production upon irradiation of laboratory-made solutions, where the $\bullet\text{OH}$ sources and sinks can be easily controlled and quantified. In the first part we investigated the pH and temperature dependence of the reactivity of TA towards $\bullet\text{OH}$, produced by irradiation of nitrate or H_2O_2 . We continued our work by investigating the role of single constituents of atmospheric cloud water such as NO_3^- , H_2O_2 and carboxylic acids, in order to assess the suitability of TA as an $\bullet\text{OH}$ probe in such media. In Table S1 (Supporting Information, hereafter SI), we report the concentration of major organic (carboxylic acids) and inorganic constituents of artificial cloud water used during this work. The adopted concentration values and the studied ranges of pH (3.9 - 7.5) and temperature (278 - 303 K) were chosen with the purpose of obtaining conditions that are relevant to atmospheric waters [1, 22]. Also note that Fe(II) and Fe(III) were not adopted here as $\bullet\text{OH}$ sources, because their complex aqueous chemistry makes it difficult to quantify their importance as sources of hydroxyl radicals in atmospheric waters, which may well be limited under many conditions [20]. Fe(II) and Fe(III) might be associated with Fenton and Fenton-like reactions that produce oxidizing species, the exact nature of which is still under dispute ($\bullet\text{OH}$ and/or ferryl ion) and, for this reason, is not exactly quantifiable [25]. These considerations do not support the use of Fe(III) and/or the Fenton reaction to test an $\bullet\text{OH}$ probe. Ozone was also not adopted as $\bullet\text{OH}$ source because, although important in the (photo)chemistry of atmospheric water droplets [12], due to its very short lifetime it would play a negligible role as $\bullet\text{OH}$ source in most laboratory investigations.

3.1. TAOH formation yield: effect of pH. To understand the pH dependence of the yield of the reaction $\text{TA} + \bullet\text{OH} \rightarrow \text{TAOH}$, solutions containing 200 μM TA and 200 μM nitrate in the pH range 3.9 - 7.5 were irradiated. The temperature of the solution was settled at 288 ± 1 K. As shown in Figure 3A, the formation yield of TAOH (Y_{TAOH}) decreased with decreasing pH, ranging from 0.23 to 0.15 at pH 7.5 and 3.9, respectively. A linear correlation between Y_{TAOH} and pH followed the relationship $Y_{\text{TAOH}} = (0.0248 \pm 0.0059) \text{pH} + (0.046 \pm 0.035)$ ($R^2 = 0.85$ from linear regression analysis). Error bounds represent $\pm 1\sigma$. The Spearman test indicated that the linear correlation is statistically significant ($p < 0.03$).

The pH values could affect the reactivity of TA towards $\bullet\text{OH}$, or the photoformation yield of $\bullet\text{OH}$ from nitrate (see reaction R1). To discriminate among the two processes, similar experiments were carried out by irradiating 4 μM H_2O_2 in the presence of 200 μM TA, at pH 4.3 and 6.7. The results, shown in Figure 3A (empty triangles), are in agreement with those obtained from nitrate photolysis. Because the $\bullet\text{OH}$ photogeneration by H_2O_2 does not depend on pH [22, 26], it is possible to conclude that the observed pH trend of Y_{TAOH} is caused by the reactivity between TA and $\bullet\text{OH}$ and, therefore, can be generalized to photochemical systems other than nitrate under irradiation. The pH trend of Y_{TAOH} should be taken into account when studying the formation of $\bullet\text{OH}$ by use of TA in natural samples.

Note that TA is a dicarboxylic acid with pK_a values of 3.52 and 4.46 [27]. Therefore, over most of the studied pH range the doubly dissociated form would prevail, which could not account for the observed pH effect. Given the relatively complex reaction pathways that define Y_{TAOH} through competition between ring addition and ring cleavage [17], it is possible that the pH effect derives from equilibria involving one or more reaction intermediates.

