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# On the existence of nitrate radicals in irradiated TiO<sub>2</sub> aqueous suspensions in the presence of nitrate ions

Francesco Parrino<sup>\*[a]</sup>, Stefano Livraghi<sup>[b]</sup>, Elio Giamello<sup>[b]</sup>, Leonardo Palmisano<sup>[a]</sup>

**Abstract:** Some evidences of the existence of nitrate radical in irradiated aqueous TiO<sub>2</sub> suspensions in the presence of nitrate ions are reported for the first time. The joint use of UV-vis and EPR spectroscopy evidenced that nitrate radicals are formed by hole induced oxidation of nitrate ions. Photocatalytic degradation of a model alkene compound allowed to highlight the presence of an intermediate organic nitrate deriving from nitrate radical attack to the double bond of the substrate. These results not only allow deeper understanding of photocatalytic processes, but open the route to new green photocatalytic syntheses initiated by nitrate radicals and to new insights in the field of atmospheric chemistry.

It is known that hydroxyl radical (OH) dominates the daytime chemistry of the atmosphere.<sup>[1]</sup> However, nitrate radical (NO<sub>3</sub>) is the most important nocturnal free oxidant radical responsible for many oxidative reactions at night-time. In the earth's atmosphere, NO<sub>3</sub> is mainly formed<sup>[2]</sup> by reaction of NO<sub>2</sub> with ozone according to equation (1) or by dissociation of N<sub>2</sub>O<sub>5</sub> [Eq. (2)].



In general, NO<sub>3</sub> is less reactive than OH with volatile organic compounds.<sup>[4]</sup> Its oxidation potential (+2.00 V vs. SCE in MeCN)<sup>[5]</sup> allows oxidation of alkenes,<sup>[6]</sup> alcohols,<sup>[7]</sup> esters,<sup>[8]</sup> ethers,<sup>[9]</sup> and amines.<sup>[10]</sup> These reactions generally proceed through direct electron transfer, by addition to  $\pi$  systems and by hydrogen atom abstraction.<sup>[11]</sup>

It is reported that OH radicals react only with undissociated nitric acid<sup>[12]</sup> according to equation (3).



NO<sub>3</sub> radical formation has been reported<sup>[13]</sup> to occur by pulse radiolysis according to equations (4),(5) or by means of equation (6):



Katsumura et al.<sup>[12a]</sup> mentioned, without giving a conclusive

prove, the hole scavenging effect of nitrate ions according to equation (7)

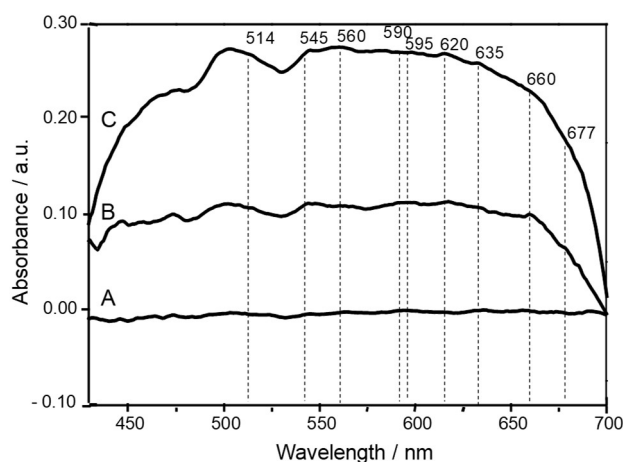


where H<sub>2</sub>O<sup>++</sup> may be formally considered as a hydrated hole, i.e. a precursor of the OH radicals. The occurrence of this reaction has been recently supported by picoseconds pulse radiolysis experiments.<sup>[14]</sup>

Although nitrate radical is one of the first species spectroscopically observed ever,<sup>[15]</sup> its potentialities as an oxidant in selective synthetic processes are under investigation. To this aim few methods to allow nitrate radical accessibility on a preparative scale have been proposed.<sup>[16,11]</sup>

