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Feed-back action of nitrite in the oxidation of nitrophenols by bicarbonate-activated

peroxide system

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Graphical abstract



Highlights

- 2-amino-4-nitrophenol and 4-nitrophenol undergo fast oxidation in the BAP system
- The oxidation follows an autocatalytic path promoted by the elimination of nitrite
- The in-situ generation of ROS led the degradation to aliphatic products

Abstract

In this study it was found that the nitrite anion greatly increases the oxidation rate of the substituted phenols by the bicarbonate-activated peroxide (BAP) system at ambient temperature. This feed-back effect was investigated in the

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BAP oxidation of 2-amino-4-nitrophenol and 4-nitrophenol, where the kinetic analysis showed that the rate determining step was the elimination of a nitro group as nitrite. Complementary oxidation experiments with 2-aminophenol in BAP system, performed in the presence/absence of sodium nitrite confirmed the catalytic role of this anion. High concentrations of nitrite/BAP prevented formation of polymeric species and favoured the degradation to aliphatic fragments such as 3-oxobutanoic and acetic acid. Indirect evidence suggested in situ generation of reactive oxygen species (ROS), other than hydroxyl, peroxyl and carbonate radicals, during the nitrite/BAP oxidation. Formation of additional ROS - peroxynitrite and nitrosoperoxycarbonate - may account the synergistic action of nitrite/ BAP system. The estimated value of the apparent rate constant of the autocatalytic step for 2-amino-4-nitrophenol ($k_{app} = (4.97\pm0.19)$ $\cdot 10^3$ M⁻³s⁻¹) demonstrates that fast degradation of this oxidation-resistant phenolic dye is feasible even in ambient conditions. These findings can be exploited for developing clean, cost-effective methods for the removal of phenolic dyes as alternative to current advanced oxidation processes.

Abbreviations: AOP advanced oxidation processes, BAP bicarbonate activated peroxide, ROS reactive oxygen species, AP 2-aminophenol, NAP 2-amino-4-nitrophenol, NP 4-nitrophenol, APX 2amino-3H-phenoxazin-3-one, OQI *o*-quinoneimine

Keywords: 2-amino-4-nitrophenol, reactive oxygen species, bicarbonate activated peroxide system

1. Introduction

The efficient degradation of contaminants from natural waters such as pharmaceuticals, dyes and detergents is still one of the targets in water- or waste treatment strategies. These xenobiotics, mostly containing phenolic rings, pose major ecological threats due to their long biological half-life and accumulation in water, soil and living organisms[1-3]. The treatment of contaminated water before discharging into the aquatic environment demands additional non-biological technologies as advanced oxidation processes (AOPs) [4-8]. (AOPs) are considered the most important technologies for environmental remediation of natural and wastewaters containing recalcitrant compounds, through the production of reactive oxygen species (ROS) [9, 10]. AOPs are based on the in-situ generation of highly reactive hydroxyl radicals (·OH) in mild conditions [11-14]. The hydroxyl radicals can oxidize any compound present in the water matrix, frequently at diffusion

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controlled rates [5]. Once formed, OH reacts unselectively and degrades efficiently the water contaminants to non-toxic, low molecular weight (LMW) compounds [15]. The use of primary oxidants (e.g. ozone, hydrogen peroxide, dioxygen) [16], energy sources (ultraviolet light) [17-19] or catalysts (titanium dioxide, iron (III), cobalt(II), potassium permanganate)[20-26] are the current pathways of generating hydroxyl radicals and other ROS such as superoxide radical (O_2^{-1}) , peroxyl radical and singlet oxygen [9]. Despite the advantage of removing organic compounds in aqueous phase AOPs hold several drawbacks which prevent their full-scale implementation; most prominently, AOPs costs are very high, requiring continuous inputs of expensive chemicals in order to maintain the operability of the oxidative system[16]. Another issue is the need of pre-treatment procedures, which are costly and technically demanding. The presence of bicarbonate anion (HCO_3) can significantly reduce the concentration of $\cdot OH$ due to scavenging processes that lead to H₂O and to a much less reactive ROS, the carbonate radical \cdot CO₃⁻[27]. Consequently, HCO₃⁻ must be removed from the contaminated samples before starting the generation of ROS in typical AOPs. The HCO_3^{-}/CO_2 buffer is ubiquitous in natural waters and stimulate the oxidation, peroxidation and nitration of several biological targets [28]. In addition Richardson et al. [27] used HCO3⁻ as activator H₂O₂ in sulphide oxidation in alcohol/water mixtures. The bicarbonate-activated peroxide (BAP) system has been highly efficient in the epoxidation of alkenes [29] through generation of \cdot CO₃⁻ and O₂⁻ \cdot . Although less oxidizing than \cdot OH (E⁰ = 2.3 V vs NHE, pH 7.0), \cdot CO₃⁻ (E⁰ = 1.78 V, pH 7.0) is a very strong one-electron oxidant that acts by both electron transfer and hydrogen abstraction mechanisms to produce radicals from the reducing substrates [30]. ROS generation from BAP system occurs according to the sequence (1) - (4):

$$H_2O_2 + HCO_3^{-} \stackrel{\rightarrow}{\leftarrow} HCO_4^{-} + H_2O \tag{1}$$

$$HCO_{4}^{-} \rightarrow \cdot CO_{3}^{-} + \cdot OH$$
⁽²⁾

$$\cdot \operatorname{CO}_{3}^{-} + \operatorname{H}_{2}\operatorname{O}_{2} \to \operatorname{HOO}_{2} + \operatorname{HCO}_{3}^{-}$$
(3)

$$HOO \rightarrow H^+ + O_2^- \, \cdot \tag{4}$$

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 \cdot CO₃⁻ is a selective ROS, attacking preferentially phenolic residues from tyrosine, indolic moieties from tryptophan and sulphides from methionine [31] especially when acting in tandem with \cdot NO₂ [32-34].