3.2. Effect of the Temperature. The temperature effect on the reaction $\text{TA} + \bullet\text{OH} \rightarrow \text{TAOH}$ was investigated upon irradiation of 200 μM TA in the presence of 200 μM NO_3^- at pH 5.4, between 278 and 303 K. The value of Y_{TAOH} at 278 K (0.13 ± 0.03) was approximately 40 % of that obtained at 303 K (0.32 ± 0.05). Moreover, as shown in Figure 3B, the data could be fitted with the linear regression $Y_{\text{TAOH}} = (0.0059 \pm 0.0011) T - (1.50 \pm 0.31)$ ($R^2 = 0.84$ from linear regression analysis). The Spearman test indicated that the linear correlation is statistically significant ($p < 0.005$).

In analogy with the case of pH, the effect of temperature on Y_{TAOH} could depend on the photogeneration yield of $\bullet\text{OH}$ from nitrate and/or on TA reactivity. To clarify this point, the degradation and formation rates of TA and TAOH were plotted as a function of solution

temperature. As shown in Figure 4, the degradation rate of TA (R_{TA}^d) is close to $\sim 7.4 \times 10^{-11}$ M s⁻¹, while the formation rate of TAOH shows a temperature dependence and ranges from 1.0×10^{-11} M s⁻¹ at 278 K to 2.4×10^{-11} at 303 K. It is also possible to obtain a linear dependence of the TAOH formation rate on the temperature: $R_{TAOH}^f = (4.73 \pm 0.71) \times 10^{-13} T - (1.21 \pm 0.21) \times 10^{-10}$. TA is the main \bullet OH scavenger in the studied systems, thus R_{TA}^d would be equal to the formation rate of \bullet OH by nitrate. Because R_{TA}^d does not show any significant temperature dependence (the value is always close to 7.4×10^{-11} M s⁻¹) compared to R_{TAOH}^f (see Figure 4), we can argue that the formation of \bullet OH upon nitrate photolysis is unaffected by temperature. The temperature variation of Y_{TAOH} would thus be accounted for by changes in the reaction pathways of the hydroxylation process.

3.3. Nitrate and hydrogen peroxide photolysis. A major issue to be tested is that the TAOH formation rate really measures the rate of \bullet OH production through the yield Y_{TAOH} . Figure S2A (SI) reports the time evolution of the fluorescence intensity at 420 nm, upon irradiation at 313 nm of solutions containing different concentrations of nitrate (from 50 μ M to 1 mM) in the presence of 50 μ M TA. The linear increase of the fluorescence intensity with the irradiation time enabled the calculation of the formation rate of TAOH from the line slope. The linearity of the TAOH initial formation rate vs. nitrate and H₂O₂ concentration is shown in Figure S2B (SI).

Irradiation of 200 μ M NO₃⁻ with different TA concentrations (50, 300 and 500 μ M) was performed to determine the amount of TA necessary to trap all the photogenerated \bullet OH. If the amount of TA is high enough to react rapidly with all the \bullet OH radicals, R_{TAOH}^f would depend on the rate of \bullet OH formation and would, therefore, be independent of the TA concentration. The experimental data confirm such a condition and suggest that the adopted 50 μ M TA is able to quantitatively trap \bullet OH produced by nitrate photolysis in water.

3.4. Quantum yield of \bullet OH production. In order to compare the use of TA with other methods of \bullet OH quantification, the quantum yield values ($\Phi_{\bullet OH}$) obtained upon nitrate photolysis in this and other studies are reported in Table 1. From the experimental data of Y_{TAOH} obtained during this work we were able to derive the quantum yield $\Phi_{\bullet OH}$ of nitrate photolysis at 313 nm, as 0.0012 ± 0.002 , 0.016 ± 0.004 and 0.014 ± 0.001 at T = 298 K, for

pH 5.1, 6.0 and 7.6, respectively. The estimated $\bullet\text{OH}$ quantum yield values ($\Phi_{\bullet\text{OH}}$) are in good agreement with the published data obtained under similar pH and temperature conditions [28-30]. It can be concluded that TA is a suitable molecule for $\bullet\text{OH}$ detection.

3.5. Effect of inorganic ions. The assessment of the role of inorganic ions, as species able to interfere with the reaction $\text{TA} + \bullet\text{OH} \rightarrow \text{TAOH}$, was carried out in the presence of acetic, formic, succinic and oxalic acids as major organic compounds identified in the cloud aqueous phase (see Table S1, SI) [31].

