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Detection of Tl(III) with luminol at physiological pH requires hydrogen peroxide as co-oxidant

Lis del Carmen Puga Molina, Sandra Viviana Verstraeten*

Department of Biological Chemistry, IQUIFIB (UBA-CONICET), School of Pharmacy and Biochemistry, University of Buenos Aires, Argentina

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ABSTRACT

The possibility that the reaction between Tl(III) (10–75 μM) and luminol at physiological pH requires the presence of a co-oxidant to produce chemiluminescence (CL) was evaluated. At pH 7.4 Tl(III) did not produce CL, unless the media was added with H_2O_2. This effect linearly depended both on Tl(III) (10–75 μM) and H_2O_2 (0.1–1 mM) concentrations. In the absence of agitation CL kinetics followed an oscillatory pattern, resembling a Belousov–Zhabotinski reaction. The optimal pH for the reaction was 7 with no CL detected below pH 6.5. The optimal temperature range for the reaction was 20–30 °C, decreasing at higher temperatures and being undetectable beyond 45 °C. The amount of Tl(I) recovered from samples matched the theoretical amount of $Tl(OH)^{2+}$ in samples, suggesting that this species may be responsible for the reaction. Proposed mechanism indicates that Tl(III) forms a complex with luminol with an apparent association constant (K) estimated to be $1.95 \times 10^{10}\ M^{-1}$. Superoxide anion was generated along the reaction, and the addition of superoxide dismutase decreased but not abolished CL. In summary, Tl(III) can be detected at micromolar concentrations at physiological pH through the reaction with luminol, provided H_2O_2 is present as a co-oxidant.

1. Introduction

Thallium (Tl) is a toxic heavy metal that is widely used in diverse industries. As a consequence of Tl mobilization by mining, together with its increased use in diverse industries, Tl is released to the environment and constitutes a hazard for human health [1,2]. Tl has two oxidation states, the monovalent (Tl(I)) and trivalent (Tl(III)) cations, and the pair Tl(III)/Tl(I) has high redox potential (ε_0: +1.25 V) [3]. The ionic radius of Tl(III) is 0.885 Å, considerably larger than those of the other metals from the same chemical group [4]. This property makes Tl(III) a medium to soft metal ion, capable to establish interactions with nitrogen and oxygen atoms with a covalent rather than ionic character [5–7]. Tl(III) can be stabilized in its trivalent form by strong complex-forming ligands [8] and the oxidation of neighbor molecules will be consequently prevented.

Luminol-based chemiluminescence (CL) is extensively used to detect the generation of a large group of oxidants including reactive oxygen species [9,10]. It has been reported that luminol detects the presence of Tl(III) in water solutions at pH 14 [11] but this reaction cannot be evidenced at neutral pH. Luminol also reacts with H_2O_2 but in order to proceed, the reaction entails the presence of catalysts, such as $K_3Fe(CN)_6$ [9] or peroxidases [12]. On this basis, and taking into account our previous findings demonstrating that Tl(III) reacts at neutral pH with the electronic spin resonance probe 5,5-dimethyl-1-pyrroline N-oxide (DMPO) [13], the aim of the present work was to investigate if in order to generate CL, the reaction between Tl(III) and luminol at physiological pH requires the presence of a co-oxidant, such as H_2O_2.

2. Materials and methods

2.1. Chemicals

Thallium (III) nitrate and thallium (I) nitrate were from Alfa Æsar (Ward Hill, MA, USA). Hydrogen peroxide solution (30% v/v) was from Riedel-de Haën (Seelze, Germany). Luminol (5-amino-2,3-dihydrophtalazine-1,4-dione), horse heart cytochrome c, bovine erythrocytes superoxide dismutase (SOD), diethylene triamine pentaacetic acid (DTPA), EDTA tetrasodium salt, sodium sulfate, sodium chloride, sodium fluoride, sodium acetate and all