$$ArH + \cdot CO_3^- \rightarrow Ar \cdot + CO_3^{2-} + H^+$$
(5)

$$Ar \cdot + \cdot NO_2 \to ArNO_2 \tag{6}$$

The BAP system can be used to build-up environmental-friendly oxidizing technologies as alternatives to current AOPs. However, the BAP system become efficient in the degradation of phenol-based compounds only when is taken in a large excess $(10^2 - 10^4 \text{ fold})$ with respect to the target concentration [35]. The issue is to ensure steady concentrations of ROS, enough to prevent polymeric by-products formation. Since both H₂O₂ and HCO₃⁻ are relatively inexpensive and nonpolluting reagents, the required high BAP/target concentration ratios could successfully be ensured either in batch or continuously-stirred reactors. In the case of nitroaromatics (e.g. nitrophenols), the elimination of nitro groups may provide supplementary ROS such as peroxynitrite (ONOO⁻), nitrosoperoxycarbonate (ONOOCO₂⁻) and NO₂ [30, 31, 36, 37], all of them potential oxidizing agents. In this work we attempted to exploit the positive feed-back action of the nitro group (consistent with an autocatalytic degradation path) on the BAP oxidation of three phenol-based dyes: 2-aminophenol (AP), 2-amino-4-nitrophenol, (NAP) and 4-nitrophenol (NP). NAP and NP are particularly resistant to chemical/biological oxidation due to the electron-withdrawing nitro group which deactivates the aromatic ring towards the electrophilic/radical attacks [38]. AP undergoes (bio)-catalysed oxidation to its stable condensation product 2-amino-3H-phenoxazin-3one (APX), which is also recalcitrant to conventional oxidative treatments [39, 40]. The oxidative degradation of NAP is by far the less studied compared to AP and NP; therefore, we focused our kinetic study on NAP oxidation. We proposed first a simplified kinetic model which highlighted the autocatalytic effect of the nitro group during the BAP oxidation and the time-evolution of NAP, H₂O₂, HCO₃⁻ and NO₂⁻ concentrations; an extended kinetic model including the time-evolution of the reaction intermediates was further developed, because their toxicity can sometimes be even

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higher than the toxicity of the initial pollutants [5]. The degradation pathways of AP and NP were depicted elsewhere [9, 11, 39]. For these substrates we developed only simplified kinetic models describing the time-evolution of spectrophotometrically detectable intermediates.

2. Materials and methodsl

2.1 Reagents

AP, NAP and NP (99%), 4-nitrocatechol (97%), methanol (HPLC grade), acetonitrile (ACN) (HPLC grade) formic acid (LC-MS grade), sodium bicarbonate (99.5%), sodium hydroxide (purity \geq 97%), sodium nitrite (purity \geq 97%), sodium nitrate (purity \geq 99) and acetic acid (purity \geq 99%) were acquired from Sigma-Aldrich (Germany). H₂O₂ obtained as a 30 % solution from Merck was diluted and the concentration was determined spectrophotometrically, using $\varepsilon_{240 \text{ nm}} = 43.6 \text{ M}^{-1} \text{ cm}^{-1}$. APX (m.p. = 249°C) was synthesized upon the oxidation of 2-aminophenol with mercury oxide followed by recrystallization from ethanol. Ultrapure water from a Millipore Simplicity 185 (conductivity < 6×10⁻⁸S·cm⁻¹, max. 5 ppb total organic compounds, TOC) system was used in the chromatographic experiments. Gaseous dioxygen was purchased from Linde (99.6% purity). *Trametes versicolor* laccase was purchased from Fluka (26U/mg specific activity) and was used to prepare 2-amino-8-nitro-3*H*-phenoxazin-3-one and 3-amino-8-nitro-1*H*-phenoxazin-2(10*H*)-one from oxidation of NAP with dioxygen. Other chemicals used were of analytical reagent grade.

2.2 Analytical methods

Spectrophotometric assays

The ultraviolet-visible (UV-VIS) measurements during the BAP oxidation of AP, NAP and NP were made on a Lambda 25 Perkin-Elmer spectrophotometer with a Peltier cell for temperature and stirring control. For IR analysis of the reaction products of AP and NAP oxidation, the collected solution after 240 min was adjusted to a pH of 2.5 with HCl to completely decompose HCO₃⁻, then dried at 30°C. The resulted solid sample was recorded in KBr pellets on a BrukerTensor 37 spectrophotometer.

Differential Scanning Calorimetry (DSC) analysis

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The DSC analysis of the reaction products of NAP oxidation was performed with DSC-2 Perkin– Elmer apparatus connected to a Tektronix TX3 multimeter and optically coupled to the interface RS 232. The scan heating rate employed was 10 K min⁻¹ in the range 300–650 K under an argon atmosphere; the apparatus sensitivity was 5 mcal s⁻¹ and the multimeter had a maximum display at 50 000 with a 0.03% error on the work domain.

Liquid chromatography-mass spectrometry (LC-MS) analysis

Experiments were conducted in an Agilent 1260 series LC system (Agilent, Waldbronn, Germany) consisting of: a binary pump, a thermostated autosampler, a thermostated column coupled with an Agilent 6410B triple-quadrupole mass analyzer with electrospray ionization (ESI) source. Data acquisition was performed using Mass Hunter software. All chromatographic runs were carried out on a Zorbax SB-C18 (50 x 2.1 mm, 1.8 µm) column from Agilent at 35°C. Isocratic elution was performed with a mobile phase composition of aq. 0.1% formic acid and acetonitrile in the volumetric ratio 90/10. A mobile phase flow-rate of 0.15 mL/min was chosen to enhance ESI ionization and sensitivity. Injection volume was 10 µL. MS detection of the substrates and their oxidation products was done in Single Ion Monitoring (SIM) and full scan mode. Both positive and negative spectra were acquired in full scan mode using the range 50 - 500 Da. ESI source parameters were: drying gas temperature 300°C, drying gas flow-rate 9 L/min, nebulizer pressure 50 psi. Sampling capillary voltage was set to 2500 V for negative mode and 4000 V for positive mode. Skimmer (fragmentor) voltage was set to 90 V. First quadrupole (Q1) resolution was set to Unit when SIM mode was used. Cell accelerator voltage of second quadrupole (Q2) was maintained at 7V. Linearity of the detector response was determined in the range $1 - 5 \mu g/mL$. Individual stock standard solutions AP, NAP and NP were prepared at a concentration of 500µg/mL in methanol. Calibration solutions were diluted in the mobile phase. All standard solutions were kept protected from light at 4°C.