Experiments were carried out with 50 μM TA and different amounts of nitrate (200 μM , 700 μM and 2 mM). No change in the initial formation rate of TAOH was observed upon addition of inorganic ions relevant to the atmospheric aqueous phase, such as Cl^- , NH_4^+ and SO_4^{2-} [32]. The data also indicate that Y_{TAOH} is independent of the ionic strength (I) of the solution in the range of $I = 250 \mu\text{M} - 2 \text{ mM}$. Therefore, it is concluded that these ions do not interfere with the TA/TAOH probe reaction, under conditions that are relevant to the atmospheric aqueous phase.

3.6. $\bullet\text{OH}$ formation rate and reaction rate constant between TA and $\bullet\text{OH}$. In order to derive the second-order rate constant between TA and $\bullet\text{OH}$, aqueous solutions of 50 μM TA were irradiated in the presence of 200 μM NO_3^- or 200 μM H_2O_2 , with the addition of different concentration values of 2-propanol (2Pr). This alcohol is a $\bullet\text{OH}$ scavenger, with a second-order rate constant $k_{2\text{Pr},\bullet\text{OH}} = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [33].

In the case of nitrate, which does not react with $\bullet\text{OH}$, there is only competition between TA and 2-propanol for reaction with $\bullet\text{OH}$. With $R_{\text{OH},\text{NO}_3^-}$ as the formation rate of $\bullet\text{OH}$ upon irradiation of nitrate one obtains:

$$R_{\text{TAOH},\text{NO}_3^-}^f = \frac{Y_{\text{TAOH}} R_{\text{OH},\text{NO}_3^-} k_{\text{TA},\bullet\text{OH}} [\text{TA}]}{k_{\text{TA},\bullet\text{OH}} [\text{TA}] + k_{2\text{Pr},\bullet\text{OH}} [2\text{Pr}]} \quad (1)$$

From the data fitting of the nitrate experiment with equation (1), which is reported in Figure 5A, and by using $Y_{\text{TAOH}} = 0.19$, we obtained $R_{\text{OH},\text{NO}_3^-} = (2.01 \pm 0.11) \times 10^{-10} \text{ M s}^{-1}$ and $k_{\text{TA},\bullet\text{OH}} = (3.9 \pm 0.1) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The photolysis of H_2O_2 is also a rather clean source of $\bullet OH$ (R3), although the reaction between H_2O_2 and $\bullet OH$ introduces some complications into the system ($k_{H_2O_2, \bullet OH} = 2.7 \times 10^7 M^{-1} s^{-1}$) [33]. However, the formation of $HO_2\bullet/O_2^{\bullet -}$ might only cause limited interference because hydroperoxide and superoxide are poorly reactive. In the presence of irradiated H_2O_2 , there is competition for photogenerated $\bullet OH$ between H_2O_2 itself, TA and 2-propanol. With $R_{\bullet OH, H_2O_2}$ as the formation rate of $\bullet OH$ upon irradiation of hydrogen peroxide and $k_{TA, \bullet OH}$ as the reaction rate constant between TA and $\bullet OH$, upon application of the steady-state approximation to $[\bullet OH]$ one derives the following equation:

$$R_{TAOH, H_2O_2}^f = \frac{Y_{TAOH} R_{\bullet OH, H_2O_2} k_{TA, \bullet OH} [TA]}{k_{TA, \bullet OH} [TA] + k_{H_2O_2, \bullet OH} [H_2O_2] + k_{2Pr, \bullet OH} [2Pr]} \quad (2)$$

From the fit with equation (2) of the H_2O_2 data, which is reported in Figure 5A, and by using $Y_{TAOH} = 0.19$ we obtained $R_{\bullet OH, H_2O_2} = (2.62 \pm 0.14) \times 10^{-9} M s^{-1}$ and $k_{TA, \bullet OH} = (4.1 \pm 0.1) \times 10^9 M^{-1} s^{-1}$. Note the very good agreement of the $k_{TA, \bullet OH}$ values obtained upon irradiation of nitrate and H_2O_2 . The agreement constitutes further evidence of the suitability of TA as $\bullet OH$ probe. The value of the second-order rate constant between TA and $\bullet OH$ obtained in these experiments compares well with the results of Saran and Summer [34]. These authors reported a reaction rate constant $k_{TA, \bullet OH} = 3.3 \times 10^9 M^{-1} s^{-1}$, showing a possible competition of the probe molecule (TA) with biomolecules under physiological conditions.