Abbreviations: CL, chemiluminescence; DTPA, diethylene triamine pentaacetic acid; EDTA, ethylendiamine tetraacetic acid; luminol, 5-amino-2,3-dihydrophtalazine-1,4-dione; NaAc, sodium acetate; SOD, superoxide dismutase

* Correspondence to: Departamento de Química Biológica, IQUIFIB (UBA-CONICET), Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires. Junín 956 (C1113AAD), Buenos Aires, Argentina. Tel.: +54 11 4964 8290x143; fax: +54 11 4962 5457.
E-mail addresses: verstraeten@ffyb.uba.ar, verstrae@qb.ffyb.uba.ar (S.V. Verstraeten).

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other reagents were of the highest quality available and were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Tl solutions

Tl(III) stock solutions were prepared by dissolving Tl(III) nitrate in Milli Q water and acidified with 3 M HCl until the attainment of a colorless solution. The amount of acidic Tl(III) solution used for the experiments did not alter the pH of the buffer solutions used in the experiments. Tl(I) stock solutions were prepared in Milli Q water without further additions.

2.3. Incubations

Two milliliters of 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4) was poured into a quartz cuvette and added with the amount of H_2O_2 indicated for the individual experiments. Basal CL emission was recorded at 431 nm for 1 min in a LS55 luminometer/fluorometer (PerkinElmer Ltd., Beaconsfield, United Kingdom) equipped with a total emission accessory and temperature control Tl(III) (10–75 μM) was added to the samples and CL was continuously recorded at the temperature indicated for the individual experiments until CL returned to the baseline value.

2.4. Luminol oxidation

The disappearance of luminol in samples was estimated as previously described [14]. Briefly, samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4) and 1 mM H_2O_2 were incubated at room temperature in the presence of 2.5–37.5 μM Tl(III) and the absorbance at 346 nm was recorded every 30 s for 16 min at room temperature (22 °C). The amount of luminol remaining in the samples was calculated using $\varepsilon = 6741\ M^{-1}\ cm^{-1}$.

2.5. Tl quantitation

The amount of Tl(I) generated upon Tl(III) reaction with luminol (0.25 mM) and H_2O_2 (1 mM) in 20 mM Tris–HCl buffer (pH 7.4) was measured using the method described by Perez-Ruiz et al. [15] with modifications. Every 30 s, 0.3 ml-aliquots were transferred to nitric acid-washed glass tubes and used to quantify Tl(I). Tl(III) remaining in the samples was chelated with 1 mM EDTA to prevent its further reduction. Samples were acidified with 0.1 M HCl (final concentration) and the fluorescence of Tl(I) was recorded at 420 nm (λ excitation: 227 nm). Tl(I) concentration in samples was calculated from a standard curve run in parallel. Since H_2O_2 quenches Tl(I) intrinsic fluorescence the standard curve was added with 1 mM H_2O_2.

2.6. Superoxide anion generation

Superoxide anion ($O_2^{\bullet -}$) generation was evaluated from the reduction of cytochrome c [16]. Samples containing 0.25 mM luminol, 0.1 mM cytochrome c, and 1 mM H_2O_2 in 20 mM Tris–HCl buffer (pH 7.4) were incubated at room temperature in the presence of Tl(III) (5–75 μM). The kinetics of cytochrome c reduction was followed at 550 nm, and $O_2^{\bullet -}$ generation was calculated ($\varepsilon = 21\ mM^{-1}\ cm^{-1}$) [17].

2.7. Calculations

Data integration, non-linear data fitting, and correlations were performed using the routines available in GraphPad Prism version 5.00 for Windows, GraphPad Software (San Diego, CA, USA).