Total organic carbon (TOC) determinations

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TOC analysis of pollutant solutions and final oxidation mixtures was performed on an Apollo 900 Combustion TOC Analyzer (Teledyne Tekmar, Mason, Ohio, USA) with a Non-dispersive Infra Red (NDIR) detector for CO_2 (0 -20 ppm calibration range). The total combustion of the samples was achieved through the 680°C combustion catalytic oxidation method. Data processing was performed with the TOC Talk Apollo 9000HS v 4.2 software.

2.3 Degradation experiments

The oxidations were conducted directly in the spectrophotometer cuvette. All phenolic substrates were dissolved in degassed bicarbonate solutions at constant temperature (25°C); their stability was checked by following the UV-VIS spectra during 240 minutes. Since no variation in the UV-VIS features was noticed, we assumed that no degradation of substrates in bicarbonate solution occurred in the considered time range. The reaction was initialized by adding different volumes of H₂O₂ stock solution such as the total H_2O_2 concentration in the reaction mixtures ranged from 1.10^{-2} to 3.10⁻¹M. In all assays at least a 100-fold excess of bicarbonate was ensured with respect to the phenolic substrates, for keeping NP and NAP as coloured phenolates, with sharp and well-defined absorption peaks in the VIS region of the spectrum (at $\lambda = 399$ nm for NP and $\lambda = 443$ nm for NAP) and also for keeping the pH at a constant value. The absorbance decrease was used further to calculate the time-evolution of the total conversion. In the case of AP, with no significant absorption in the VIS region, the absorbance measurements were achieved at $\lambda = 434$ nm, where the stable oxidation product APX has a molar absorptivity of $\varepsilon = 23200$ cm⁻¹·M⁻¹ or at $\lambda = 401$ nm where the formation of a coloured intermediate was observed. NaHCO3 concentrations were within 1.10⁻² to 3.10⁻¹M, while the AP, NAP and NP ranged within 3.10⁻⁶ M to 3.10⁻⁴ M. No pH shifting from the value of 8.5 in the reaction solutions was observed during the reaction time. Blank experiments were performed by replacing NaHCO₃ with NaOH, adjusting NaOH concentration to increase the pH value from 8.5, as in the presence of NaHCO₃ to 12, to strong alkaline medium. While the UV-VIS features of NP and NAP remained unchanged during 240 minutes, a slight

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increase of the absorption peak at 434 nm, assigned to APX formation was noticed during the AP oxidation. Since the AP oxidation follows the same pattern to APX formation as described elsewhere [39], whereas NP and NAP underwent no oxidation, we assumed that the fast fading of NP and NAP solutions occurred in the BAP system only. LC-MS analysis was performed first on the bicarbonate solutions of AP, NAP and NP, then at different times till the end of the oxidation experiments, when the total conversion of the substrates remained constant. Samples from the reaction mixtures with low conversions of substrates were kept at ambient temperature and their compositions were analysed after 2-5 days. The identification of the same LC-MS conditions as the substrates. The experiments were also conducted in 3 main sets according to the concentrations' ratio of the substrate/BAP system (*i.e.* equal concentrations of HCO₃⁻ and H₂O₂): 1:10², 1:10³, and 1:10⁴ because this shifting caused significant changes in the composition of the final reaction mixtures. Finally, the oxidation assays of AP, NAP and NP with BAP + NaNO₂, were achieved for 1: 1:10⁴ concentrations' ratio of substrate/BAP system along with blank experiments with NaHCO₃ + NaNO₂ and H₂O₂ + NaNO₂ with NaNO₂ ranging from 1·10⁻⁵ to 1·10⁻²M.

2.4 Synthesis of 2-amino-8-nitro-3H-phenoxazin-3-one and 3-amino-8-nitro-1H-phenoxazin-2(10H)-one

The enzymatic oxidation of NAP with dioxygen was conducted in aqueous solution in a bubbling stirred semi-batch reactor at 25°C. The gaseous stream was passed through two saturation vessels with water to avoid the evaporation of the solution from the reaction vessel; an aqueous solution of $1 \cdot 10^{-3}$ M 2-amino-4-nitrophenol was incubated with $1 \cdot 10^{-5}$ M laccase and continuously stirred for 12 h. The yellow-brown precipitate was collected, washed with water and then recrystallized from ethanol and gently dried under an argon stream.

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3. Results and discussion

3.1 Efficiency of the BAP system

The calibration plots from colorimetric and LC-MS analyses were built up to calculate and eventually compare the conversion of substrates with both methods. The absorbance – concentration data of NAP and NP standard solutions at pH 8.5 provided the molar absorption coefficients: at $\epsilon_{\lambda=443}$ nm = 12621M⁻¹cm⁻¹ for NAP and $\epsilon_{\lambda=399}$ nm = 18100M⁻¹cm⁻¹ for NP, which were used further to calculate AP, NAP and NP concentrations for the extended progress curves during the degradation experiments. The oxidant systems containing 10², 10³ and 10⁴ fold excesses of BAP for all 3 phenolic substrates yielded different oxidation products as well as significant changes of conversion. The half-lives of the phenolic substrates ($\tau_{1/2}$) were calculated with respect to substrate/BAP molar ratio (Fig.1 A-B) together with the degradation frequencies in initial conditions, when the catalytic effect of nitrite was negligible (conversions below 5%). The degradation frequencies were calculated as slopes of linear parts of the extended progress curves conversion *vs.* time for the optimized 1:10³ and 1:10⁴ substrate/BAP ratio (Fig. 1 B-C).