The data obtained with both NO_3^- and H_2O_2 suggest that TA undergoes selective reaction with $\bullet OH$, with rate constant $k_{TA, \bullet OH} = (4.0 \pm 0.1) \times 10^9 M^{-1} s^{-1}$.

3.7. $\bullet OH$ quantification in artificial cloud water. As discussed in the materials and methods section, synthetic solutions were used as proxies of cloud water composition.

To evaluate the adequate concentration of TA needed to quantitatively determine $\bullet OH$ photoformation in synthetic cloud water, a series of experiments was performed and the results indicated a plateau of R_{TAOH}^f for $[TA] > 900 \mu M$.

Further experiments were carried out with 1 mM TA in artificial cloud water, with the composition reported in Table S2. Figure 5B reports R_{TAOH}^f , upon 313 nm irradiation of

artificial cloud water, as a function of the concentration of added 2-propanol. In the systems under study, the expected source of $\bullet\text{OH}$ is nitrate and the possible scavengers are TA, 2-propanol and the organic acids. The reaction rate constants with $\bullet\text{OH}$ are $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (2-propanol), $7.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (acetic acid), $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (formic acid), $5.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (succinic acid), and $7.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (oxalic acid) [33, 35]. For the reaction rate constant of TA with $\bullet\text{OH}$, we used $4.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ as previously evaluated in this paper. The experimental data reported in Figure 5B were fitted with the following equation:

$$R_{TAOH}^f = \frac{Y_{TAOH} R_{\bullet\text{OH}, \text{NO}_3^-} k_{TA, \bullet\text{OH}} [TA]}{k_{TA, \bullet\text{OH}} [TA] + k_{2\text{Pr}, \bullet\text{OH}} [2\text{Pr}] + \sum_i k_{S_i} [S_i]} \quad (3)$$

where $Y_{TAOH} \times R_{\bullet\text{OH}, \text{NO}_3^-}$ was the only fit variable. The value of $\sum_i k_{S_i} [S_i]$ was calculated as the sum of the contributions of 20.0 μM acetic acid, 14.5 μM formic acid, 1.5 μM succinic acid and 3.0 μM oxalic acid, with the reaction rate constants reported above. $\sum_i k_{S_i} [S_i] = 4.0 \times 10^4 \text{ s}^{-1}$ was obtained. Figure 5B shows the very good fit of equation (3) to the experimental data, taking into account the detection limit of our measures quantified as $5 \times 10^{-12} \text{ M s}^{-1}$ (obtained by taking into account the signal-to noise ratio of the fluorescence detection system). It is further confirmed that TA is a good $\bullet\text{OH}$ probe under the adopted conditions and that, for instance, its reaction yield with $\bullet\text{OH}$ is not modified by the adopted cloud water components (organic acids and inorganic anions). This conclusion is further supported by the agreement between the value of $R_{\bullet\text{OH}, \text{NO}_3^-}$ measured in artificial cloud water containing 200 μM nitrate ($(2.00 \pm 0.03) \times 10^{-10} \text{ M s}^{-1}$) and that reported in Figure 5A for 200 μM nitrate alone ($(2.01 \pm 0.11) \times 10^{-10} \text{ M s}^{-1}$).

4. Conclusions and atmospheric implications.

This paper shows that the reaction between TA and $\bullet\text{OH}$ in oxygenated solution gives TAOH, with pH and temperature trends that should be taken into account for a laboratory quantification of $\bullet\text{OH}$ photogeneration in atmospheric waters. The values of Y_{TAOH} are not affected by common cloud water components such as inorganic anions (Cl^- , NH_4^+ and SO_4^{2-}) and carboxylic acids (formic, acetic, succinic, oxalic), at atmospherically relevant concentration. TA appears as a more selective $\bullet\text{OH}$ probe compared to nitrobenzene and

benzoic acid, which undergo significant interference by additional reactive species (possibly nitrogen dioxide and atomic oxygen) that are produced by nitrate photolysis [36]. In oxygenated solution the TAOH yield is relatively low compared to the phenol yield from benzene, but the reverse is true in oxygen-free solution [17, 37]. Two important advantages of TA versus benzene are the safer use and the limited volatility, which allows the degradation rate of TA to be taken into account. In contrast, that of benzene is often biased by volatilization [30, 36]. The accurate determination of the rate of TA degradation in addition to TAOH formation is interesting as it allows the use of Y_{TAOH} to identify possible interference. That would be more useful in surface-water photochemistry, where the excited triplet states of organic compounds are likely to play a more important role than in atmospheric waters [38, 39]. Moreover, the fluorescence of TAOH allows more sensitive detection (by direct fluorescence spectroscopy or HPLC-Fluorescence) compared to non-fluorescent compounds.