3. Results and discussion

In 1982, Fritsche et al. described a method to quantify Tl(I) in aqueous solutions based on its oxidation to Tl(III) with bromine and further detection with luminol in alkaline conditions [11]. To investigate if the reaction between Tl(III) and luminol can be evidenced at physiological pH, samples containing 0.25 mM luminol in 20 mM Tris–HCl solution (pH 7.4) were added with 75 μM Tl(III) and CL was recorded at 431 nm. Under these conditions no significant CL was detected (Fig. 1, (a)). The possibility that the components of the system under study, rather the pH of the media, may impair CL production was evaluated by performing the reaction in a 20 mM Tris solution adjusted to pH 13. In agreement with the previous data from Fritsche et al. [11], a rapid increase in CL was observed, returning to a baseline value within the first 2 min from reaction onset (inset to Fig. 1).

Luminol is able to detect a wide range of oxidants, including reactive oxygen species and other free radicals, as well as certain transition metals (for comprehensive review see [9]). In addition, luminol can react with a number of compounds without producing CL unless the reaction media is added with a co-oxidant, such as H_2O_2 [9]. On this basis, we investigated if in order to produce CL, the reaction between Tl(III) and luminol at neutral pH required the presence of H_2O_2. As observed for Tl(III), H_2O_2 alone did not produce CL from luminol (data not shown). On the other hand, CL was detectable in samples containing 0.25 mM luminol, 75 μM Tl(III) and 1 mM H_2O_2 (Fig. 1, (b)). Kinetics of CL production showed a maximum around 1 min from the reaction start, followed by a progressive decrease toward a baseline value 10–12 min later. Therefore, subsequent experiments were standardized by recording CL until 16 min from the start of the reaction, when no further CL was detectable for any experimental condition. To notice, when the reaction was carried out in the absence of agitation, luminol CL showed an oscillatory pattern (Fig. 1) resembling those that proceed through the Belousov–Zhabotinky reaction [18]. This kind of oscillatory pattern was not observed when the reaction was performed under continuous stirring at 100 rpm, with CL kinetics showing a maximum within the first 5 s from the onset followed by a monotonic decrease toward the baseline value (data not shown).

The dependence of luminol CL emission on both Tl(III) and H_2O_2 concentrations was next evaluated. In the presence of

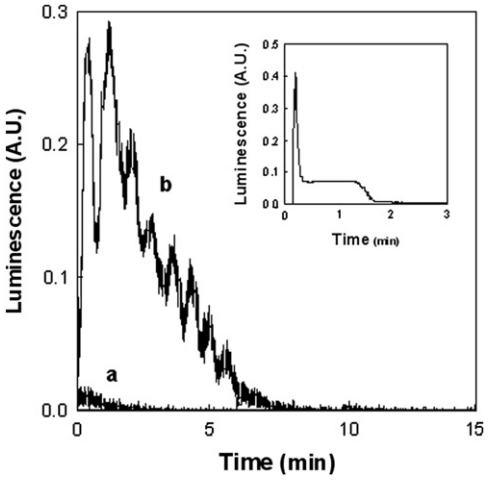

Fig. 1. Kinetics of Tl(III)-mediated luminol chemiluminescence. Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4) without (a) or with 1 mM H_2O_2 (b) were added with 30 μM Tl(III) and luminescence emission was recorded at 431 nm. Traces correspond to a representative experiment. A.U.: arbitrary units. Inset: Kinetics of the reaction between 30 μM Tl(III) and 0.25 mM luminol in 20 mM Tris–HCl (pH 13).

75 μM Tl(III), total CL intensity increased linearly ($r^2 = 0.74$, $P < 0.0001$) with H_2O_2 concentration (0.1–1 mM) in the media (Fig. 2(A)); beyond this concentration CL reached a plateau (data not shown). Similarly, a linear relationship ($r^2 = 0.89$, $P < 0.0001$) between total CL production and the concentration of Tl(III) in the media was observed within the 10–75 μM range (Fig. 2(B)). This finding is in accordance with the previous work by Fritsche et al. [11] who reported that in alkaline conditions, luminol CL linearly depended on Tl(III) concentration over the range 4.9–49 μM. The amount of luminol oxidized along the reaction was quantified from the decrease in the absorbance at 346 nm (Fig. 3). Based on the obtained data, the pseudo-first order constant rate of luminol oxidation for the Tl(III)/H_2O_2 system was estimated to be $0.135 \times 10^{-3}\ s^{-1}$.