Figure 1

The 1:10³ phenol/BAP ratio was efficient only for AP degradation giving a half-life of 7122 s. NAP was more resistant to degradation than NP which can be assigned to their different oxidation mechanisms. Interestingly, for 1:10⁴ ratios the half-life of NAP was shorter than NP (600 s *vs.* 7200 s), presumably due to the faster generation of nitrite. The degradation frequencies show a much higher value for AP compared to NAP and NP (Fig. 1 C). Apparently, the amino substituent in the o- position decreases the stability of the aromatic ring of both AP and NAP and is consistent with fact that the degradation frequency of NAP is 10 times higher than NP's (Fig. 1 D).

 $1:10^2$ substrate /BAP molar ratios provided low conversions of the phenolic substrates, even after 240 minutes. Conversely, for $1:10^4$ substrate/BAP molar ratios, AP and NAP underwent 99.9 % conversion after 70 minutes, while NP attained only 21 % (Fig. 2).

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Figure 2

The oxidation mechanism of AP was widely studied and its conversion to APX in the presence of mild oxidants is well known [41, 42]; it was expected NAP to follow a similar pattern. The LC-MS analysis of the final reaction mixtures supported by literature data [43-46] provided mechanistic insights regarding the BAP oxidation of AP, NAP and NP. The relevant MS spectra of oxidation intermediates along with the corresponding chromatograms are summarized in the supporting information (SI) Figs. SI-1-4. The characteristic precursor ions and molecular masses of the substrates and of the presumable degradation products are given in Tables SI-1 A-C. It is commonly accepted that the six-electron oxidative condensation of two molecules of AP to form APX occurs via *o*-quinoneimine (OQI), a highly reactive intermediate [46, 47] which was not identified with the LC-MS analysis. However, while the experiments of AP degradation at 1:10³ AP/BAP molar ratio vielded APX (Table SI-1-A), whose formation was monitored by absorbance measurements, the assays conducted at a 1:10⁴ AP/BAP molar ratio gave LMW products in the final reaction mixture. It was noticed the fast appearance/disappearance of an absorption band at 401 nm which can be assigned to OQI formation/decay (Fig.SI-5). At high concentrations of BAP system the decomposition of the OQI is faster than the condensation with another AP molecule to give APX. Since no other possible intermediate with less chromophore groups than APX, stable enough to be observed from absorbance measurements were reported so far, we assumed that the coloured compound is OQI. The assumption is supported by the fact that the oxidation of NAP yielded the corresponding 4-nitro-1,2-quinoneimine, a relatively stable by-product, identified with LC-MS (Table SI-1-B). Its stability might be assigned to the electron-withdrawing nitro group which enhances the double bond character of the carbon-oxygen bond. In the given reaction conditions OQI undergoes apparent first-order decay. The rate constant was estimated by non-linear regression, fitting an exponential decay equation on the experimental data which gave $k_{apparent} =$ (0.463 ± 0.021) s⁻¹ with a coefficient of determination r² =0.9955, for a significance level $\alpha = 0.05$. Consequently, the apparent half-life of OQI (1:10⁴ AP/BAP molar ratio) was around 1.5 s, a

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plausible value for an active intermediate. The composition of the reaction mixtures of AP oxidation at different AP/BAP molar ratio corroborated with the formation of the coloured intermediate absorbing at 401 nm sustain the hypothesis that at high concentrations of BAP, the formation of APX doesn't occur and OQI decomposes to aliphatic compounds (Table SI-1-A). To confirm this hypothesis, solutions with concentrations from $3 \cdot 10^{-6}$ to $3 \cdot 10^{-5}$ M were prepared in $1:10^4$ APX/BAP molar ratios and their VIS spectra were recorded during 240 minute when no decrease of the characteristic sharp peak of APX was observed. Thus, a degradation pathway for AP involving the decomposition of OQI to aliphatic compounds (Scheme 1) might serve as well to explain a similar behaviour of NAP oxidation in the BAP system.

Scheme 1

At lower AP/BAP molar ratios the oxidation yield mainly APX, while higher ratios prevent the formation of polymeric species In the case of NAP, the 4-nitro-quinoneimine is the key intermediate either to condensation products such as 3-amino-8-nitro-1H-phenoxazin-2(*10H*)-one and 2-amino-8-nitro-3H-phenoxazin- 3-one, or to the decomposition products such as 4-hydroxy-1,2-benzoquinone. These compounds with 257, respectively 259 molecular weights were obtained in control experiments from oxidation of NAP with dioxygen in the presence of laccase as previously described. The solid mixture recrystallized from ethanol contained yellow and brown crystals which were further separated mechanically and their distinct IR spectra were recorded (Figs. SI-6, 7 and Table SI-2). Solid samples of the two nitrophenoxazones, analyzed with DSC revealed close melting points (221 and 231.5°C), consistent with the melting points assigned to phenoxazones. According to all evidence provided by LC-MS, UV-VIS, IR spectral data and DSC analysis, a reaction path for NAP degradation in the BAP system was proposed (Scheme 2).

Scheme 2

The main degradation product generated in the BAP system during the oxidation of NAP is 4hydroxy-1,2-benzoquinone. At higher substrate/BAP molar ratios, the degradation products of NAP

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are mostly the same obtained at NP oxidation, while a lower substrate/BAP molar ratios NAP yields phenoxazones.

3.2 Degradation kinetics of 2-amino-4-nitrophenol and 4-nitrophenol

A simplified kinetic model was developed for NAP and NP taking into account the degradation path and the chemistry of the BAP system. In order to estimate the apparent kinetic constants, the conditions implying the large excess of BAP species (1: 10⁴ substrate/BAP molar ratios) were preferred. The progress curves as total conversions of phenolic substrates *vs*. time were drawn in the following experimental set-up (Fig.3):

- Keeping the initial concentration of substrates at a constant value *i.e.* 3·10⁻⁵M and first varying the initial concentration of bicarbonate from 0.001 to 0.3M, then varying the initial concentration of hydrogen peroxide from 0.001 to 0.3M. The decomposition of both BAP species was considered negligible with respect to substrate depletion;
- Keeping the initial concentration of both BAP species at the optimized value of 0.3M and varying the concentration of the substrates from $3 \cdot 10^{-6}$ M to $3 \cdot 10^{-4}$ M.