Heterogeneous photocatalysis has attracted attention as a sustainable tool for the green synthesis of valuable compounds.<sup>[17]</sup> Reduction of nitrate ions is known to occur by means of heterogeneous photocatalysis in anaerobic conditions, in the presence of hole scavengers<sup>[18]</sup> or with noble metals doped photocatalysts.<sup>[19]</sup> On the other hand, oxygen efficiently competes with nitrate ions for the photogenerated electrons so that nitrate ions concentration remains virtually unaltered in irradiated TiO<sub>2</sub> aqueous suspensions [see the following Eqs. (8), (13)-(15)].<sup>[20]</sup> The presence of nitrate ions only slightly influences the photocatalytic degradation of many organic pollutants<sup>[21]</sup> and the bactericidal activity<sup>[22]</sup> of TiO<sub>2</sub>. For these reasons, to the best of our knowledge, nitrate ions have been considered as an "inert" species in aqueous oxygenated TiO<sub>2</sub> photocatalytic suspensions.

To get direct evidences of the presence of nitrate radicals in irradiated TiO<sub>2</sub> suspensions, UV-vis spectra of a rear side irradiated mixture containing H<sub>2</sub>O, P25 TiO<sub>2</sub> (Evonik) and O<sub>2</sub> with or without nitrate ions have been recorded (see Figure S1 for experimental details). Results are shown in Figure 1.



**Figure 1.** UV-vis spectra obtained on rear side illuminated mixture of water, TiO<sub>2</sub> P25 in the presence of oxygen without (A) and with (B,C) nitrate ions. Spectrum C is obtained under the same experimental conditions of spectrum B, but at a lower temperature (sample frozen by pouring liquid nitrogen).

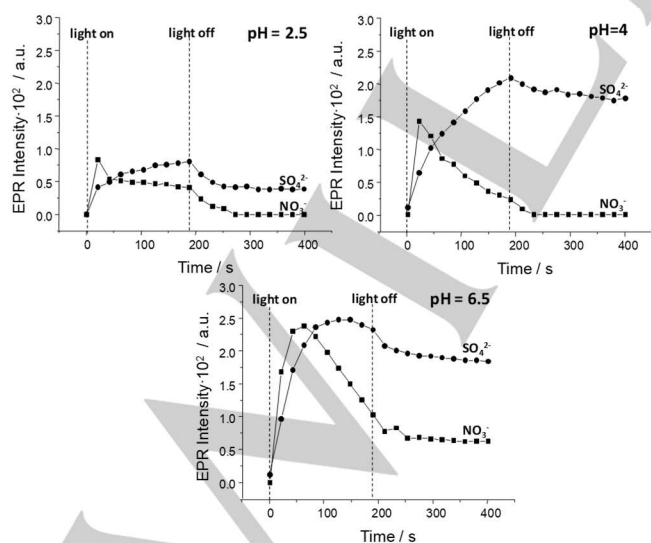
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Spectrum A has been obtained when the sample consisting of a mixture of TiO<sub>2</sub> P25 and few drops of water, previously blown with pure oxygen during 15 minutes, was irradiated from the rear side and simultaneously analyzed against a P25 TiO<sub>2</sub> reference. In the region between 420 and 700 nm no absorption occurred. The LED irradiating from the rear side did not emit in this range so that, although photons could reach the front side of the sample, they did not influence the analysis. The wavelength range in Figure 1 starts from 420 nm because signals below this value derive from the LED emission. Blowing oxygen on the sample prior to analysis was necessary in order to remove the Ti<sup>3+</sup> centres. The latter ones would be otherwise formed under irradiation, thus producing their characteristic bands in the visible range. The presence of nitrate ions in the sample (spectra B and C) increased the absorbance in the range between 430 and 700 nm. Notably, spectrum B is obtained at ambient temperature while spectrum C is obtained on a sample previously frozen by pouring liquid nitrogen on its surface.