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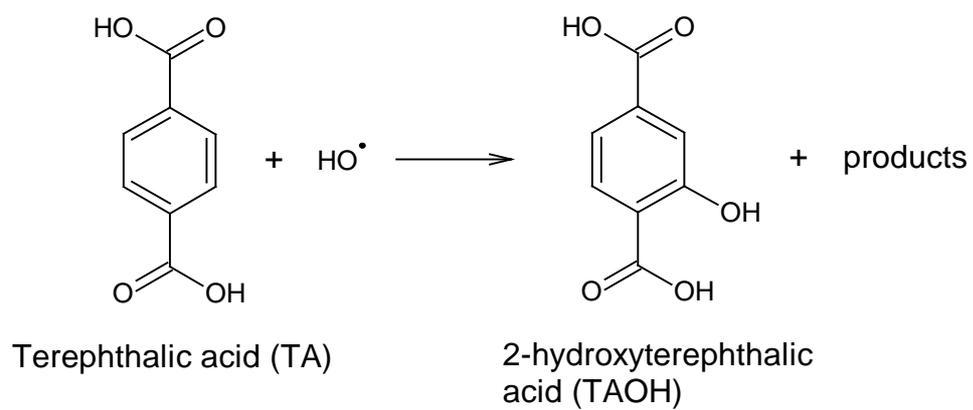


Figure 1. TA and TAOH chemical structures.