Figure 3

The sigmoidal-shaped curves conversion vs. time, suggest an autocatalytic pattern. Changing NAP/BAP ratio from 10⁴ to 10³ caused a sharp drop of conversion this occurring probably because the generated ROS from the BAP system reacted at low rates with NAP and consequently the autocatalytic species evolved slowly, at low yields, in insufficient amounts to oxidize the substrate. The main issue was to identify the possible autocatalytic species derived from NAP. To do this, we followed the oxidation of 2-aminophenol in a 1:10³ AP/BAP molar ratio, one experiment being performed in the presence of NO₂⁻. At this AP/BAP molar ratio the oxidation product is APX as resulted from the LC-MS analysis.

Figure 4

In the absence of nitrite, the formation of APX follows an apparent first- order exponential growth while in the presence of nitrite the shape of the progress curve changed to sigmoidal, finally

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yielding lower concentrations of APX. The LC-MS analysis of the latest proved the formation of 2butenoic acid along with APX. This is consistent with the fact that the NO_2^- favours the decomposition of AP to LMW compounds and not the oxidative coupling to APX. Another experiment performed in similar conditions with NAP, gave a decrease of NAP's half-life from 600 to 124 s (data not shown).

A sigmoidal-shaped dependence was observed for the time-evolution of NP conversion, supporting the hypothesis of a catalytic effect of nitrite. Accordingly, the time-evolution of the reactant system for $1:10^4$ substrate/BAP molar ratio, can be described by the two-step model:

$$A \xrightarrow{k_1'} P_1 + M \tag{7}$$

$$A + M \xrightarrow{k_2} P_1 + 2M \tag{8}$$

Where A is the nitrophenolic substrate, P₁ is a stable intermediate, possibly 4-hydroxy-1-2 benzoquinone and M is the autocatalytic species NO₂⁻; k'_1 is the apparent first-order rate constant of the non-catalytic step when a large excess of HCO₃⁻ and H₂O₂ towards nitrophenols was considered and k_2 is the apparent second-order rate constant of the autocatalytic process.

The reaction rate of the autocatalytic step is:

$$r_{R_2} = k_2[A][M]$$

The rate of the overall process becomes:

$$r_{R} = -\frac{d[A]}{dt} = k_{1}' \cdot [A] + k_{2}[A][M]$$
(9)

From the mass-balance one obtains:

$$[M] - [M]_0 = [A]_0 - [A] = [P_1]$$
(10)

If y is the conversion, then:

$$r_{R} = -\frac{d[A]}{dt} = [A]_{0} \frac{dy}{dt} = k_{1}'[A]_{0}(1-y) + k_{2}[A]_{0}(1-y)([M]_{0} + [A]_{0}y)$$
(11)

and

$$\frac{dy}{dt} = k_2 [A]_0 \left(1 - y\right) \left(\frac{k_1' + k_2 [M]_0}{k_2 [A]_0} + y\right)$$
(11)

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If
$$k_2 \cdot [A]_0 = k$$
; $\frac{k_1' + k_2[M]_0}{k_2[A]_0} = \rho$ then:
 $\frac{dy}{dt} = k(1-y)(\rho + y)$
(12)

The integrated form of the equation becomes:

$$y = \frac{\rho(e^{k(1+\rho)t} - 1)}{(1+\rho \cdot e^{k(1+\rho)t})}$$
(13)

Eq. (13) was fitted on the experimental data NAP and NP conversion *vs*. time and the parameters *k* and ρ were estimated through non-linear regression. Eq. (13) represents the analytical form of the sigmoidal-shaped curve characteristic for autocatalytic processes. The coordinates of the inflection point are the dimensionless parameter ρ and the induction period τ ; the smaller the value of ρ , the longer the value of τ .

From the dependence of k and ρ on the concentration of bicarbonate and H₂O₂ at a settled concentration of NAP, the rate constants k'_1 and k_2 , as well as the empirical reaction orders towards HCO₃⁻ and H₂O₂ were estimated. With $k'_1 = k_1 [HCO_3^{--}]_0^m [H_2O_2]_0^n$ and $k_2 = k'_2 [HCO_3^{--}]_0^p [H_2O_2]_0^r$ the expressions of k and ρ become:

$$k = k_{2}' \Big[HCO_{3}^{-} \Big]_{0}^{p} \Big[H_{2}O_{2} \Big]_{0}^{r} \Big[NAP \Big]_{0}$$

$$\rho = \frac{k_{1} \Big[HCO_{3}^{-} \Big]_{0}^{m} \Big[H_{2}O_{2} \Big]_{0}^{n} + k_{2}' \Big[HCO_{3}^{-} \Big]_{0}^{p} \Big[H_{2}O_{2} \Big]_{0}^{r} \Big[NO_{2}^{-} \Big]_{0}}{k_{2}' \Big[HCO_{3}^{-} \Big]_{0}^{p} \Big[H_{2}O_{2} \Big]_{0}^{r} \Big[NAP \Big]_{0}}$$
(14)
(14)

and

$$\rho = \frac{k_1 \left[HCO_3^{-} \right]_0^{m-p} \left[H_2O_2 \right]_0^{n-r}}{k_2' \left[NAP \right]_0} + \frac{\left[NO_2^{-} \right]_0}{\left[NAP \right]_0}$$
(16)

In order to estimate the rate constants k_1 and k'_2 together with the partial empirical reaction orders *m*, *n*, *p* and *r*, the parameters *k* and ρ were represented as functions of H₂O₂ and HCO₃⁻ initial concentrations. Equations (14) and (16) were used along a multiple nonlinear regression analysis