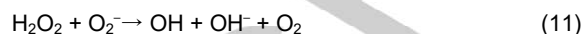
None of the species which, according to literature, may be produced when TiO<sub>2</sub> is irradiated in the presence of water and nitrate, absorbs in this region (with the exception of blue coloured Ti<sup>3+</sup> species whose presence, as above mentioned, can be neglected under the experimental conditions used). Spectra B and C show more than 20 bands from 420 to 700 nm which are in good agreement with those reported in the literature for nitrate radical in gas or condensed phase (see Table S1 in the Supporting Information).

Figure 2 shows the trend of the EPR signal intensity versus time corresponding to the DMPO-OH adduct [DMPO: 5,5-dimethyl-1-pyrroline-N-oxide, Eq. (S1), Supporting Information] for TiO<sub>2</sub> suspensions in the presence of 4mM nitrate (black curves) and 4mM sulphate (red curves) at pH 2.5, 4.0 and 6.5. EPR intensity values have been recorded under irradiation during ca. 200 seconds and in the dark for the remaining time. It is worth to remind that a higher EPR intensity indicates higher amount of hydroxyl radicals detected.



**Figure 2.** EPR signals intensity versus time for TiO<sub>2</sub> suspensions in the presence of 4 mM nitrate (squares) and 4 mM sulphate (circles) ions at pH 2.5, 4.0, and 6.5.

Irradiation caused a steep increase of the signal for all of the curves, indicating the photocatalytic production of OH radicals according to equations (8)–(12).



The main information derived from the experiments of spin trapping in Figure 2 are the following:

a) Increasing the pH of the suspension results in a generally higher amounts of detected hydroxyl radicals. This may be, in principle, attributed to two distinct factors: (i) the OH radicals trapping efficiency of DMPO is lower at acidic pH values,<sup>[23]</sup> and (ii) the OH radicals photogeneration increases when pH rises from 3 to 7.<sup>[24]</sup>

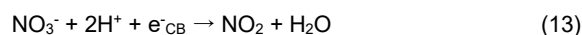
b) In the initial steps of irradiation (from 0 to ca. 30–50 s) the hydroxyl radical generation rate is slightly higher in the presence of nitrate ions than sulphate ions. This occurs for all of the considered pH values.

c) Upon further irradiation the two curves diverge. While in the presence of sulphate ions, the OH radical production increases attaining a plateau, a net decrease of the OH radical detection is observed in the presence of nitrate ions. This effect is more evident at pHs 4 and 6.5.

Therefore, it can be concluded that the presence of nitrate ions limits the production of OH radicals or, alternatively, nitrate ions act as scavengers of the radical species.

Nitrate radical formation by direct hydroxyl radical attack to undissociated nitric acid [Eq. (3)] may be considered negligible in the present experimental conditions (diluted HNO<sub>3</sub>, 4mM).

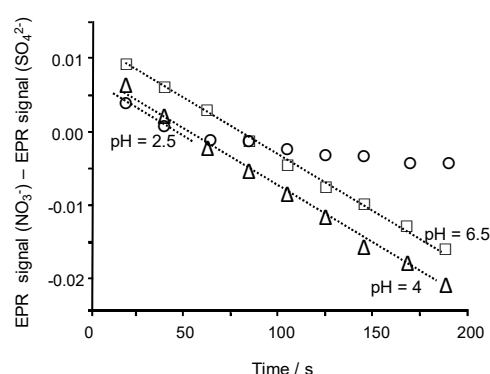
On the other hand, nitrate might be firstly reduced by the photogenerated electrons ( $\text{e}^-_{\text{CB}}$ ) to NO<sub>2</sub> [Eq. (13)] which in turn acts as the OH radical sink [Eq. (14)] affording peroxynitrite (HO<sub>2</sub>NO). The latter fastly decomposes back to H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> [Eq. (15)].