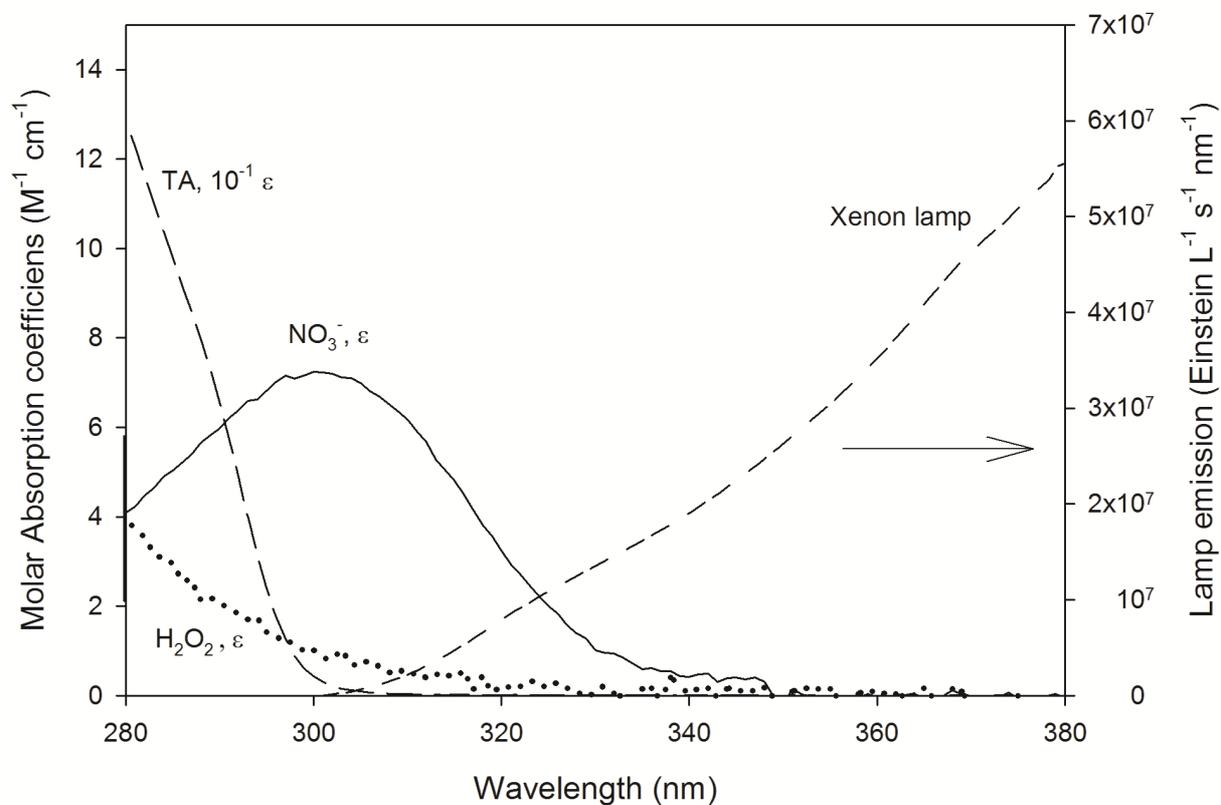


Figure 2. Emission spectrum of the 1000 W xenon lamp (with Pyrex filter) (long-dashed line), molar absorption coefficients of the aqueous solutions of terephthalic acid (short-dashed line), nitrate (solid line) and H_2O_2 (dotted line).