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(Figs. SI-8 A - B). The estimated values were: $p = 1.85\pm0.18$, $r = 1.15\pm0.14$, $k'_2 = (4.97\pm0.19)\cdot10^3$ L³·mol⁻³s⁻¹ from the plot of k vs. [H₂O₂]₀ and [HCO₃⁻]₀ (with $r^2 = 0.9833$, for $\alpha = 0.05$); and $m = 0.974\pm0.011$, n = 1.06, $k_l = (4.16\pm)\cdot10^{-3}$ s⁻¹ from the plot of ρ vs. [H₂O₂]₀ and [HCO₃⁻]₀. In the case of 4-nitrophenol all the extended progress curves conversion vs. time displayed a similar sigmoidal shape described in eq. (13); for example, at [NP]₀ = $3\cdot10^{-5}$ M, ρ was (0.737±0.048) and k was (9.76 ± 0.41)· 10^{-5} s⁻¹ (with $r^2 = 0.9994$ for $\alpha = 0.05$), while for NAP ρ was (0.1691 ± 0.0053) and k was (3.02 ± 0.012)· 10^{-3} s⁻¹ (with $r^2 = 0.9955$ for $\alpha = 0.05$). It appears that the induction period was longer for NAP oxidation, but the autocatalytic step in the case of NAP was faster than for NP. This may suggest that the generation of NO₂⁻ from oxidation of 4-nitro-1,2-quinoneimine is the rate determining step for NAP oxidation; compared to NP, the elimination of NO₂⁻ from 4-nitrocatechol occurs at a higher rate. To plausibly explain the catalytic effect of NO₂⁻ in the presence of ROS from the BAP system, an extended kinetic model was further developed suitable for oxidation undergoing in batch reactors.

3.3 Extended kinetic model

The previous simplified kinetic model described the time-evolution of the overall degradation process of NAP and NP in the BAP system, provided that the molar ratio substrate /BAP remains $1:10^4$, as long as the degradation route to 4-hydroxy-1,2- benzoquinone is considered the main path of NAP and NP decomposition. These conditions are difficult to attain in practice. In order to make the entire process feasible, a more realistic kinetic model was build-up, taking to account the reported data about the generation of ROS in HCO₃⁻/H₂O₂ system and the LC-MS results from the AP, NAP and NP oxidation; here SH⁻ represents the 2-amino-4-nitrophenolate, S is the corresponding 4-nitro-quinoneimine, P₁ is 4-hydroxy-1,2-benzoquinone, P₂ and P₃ are 3-amino-8-nitro-1H-phenoxazin-2(10*H*)-one and 2-amino-8-nitro-3*H*-phenoxazin-3-one, respectively; P₄ is 3-oxobutanoic acid.

$$H_2O_2 + HCO_3 \xrightarrow{k_1} HCO_4 + H_2O$$
(17)

$$HCO_4^{-} + H_2O_{-} \xrightarrow{k_1} H_2O_2 + HCO_3^{-}$$
(18)

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$HCO_4^- \xrightarrow{k_2^a} \cdot CO_3^- + \cdot OH$	(19)
$HCO_3^- + OH \xrightarrow{k_3} OT O_3^- + H_2O$	(20)
$\cdot \operatorname{CO}_3^- + \operatorname{H}_2\operatorname{O}_2 \xrightarrow{k_4} \operatorname{HOO} \cdot + \operatorname{HCO}_3^-$	(21)
$HOO \cdot \xrightarrow{k_5} H^+ + O_2^- \cdot$	(22)
$O_2^- \cdot + HCO_3^- \xrightarrow{k_6} HOO \cdot + CO_3^{2-}$	(23)
$\cdot OH + H_2O_2 \xrightarrow{k_7} HOO \cdot + H_2O$	(24)
$SH^{-} + CO_{3}^{-} + O_{2}^{-} \cdot \xrightarrow{k_{8}} S + CO_{3}^{2-} + HOO \cdot$	(25)
$CO_3^{2-} + H^+ \xrightarrow{k_9} HCO_3^{-}$	(26)
$\cdot OH + \cdot OH \xrightarrow{k_{10}} H_2O_2$	(27)
$\mathbf{S} + \mathbf{O}_2^{-} \cdot + \cdot \mathbf{CO}_3^{-} \xrightarrow{k_{11}} \mathbf{P}_1 + \mathbf{NO}_2^{-} + \mathbf{CO}_3^{2-} + \mathbf{H}^+$	(28)
$H_2O_2 + NO_2^- \xrightarrow{k_{12}} ONOO^- + H_2O$	(29)
$ONOO^{-} + CO_2 \xrightarrow{\vec{k}_{13}} ONOOCO_2$	(30)
$ONOOCO_2 \xrightarrow{\tilde{k}_{13}} ONOO + CO_2$	(31)
$ONOOCO_2^{-} \xrightarrow{\vec{k}_{14}} OO_3^{-} + OO_3^{-} + OO_2^{-}$	(32)
$\cdot \operatorname{CO}_{3}^{-} + \cdot \operatorname{NO}_{2} \xrightarrow{\overline{k}_{14}} \operatorname{ONOOCO}_{2}$	(33)
$\cdot \operatorname{CO}_3^{-} + \cdot \operatorname{NO}_2 \xrightarrow{k_{15}} \operatorname{CO}_2 + \operatorname{NO}_3^{-}$	(34)
$ONOO^{-} \xrightarrow{k_{16}} NO_3^{-}$	(35)
$SH^- + \cdot NO_2 + \cdot CO_3^- \xrightarrow{k_{17}} P_1 + 2NO_2^- + CO_3^{2-} + 2H^+$	(36)
$S + SH^{-} \xrightarrow{k_{18}} P_2$	(37)
$S + SH^{-} \xrightarrow{k_{19}} P_{3}$	(38)
$\cdot \operatorname{CO}_3^{\scriptscriptstyle -} + \operatorname{P}_1 \xrightarrow{k_{20}} \operatorname{P}_4 + \operatorname{CO}_3^{2-} + \operatorname{CO}_2 + \operatorname{H}^+$	(39)

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 $\cdot OH + CO_3^2 \xrightarrow{k_{21}} HO^- + \cdot CO_3^-$

(40)

The reaction steps from eqs. 17-24, 26-27, 39-40 are typical for the BAP system and their rate constants estimated [4, 28, 34, 35].

Steps 25, 28, 37-39 were derived from the "empirical" kinetics developed in the previous paragraph and consistent with literature data regarding the reactions of $\cdot CO_3^-$ with anilines and phenols [13, 48].