To assess the optimal temperature for Tl(III) detection with luminol, reactions were carried out in the temperature range between 20 and 45 °C. Maximal CL production was achieved between 20 and 30 °C. At higher temperatures a dramatic decrease in CL was evidenced (Fig. 4), with negligible CL detected beyond 45 °C. The adjustment of experimental data to a sigmoidal curve (r^2: 0.87) indicated that the temperature necessary to reduce CL to a 50% was 36.2 °C. These results are in agreement

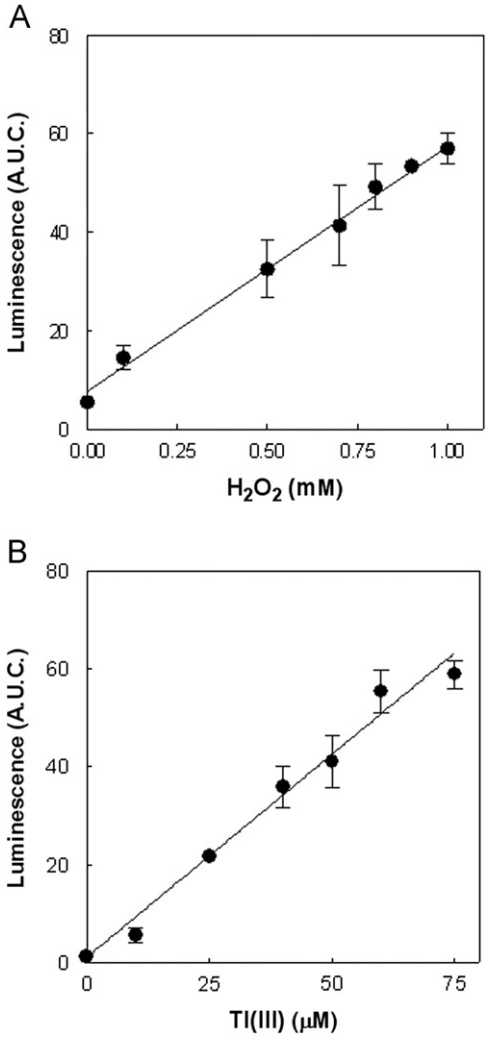

Fig. 2. Influence of Tl(III) and H_2O_2 concentrations. Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4) were incubated at room temperature for 16 min in the presence of (A) 0.1–1 mM H_2O_2 and 75 μM Tl(III), or (B) 1 mM H_2O_2 and 10–75 μM Tl(III). CL was measured as described in Fig. 1. Results are shown as total CL calculated as the area under the curve (A.U.C.) of CL production kinetics, and are the mean ± SEM of four independent experiments.

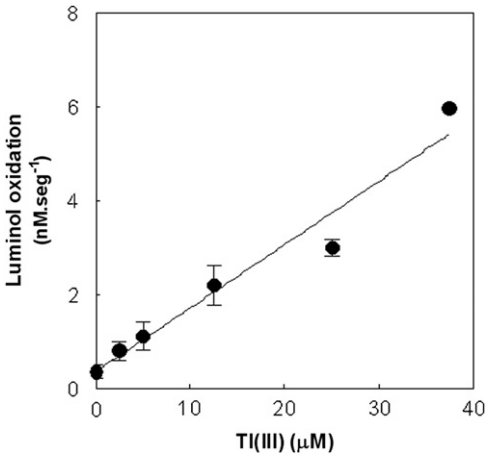

Fig. 3. Luminol oxidation. Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4) and 1 mM H_2O_2 were incubated at room temperature for 16 min in the presence of variable amounts of Tl(III) and luminol oxidation was quantified as described in Section 2.4. Results are shown as the mean ± SEM of five independent experiments.