If the latter mechanism holds, the rate of OH radicals decay should depend on both pH and OH radical concentration. The rate of disappearance of OH radicals in the presence of nitrate ions is not accessible from Figure 2. In fact, although a decrease of OH radicals concentration may be easily observed, their generation simultaneously occurs under constant irradiation. The slope of the curve in Figure 2 may be strongly affected by the fact that the trapping efficiency of DMPO increases with increasing pH.<sup>[23]</sup> Moreover, the OH radicals generation and related detection via spin trapping is more efficient at higher pH values.<sup>[24]</sup> These factors somehow mask the pH dependence of

the OH radical decay in the presence of nitrate.

At constant pH the OH radical concentration at a given time is determined by two opposite processes, i.e. OH generation and OH consumption. By considering that the  $\text{SO}_4^\cdot$  radical is produced only by reduction of peroxodisulfate ion with various one-electron reductants or via direct photolysis,<sup>[25]</sup> the presence of sulphate ions may be assumed as ineffective on OH consumption. In fact, OH radical trapping experiments carried out at different sulphate ions concentration (see Figure S2, Supporting information) did not show significant differences in terms of detected OH radicals. The effect of nitrate ions on the consumption of OH radicals can be therefore simply expressed as the difference between the curves in the presence of sulphate and those in the presence of nitrate ions reported in each panel of Figure 2. The results of this procedure are shown in Figure 3.



**Figure 3.** Difference between the EPR signals recorded in the presence of nitrate and sulphate ions versus irradiation time at pH = 2.5 (circles), 4 (triangles), and 6.5 (squares).

The differences of the EPR signals in the presence of nitrate and sulphate ions, reported in Figure 3 show a linear dependence with time. Remarkably, two of the lines (pH 4 and 6.5) have the same slope which is also that of the first two points recorded at pH 2.5. In this case, in fact, the slope changes after 80 seconds of irradiation, due to the lower trapping efficiency of DMPO at this acidic pH. The slope of the curves represents the rate of the overall process consuming OH radicals in the presence of nitrate ions. As the slope does not significantly change with pH, the pH dependence of the OH radical decay in the presence of nitrate ions may be considered negligible. Therefore, the mechanism reported in equation (13)-(15) seems to be less probable in these conditions as it would imply a pH dependent OH radical consumption.

Moreover, as the points in Figure 3 may be satisfactorily fitted by a straight line in all cases, the kinetics of OH radicals decay during irradiation is of zero order with respect to OH radicals concentration. This suggests that the observed OH radical decrease is not due to their direct reaction with nitrate ions but rather to the reaction of the latter with a precursor of OH radical i.e. with a photogenerated hole, in its free form [ $\text{h}^+$ , Eq. (16)], hydrated [ $\text{H}_2\text{O}^{+\cdot}$ , Eq. (7)], or trapped on an active site at the  $\text{TiO}_2$  surface [ $\text{Ti-OH}^{+\cdot}$ , Eq. (17)],

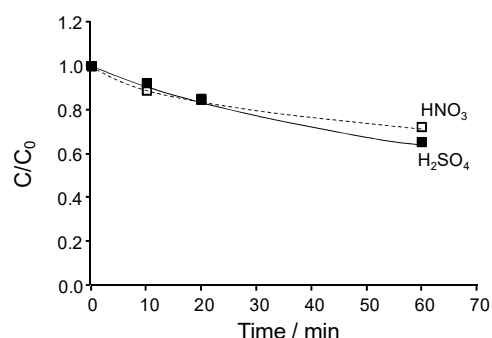


thereby competing with the formation of OH by reaction with water [Eq. (12)]. The competition between water and nitrate ions for the hole induced oxidation, previously reported in literature in other systems,<sup>[14]</sup> might be effective also in the present system (at pH values lower than the zero point charge of  $\text{TiO}_2$ , i.e. ca. 6.5). In fact, even if water is present in very large excess, the density of nitrate anions on the positively charged surface can be very high. Notably, both equations (16) and (17) imply a dependence of the slope of the curves in Figure 3 from nitrate ions concentration. Accordingly, increasing nitrate ions concentration resulted in increased slope, keeping constant other experimental conditions (Figure S3, Supporting information). In fact, competition with water for the photogenerated holes is higher at higher nitrate ions concentration, thus producing faster decline of the amount of detected OH radicals.