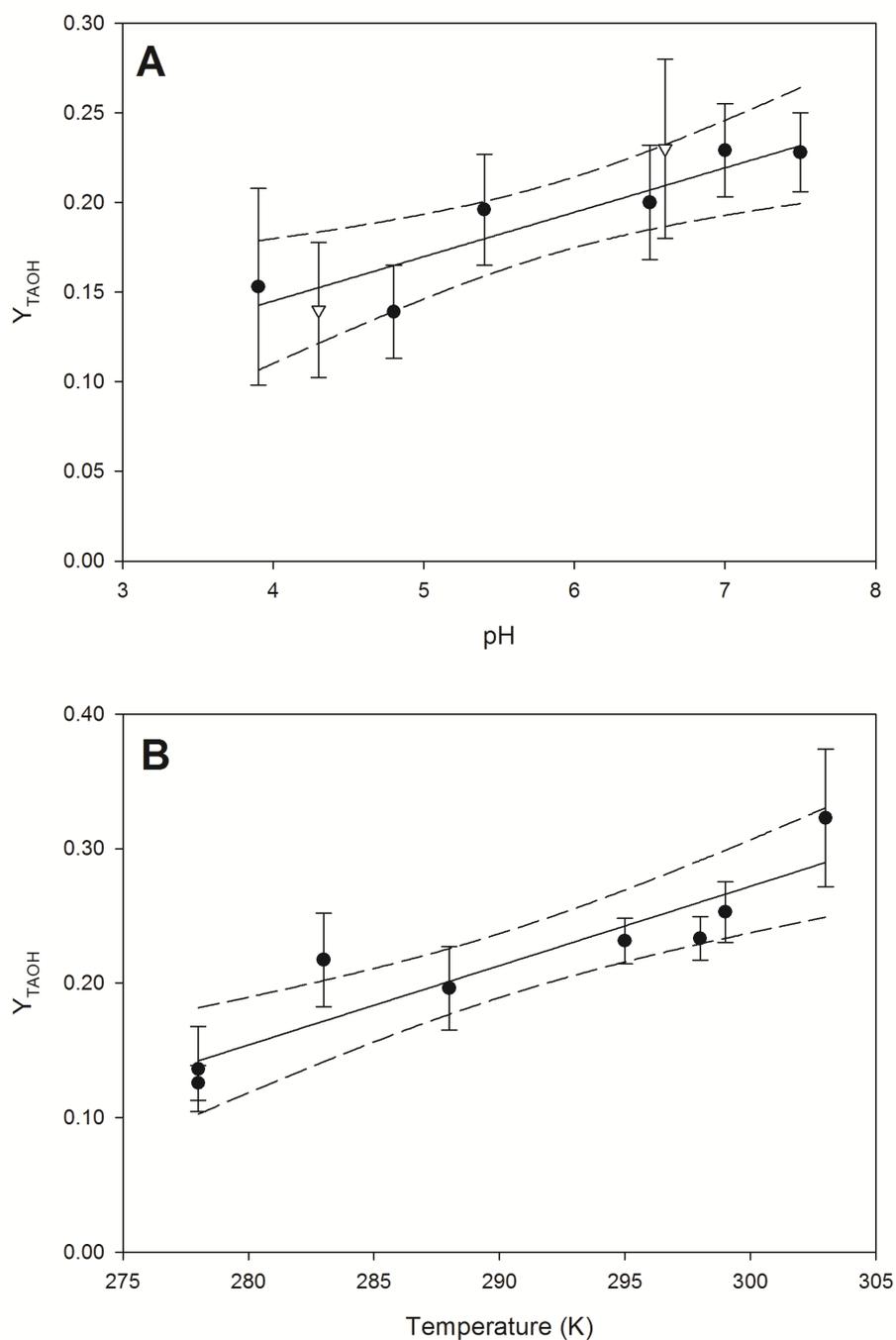


Figure 3. pH (A) and temperature (B) dependence of the TAOH yield, obtained under polychromatic wavelength irradiation ($\lambda > 300$ nm) of aqueous solutions containing 200 μM TA and 200 μM nitrate (filled circles) or 4 μM H_2O_2 (empty triangles). The temperature of (A) was settled at 288 ± 1 K and pH was changed by using HClO_4 or NaOH . The experiments in (B) were performed at pH 5.4. The solid line represents the linear fit of the experimental data and the dashed line denotes the 95% confidence interval of this fit.

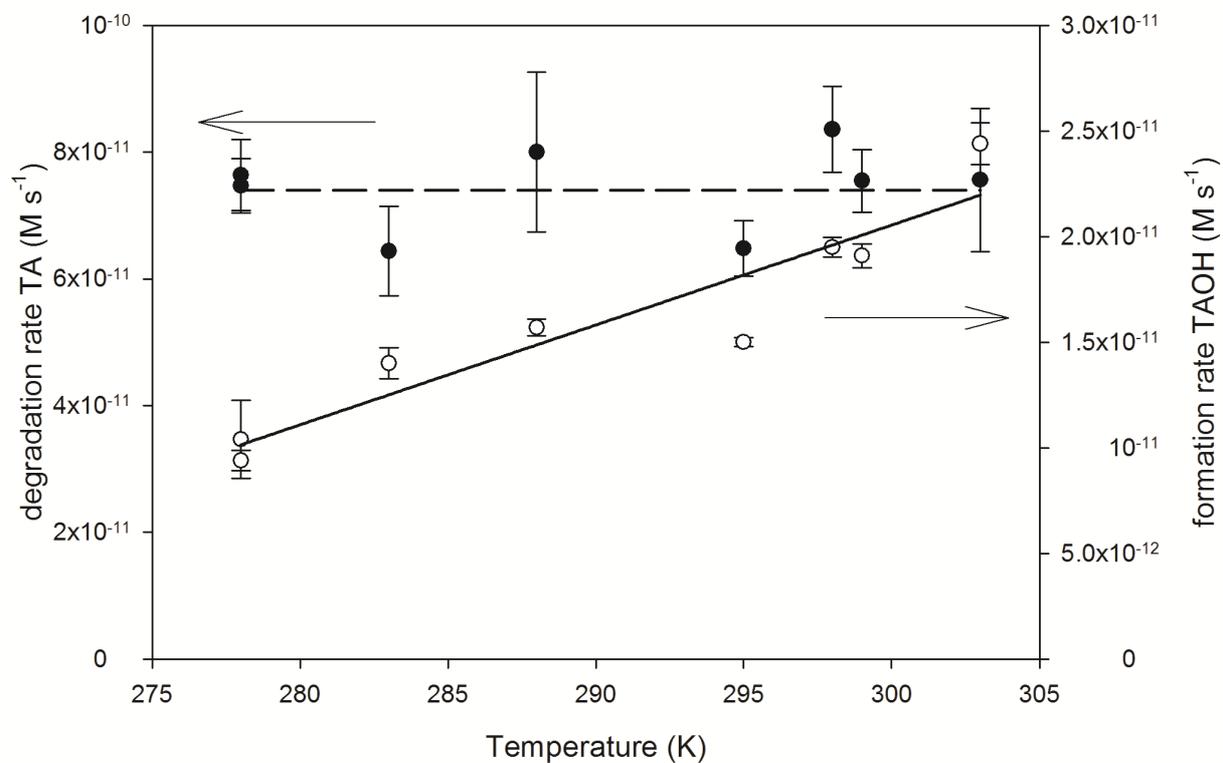


Figure 4. Degradation and formation rates (M s^{-1}) of TA (filled circles, dashed line) and TAOH (empty circles, solid line), respectively, as a function of solution temperature. The errors bars represent $\pm 1\sigma$, based on the fit of the experimental data.