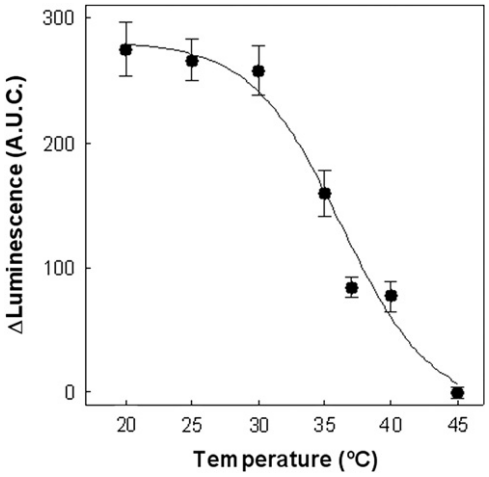

Fig. 4. Influence of temperature. Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4) were preincubated for 5 min in the 20–45 °C temperature range, added with 1 mM H_2O_2 and 75 μM Tl(III) and further incubated at the same temperature for 16 min. Results are expressed as the difference between total CL recorded at each temperature and that obtained at 45 °C, and are the mean ± SEM of four independent experiments. A.U.C.: area under curve.

with early reports from Lind et al. [19] who observed that CL resulting from the oxidation of luminol analog 4-(dimethylamino)phthalhydrazide decreased with the increase in the temperature of the reaction media. This effect was ascribed to a decrease in CL quantum yield rather to a lower chemiexcitation of the resulting phthalate [19].

The influence of the pH of the media on the extent of the reaction was next evaluated. For that purpose, the pH of the 20 mM Tris–HCl solution used for the experiments was adjusted to span the range 4–10. When the reaction was carried out within the 4.0–6.5 pH range, no luminol CL was detected (Fig. 5(A)). This finding is in agreement with the fact that the reactive form of luminol is the monoanion (pKa = 6.7, Fig. 9) [9] and, therefore, no CL should be expected in acidic conditions.

At pH 7, maximal CL for this reaction was achieved, with a progressive decrease in CL emission with pH increase (Fig. 5(A)). Like other metals from the same chemical group (p.e., aluminum), Tl(III) is an amphoteric cation and forms poly-hydroxylated species according to the pH of the media [20]. In order to further understand the possible causes of CL decrease as the incubation

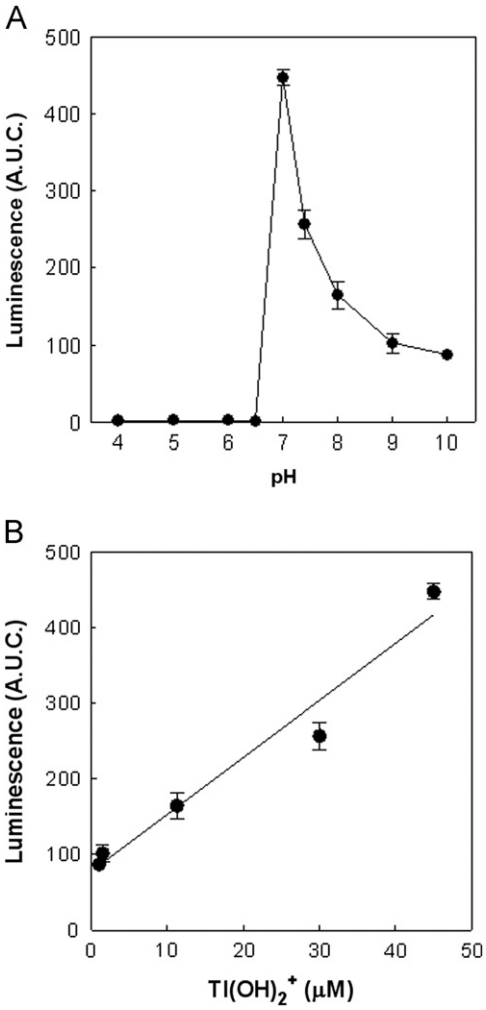

Fig. 5. Influence of pH. (A) Samples containing 0.25 mM luminol in a 20 mM Tris–HCl solution adjusted to pH 4–10, and 1 mM H_2O_2 were incubated for 15 min at room temperature in the presence of 75 μM Tl(III). Results are shown as total CL calculated as the area under the curve (A.U.C.) of CL production kinetics, and are the mean ± SEM of four independent experiments. (B) Correlation between CL measured at pH 7–10 and the calculated concentration of $Tl(OH)_2^+$ in the samples (total Tl(III) concentration: 75 μM).