Nitrate ions hole trapping effect has been recently demonstrated by picoseconds pulse radiolysis measurements in the case of  $\text{Cl}^-$  and  $\text{Br}^-$  concentrated solutions.<sup>[14]</sup> The capability of  $\text{H}_2\text{O}^{+\cdot}$  radical cation to oxidize nitrate ions according to equation (7) is reported to occur in ultrafast regime<sup>[14]</sup> and to compete with OH radical generation by water oxidation. Recently, Shkrob et al.<sup>[26]</sup> reported  $\text{NO}_3^\cdot$  radicals formation by hole scavenging of nitrate ions in imidazolium ionic liquids.

Equations (7), (16), and (17) allow to justify the results shown in Figure 3, i.e. that the OH radical decay does not depend on the OH radical concentration and pH. In fact, OH radicals are not directly consumed by direct reaction with nitrate, but through reaction of the latter with photogenerated holes. Therefore, the presence of nitrate radicals in irradiated  $\text{TiO}_2$  aqueous suspensions in the presence of nitrate ions can be proposed also on the basis of EPR indirect evidences. The EPR signal of  $\text{NO}_3^\cdot$ , in fact, could not be obtained in the present working conditions as the direct observation of this radical species has been performed at very low temperature in the case of an irradiated crystalline solid.<sup>[3]</sup>

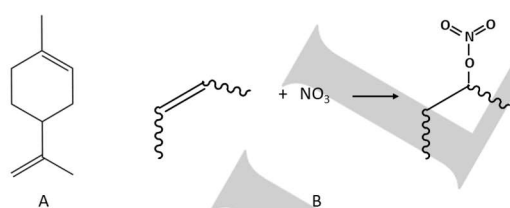
Figure 4 reports the results of the photocatalytic oxidation of phenol in the presence of  $\text{TiO}_2$  P25 and  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$ .



**Figure 4.** Normalized phenol concentration versus irradiation time in the presence of  $\text{TiO}_2$  P25 ( $0.5 \text{ g L}^{-1}$ ) at pH ca. 1.5 in the presence of  $\text{HNO}_3$  (empty squares) and  $\text{H}_2\text{SO}_4$  (full squares). Initial phenol concentration,  $C_0 = 0.5 \text{ mM}$ .

It is evident that the presence of sulphuric or nitric acid did not significantly influence the photocatalytic degradation rate of phenol. Although this finding is in accord with the relevant literature,<sup>[21]</sup> it appears in conflict with the above reported EPR results (Figure 2). In fact, the hydroxyl radical concentration increases in the presence of sulphate ions eventually reaching a plateau. On the contrary, it initially increases in the presence of nitrate ions and after few seconds monotonically decreases. By taking into account that the photocatalytic degradation of phenol occurs mainly through hydroxyl radical attack,<sup>[27]</sup> the photocatalytic degradation rate should dramatically decrease in the presence of nitric acid with respect to sulphuric acid. Therefore, some other reaction paths involving nitrate ions must be hypothesized to justify the results shown in Figure 4. The presence of nitrate radicals may suggest an explanation. In fact, the oxidizing power of nitrate radicals is close to that of hydroxyl radicals. Furthermore, both nitrate and hydroxyl radical attacks proceed through hydrogen abstraction<sup>[28]</sup> so that the oxidation products in the two cases are possibly the same. Therefore, the reaction mechanism may be very different from that occurring in the presence of sulphuric acid, although the presence of nitrate does not macroscopically affect the phenol degradation. Notably, traces of paranitrophenol have been detected in the presence of HNO<sub>3</sub> only within the first 10 minutes of reaction but not at longer irradiation times. This is in agreement with Djengel et al.<sup>[29]</sup> which did not observe nitration of phenol in samples taken after 1 hour irradiation. Nitration may occur through NO<sub>2</sub> radicals generated according to equation (13), as described by Bedini et al.<sup>[30]</sup>, but also through NO<sub>3</sub> initiated hydrogen abstraction<sup>[28]</sup> and subsequent NO<sub>2</sub> addition. The probability of this occurrence could be very low in photocatalytic aqueous systems, thus explaining the trace amounts of nitrophenol detected.