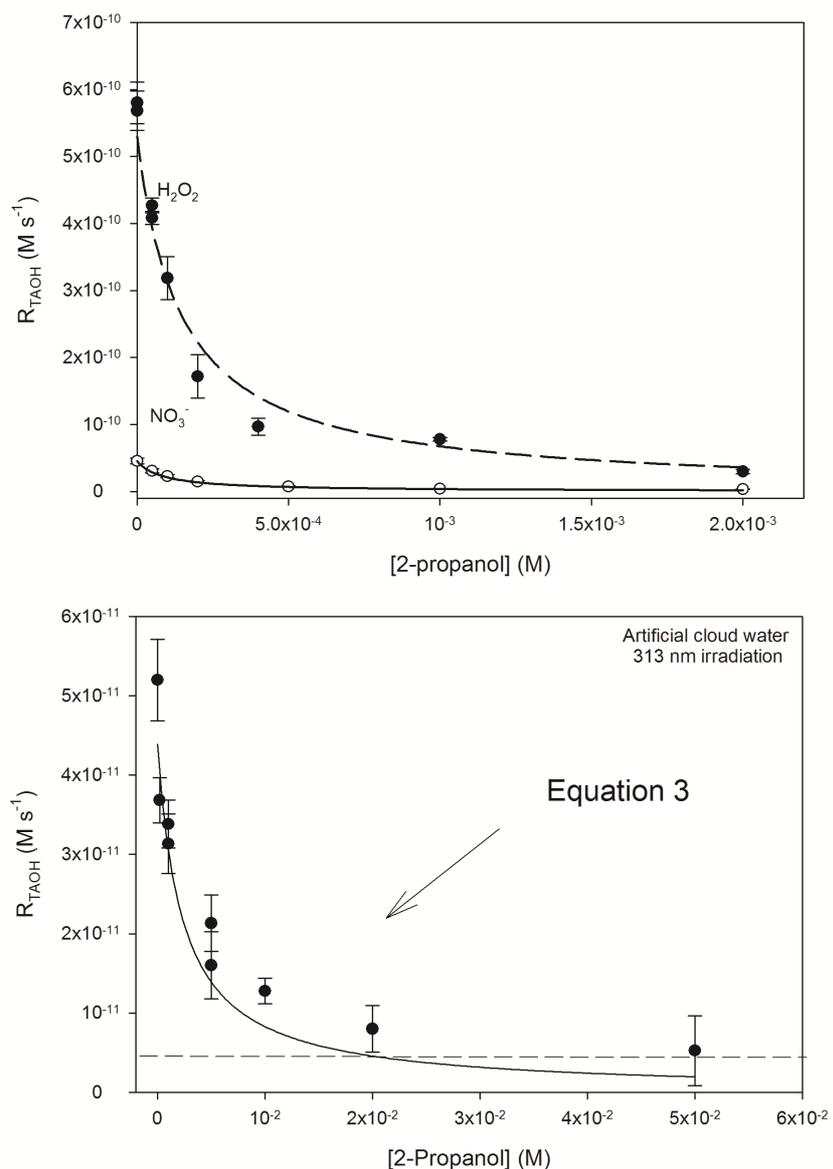


Figure 5. A. Initial formation rate of TAOH from 50 μM TA, upon 313 nm irradiation of 200 μM H_2O_2 (filled circles, dashed line) and 200 μM NO_3^- (empty circles, solid line), as a function of the concentration of 2-propanol. The solid curve shows the fit with eq. (1) and the dashed curve the fit with eq. (2).

B. Initial formation rate of TAOH from 50 μM TA, upon 313 nm irradiation of artificial cloud water, as a function of the concentration of 2-propanol. The solid curve shows the fit with eq. (3). The errors bars represent $\pm 2\sigma$, based on the fit of the experimental data. The dashed line represents our detection limit for $R_{TAOH}^f \sim 5 \times 10^{-12} M s^{-1}$.