The sequence 29-35 includes steps from literature about peroxynitrite ONOO⁻ formation from the reaction of H₂O₂ and nitrite [33]. Still, since control experiments with NAP and NP in H₂O₂/NO₂⁻ system did not display any transformation of NAP and NP, we assumed that the key species in the overall autocatalytic process is the nitrosoperoxycarbonate (ONOOCO₂⁻) which decomposes in \cdot CO₃⁻ and \cdot NO₂[30, 31]. Reactions 25, 28, 37-39 were considered apparent single steps, comprising several elementary steps where the mass - balance was neglected for H⁺ and the other degradation products, because their entire mechanisms are not completely elucidated. The mass- and charge balance was applied for the species of interest: 4-nitro-1,2-quinoneimine, 4-hydroxy-1,2-benzoquinone, 3-amino-8-nitro-1H-phenoxazin-2(10*H*)-one, 2-amino-8-nitro-3*H*-phenoxazin-3-one and 3-oxobutanoic acid, in agreement with the previously estimated apparent reaction orders from the simplified kinetic model.

3.3.1 Simulation assays

The simulation providing the kinetic behaviour of the NAB/BAP system started from a set of rate constants and initial concentrations of the chemical species involved. The rate constants from literature are summarized in Table 1.

The initial concentration of CO₂ was estimated using the equilibrium constant (K_{CO2/HCO3} = 4.3 $\times 10^{-7}$ M)[31], the initial concentration of bicarbonate, the pH of the solution, and the solubility of CO₂ in water at 25°C and 1 atm [49]. Since for all experiments the concentration of CO₂ does not exceed the solubility limit of 3.3 $\cdot 10^{-2}$ M, no absorption/desorption equilibrium was considered here. NAP was considered as 2-amino-4-nitrophenolate at pH 8.5 (pK_a = 7.6 [50]). The mass-balance for

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 H^+ and HO^- was neglected because the pH remained constant during the kinetic assays; hence the concentrations of H^+ and HO^- were kept at $3.16 \cdot 10^{-9}M$ and $3.16 \cdot 10^{-6}M$ respectively in the simulation runs.

The time-evolution of the NAP/BAP system was described by the differential equations derived from steps 17 - 40. The rate constants' optimization was performed with Kintecus [51] for 10 experimental sets.

3.3.2 Sensitivity analysis

The sensitivity analysis was accomplished with Atropos [52] at three different time intervals to avoid over-parametrization. Accordingly, all rate constants influenced the shape of the simulated progress curves, therefore all proposed steps were considered kinetically significant. The optimized rate constants (with $\alpha = 0.05$) are summarized in Table 2.

The rate constants k_3 and k_6 were estimated during the optimization process; steps 20 and 23 were assumed unilateral in the reaction conditions, even if they were reported in literature as bilateral [27]. The by-and final products appear to accumulate in amount consistent with the data obtained by LC-MS analysis in the final reaction mixtures (Fig.5).

Figure 5

Simulated and experimental kinetic curves of the reaction intermediate and products confirmed the disappearance of NAP in less than 2 hours and the efficiency of nitrite/BAP system. The simulated and experimental progress curves NAP vs. time matched well to obtained data for BAP concentrations ranging from $1 \cdot 10^{-3}$ to 0.3M, either with NO₂⁻ generated in reaction or with NO₂⁻ added at the beginning of the experiment. Once again, the proposed path is in agreement with the obtained results and describes satisfactorily the nitrite mediated oxidation of phenolic substrates in the BAP system. There are some limitations of the extended model regarding the fate of intermediates comprised in equations 36-39, which is difficult to trace. Therefore, we assume that the overall equations 36-39 respect the mass-balance for the species of interest being in agreement with the reaction sequence depicted in Scheme 2.

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3.3.3 Quantification of the mineralization level

The kinetic analysis coupled with the LC-MS results demonstrate that BAP system cannot achieve complete mineralization, even at high substrate/BAP molar ratios (though 100% conversion of the nitro-aromatic pollutants was obtained within 240 minutes). The main concern here, as in other similar oxidative water treatments, is the formation of toxic or less biodegradable intermediates/final products [53]. However, for high substrate/BAP molar ratios, AP and NP yielded small aliphatic compounds, mainly acetate, whose toxicity is far less than of the initial pollutants. Potentially toxic aromatic compounds were identified in the final reaction mixture after BAP oxidation of NP (Table SI-1 C); therefore, the TOC analysis was performed first on AP, NAP and NP in bicarbonate solutions without H_2O_2 (*TOC*₀) and secondly, on reaction mixtures with the optimized substrate/BAP molar ratio 1:10⁴ after 240 minutes (*TOC*_∞) The TOC percentage removal was calculated as:

$$\% \ TOC_{removal} = \frac{TOC_0 - TOC_{\infty}}{TOC_0} \cdot 100$$
(40)

The results (summarized in Table SI-3) showed that TOC removal was 75 – 78 % for AP and NAP and 62% for NP. Since high molar ratios of substrate/BAP were already used, and increasing this ratio does not suit environmentally realistic conditions, we attempted to exploit the catalytic effect of nitrite in order to achieve complete mineralization. Several experiments were performed using substrate/BAP/NO₂⁻ molar ratios from 1:10⁴:10² to 1:10⁴: 1. Surprisingly, all gave around 100% TOC removal for the three phenolic substrates, confirming the feed-back action of nitrite in the BAP oxidation system. Consequently, the molar ratio with the lowest content of nitrite to achieve complete mineralization (Table SI-3) was considered compatible with more environmental friendly technologies. Thus, it was demonstrated that the final reaction mixtures of the first cycle of BAP oxidation contain large amounts of nitrate, nitrite and bicarbonate anions. The bicarbonate anion can be re-used simultaneously with nitrate and nitrite in a subsequent step through the photolysis of nitrate with UV radiation at $\lambda = 254$ nm to generate peroxynitrite, carbonate and hydroxyl radical together with other ROS species in the absence of hydrogen peroxide [54]. These findings may