Different is the case of the photocatalytic degradation of an alkene like limonene (Figure 5A). In fact, NO<sub>3</sub> radicals, unlike OH radicals, are reported to add to double bond giving rise to organic nitrates.

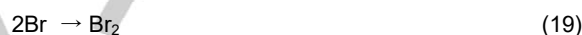


**Figure 5.** A: molecular structure of limonene; B: nitrate radical addition to C=C double bond.

Photocatalytic degradation of limonene in gas phase over an aqueous slurry of TiO<sub>2</sub> P25 has been carried out in the presence of nitric acid and sulphuric acid. The experimental details are reported in the Supporting Information. Although with different relative amounts, some degradation products were detected both in the presence of nitric and sulphuric acids. Other compounds were present only in the presence of nitric acid. In particular, even if standards of the possible compounds deriving from reaction of NO<sub>3</sub> and limonene were not available, a species

whose mass spectrum was compatible with a nitric acid alkyl ester was detected (see Figure S4, Supporting information). This compound may be possibly obtained by preferential NO<sub>3</sub> radical addition to the endocyclic double bond of limonene or of possible unsaturated intermediates photocatalytically generated (Figure 5B).<sup>[31]</sup> In any case, this result is an additional demonstration of the existence of nitrate radicals in the presence of nitrate ions on irradiated semiconductors.

The presence of nitrate radicals may provide an additional mechanistic hypothesis to that reported by Parrino et al.<sup>[20]</sup> for the photocatalytic bromine formation in the presence of nitrate at acidic pHs. By taking into account the above mentioned considerations, another possible “first step” might be the nitrate ions oxidation to nitrate radical. Hole transfer to the nitrate ions may be favoured by considering the positively charged TiO<sub>2</sub> surface at the given acidic conditions and the consequently higher nitrate (and bromide ions) density close to the surface with respect to the bulk. Furthermore, bromide ions are reported as efficient nitrate radical traps because of their fast reaction<sup>[32]</sup> affording elemental bromine [Eqs. (18)–(19)].



The existence of nitrate radicals in irradiated TiO<sub>2</sub> suspensions in the presence of nitrate ions can be firmly proposed on the basis of UV-vis and EPR spectroscopy results. Furthermore, photocatalytic tests in the presence of a model olefin allowed to highlight the specific nitrate radical attack to the double bond of the substrate affording the corresponding organic nitrate. Formation of nitrate radical may be hypothesized to occur through direct or mediated hole induced oxidation of nitrate ions. This finding not only provides a deeper understanding of photocatalytic processes, but it interdisciplinarily highlights the possibility of nitrate radical production in mild conditions with dramatic consequences in the field of atmospheric Chemistry, green organic synthesis and environmental remediation.

**Keywords:** Photocatalysis • Radicals • Nitrate • TiO<sub>2</sub>

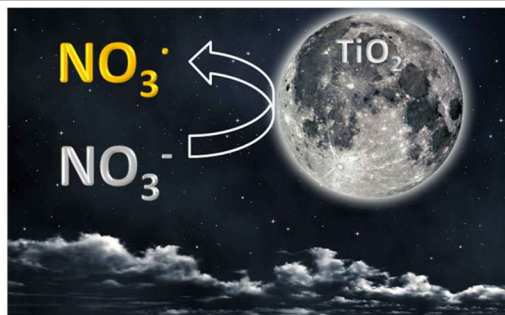
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## Entry for the Table of Contents

## COMMUNICATION

Evidences of the existence of nitrate radicals in irradiated aqueous  $\text{TiO}_2$  suspensions in the presence of nitrate ions are reported for the first time. The joint use of UV-vis and EPR spectroscopy evidenced that nitrate radicals are formed by direct or indirect oxidation of nitrate ions by photogenerated holes.



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