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allow decreasing the molar ratio H₂O₂/HCO₃⁻ required for the TOC removal trough the cyclic regeneration of ROS species. Another alternative is to remove nitrate from the final reaction mixtures. Nitrate/nitrite removal from natural or waste water is usually achieved through reverse osmosis, ion exchange, electrodialysis and activated carbon adsorption coupled with pH adjustment [55, 56]. On the other hand, the biological denitrification by which denitrifying bacteria use nitrate as terminal electron acceptor in their respiratory process, finally yielding gaseous nitrogen, may well compete with the conventional treatment procedures in terms of economic feasibility [57]. It was shown that autotrophic microorganisms such *as Parcoccus* could use molecular hydrogen as a substrate and bicarbonate as carbon source for the complete reduction of nitrate (0.35 mg H₂ being required to complete the reduction of 1 mg nitrate nitrogen at 25°C)[58]. Therefore, we consider that a working sequence comprising: BAP/nitrite oxidation combined with UV photolysis, biological removal of nitrate and another subsequent BAP-assisted removal of the denitrifying microorganisms may be amenable for wastewater treatment technologies.

4. Conclusions

We attempted to demonstrate that BAP system in tandem with nitro-aromatic compounds can provide a feasible in situ "self-destroying" technology of stable nitro-derivatives in natural and waste water amenable for batch reactors; The bicarbonate anion, which is the main source of carbonate radical regenerates during the oxidation cycles and, as long as a stationary concentration of H₂O₂ is ensured, the system can be implemented and developed along other AOP technologies for nitro-derivatives removal. For example, a faster generation of ROS derived either from H₂O₂ or from nitrate in the presence of bicarbonate can be achieved in photochemical reactors. The simplified kinetic model is applicable to any nitro-derivative undergoing oxidation in a large excess of BAP species, without requiring advanced knowledge of the reaction mechanism; on the other side, the extended kinetic model accounted for the chemistry of BAP.

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Figure 1 Degradation efficiency of BAP system expressed as: (A-B) half-lives of phenolic substrates for $1:10^3$ and $1:10^4$ phenolic substrate/BAP molar ratios and (C-D) degradation frequencies for $1:10^4$ phenolic substrate/BAP molar ratios (pH = 8.5, T = 25° C)



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Figure 2 Fractional conversions of the phenolic substrates vs. phenolic substrate/BAP molar ratios

after 70 minutes (pH = 8.5, T = 25° C)



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Figure 3 Optimization of initial molar ratios NAP/BAP system according to the time-evolution of NAP conversion: A) Variation of $[HCO_3^-]_0$ when $[NAP]_0 = 3 \cdot 10^{-5} M$ and $[H_2O_2]_0 = 0.3M$; B) variation of $[H_2O_2]_0$ when $[NAP]_0 = 3 \cdot 10^{-5} M$ and $[HCO_3^-]_0 = 0.3M$; C) variation of $[NAP]_0$ when



 $[HCO_3^-]_0 = [H_2O_2]_0 = 0.3M$

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Figure 4 Evidence of autocatalytic effect of nitrite on 2-aminophenol oxidation in BAP system;

 $[AP]_0 = 3 \cdot 10^{-5} M$, $[HCO_3]_0 = [H_2O_2]_0 = 3 \cdot 10^{-2} M$



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Figure 5 Simulated and experimental kinetic curves of the reaction intermediate and products

 $([NAP]_0 = 1.85 \cdot 10^{-5}M, [HCO_3]_0 = 0.3M, [H_2O_2]_0 = 0.3M, pH = 8.5, T = 25^{\circ}C)$



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Scheme 1 Proposed degradation pathway of AP for different molar ratios AP/BAP system



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Scheme 2 Possible degradation route of NAP in the BAP system based on LC-MS analysis of the

oxidation by-product



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Table 1 Rate constants in aqueous medium used in the optimization procedure

Rate constant	Value	reference
Ř ₁	$3.8 \times 10^{-4} \text{ M}^{-1} \cdot \text{s}^{-1}$	[27, 48]
κ̄ ₁	$1.2 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$	[27, 48]
k4	$5 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$	[26, 48]
k5	5×10 ⁵ s ⁻¹	[4, 33]
k7	$2 \times 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$	[33]
k9	$5 \times 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$	[26]
k10	$5.5 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$	[4]
<i>k</i> ₁₃	$3 \times 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$	[30]
k ₁₃	$1.5 \times 10^6 \text{ s}^{-1}$	[30]
<i>k</i> ₁₄	1.9×10 ⁹ s ⁻¹	[30]
k ₁₄	$5 \times 10^8 \text{ M}^{-1} \cdot \text{s}^{-1}$	[30]
k21	4.2×108 M-1·s-1	[48]

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Table 2 Optimized rate constants in BAP system

Rate constant	Value
k_2^a	$(2.65\pm0.11) \text{ s}^{-1}$
k3	$(5.11\pm0.48)\times10^{-3}$ M ⁻¹ s ⁻¹
	2 1 1
k6	$(1.03\pm0.05)\times10^{-3}$ M ⁻¹ s ⁻¹
k ₈	$(4.71\pm0.42) \times 10^2 \text{ M}^{-1} \cdot \text{s}^{-1}$
kıı	$(1.09\pm0.23)\times10^3 \text{ M}^{-2}\cdot\text{s}^{-1}$
k12	$(1.510\pm0.004)\times10^{-1} \text{ s}^{-1}$
k15	$(1.840\pm0.092)\times10^2 \text{ M}^{-1}\cdot\text{s}^{-1}$
k16	(5.037 ± 0.046) s ⁻¹
k17	$(3.73\pm0.22)\times10^3 \text{ M}^{-2}\cdot\text{s}^{-1}$
k18	$(1.83\pm0.15) \mathrm{M}^{-1} \cdot \mathrm{s}^{-1}$
k19	$(1.54+0.13)\times10^1 \mathrm{M}^{-1}\cdot\mathrm{s}^{-1}$
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k20	$(2.97\pm0.14)\times10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$