media became alkaline, the relative amount of Tl(III) hydroxyl species was calculated at the assessed pH. Based on the distribution of those species as a function of pH reported by Lin and Nriagu [20], we estimated that at pH 7, around 60% of total Tl(III) in the samples was present as $Tl(OH)^{2+}$. The remaining 40% was equally divided into $Tl(OH)^{2+}$ and $Tl(OH)_3$. $Tl(OH)_3$ being highly insoluble in aqueous solutions (pKps=45.2 [20]), it seems unlikely that it could be responsible for the CL detected. Thus, $Tl(OH)^{2+}$ and/or $Tl(OH)_2^+$ might be the species involved in this reaction. However, it is important to point out that $Tl(OH)^{2+}$ is no longer present beyond pH 8 although CL was still detectable in samples, thus leaving $Tl(OH)_2^+$ as the main candidate to react with luminol and to generate CL. Interestingly, a linear relationship between the estimated concentration of $Tl(OH)_2^+$ in the samples for each pH assessed and CL generation was observed (r^2: 0.96, $P<0.005$) (Fig. 5(B)). This result points to $Tl(OH)_2^+$ as the main species responsible for the reaction with luminol in neutral and mild alkaline conditions. However, the contribution of $Tl(OH)^{2+}$ to the reaction may not be ruled out since this species is formed in the 2–8 pH range, and because $Tl(OH)^{2+}$ and $Tl(OH)_2^+$ will be rapidly interconverted as their reaction with luminol displaces the equilibrium between them.

In the case that CL resulted from a 2-electron oxidation of luminol by Tl(III), the generation of Tl(I) would be expected. To corroborate that, the amount of Tl(I) in the samples was quantified throughout the reaction. In experiments performed in the presence of 75 μM Tl(III), the average concentration of Tl(I) achieved was 35.2 ± 0.6 μM (Fig. 6). This result is in agreement with the concentration of $Tl(OH)_2^+$ expected in the samples, estimated as 35 μM at pH 7.4 for a total concentration of Tl(III) of 75 μM, and supports the involvement of this species in this reaction.

To estimate the apparent association constant (K) of the Tl(III)-luminol complex, the inhibition of the reaction by a series of compounds with known Tl(III)-chelating capacity was investigated. For this purpose, samples containing 0.25 mM luminol in 20 mM Tris–HCl (pH 7.4) and 1 mM H_2O_2 were added with 0.05–1 mM of the following Tl(III) chelators: DTPA (log K: 46), EDTA (log K: 22.5), Na_2SO_4 (log K: 9.02), NaAc (log K: 8.41), NaCl (log K: 8.14), or NaF (log K: 6.44), and the reaction was started by the addition of 75 μM Tl(III). For each chelator assessed, the inhibition of the reaction adjusted to a one phase exponential association curve (inset to Fig. 7), and the maximal inhibition achieved was calculated. The relationship between the maximal inhibition of the reaction by the chelating agent and the constant association of Tl(III)-chelator complex adjusted to a sigmoidal curve (r^2: 0.97) (Fig. 7). Based on this, the apparent association constant between Tl(III) and luminol was estimated to be $1.95\times10^{10}\ M^{-1}$.

Superoxide anion ($O_2^{\bullet-}$) is generated from one-electron reduction of molecular oxygen. Even when the redox potential of the pair $O_2^{\bullet-}/H_2O_2$ is relatively high (+0.94 V) [21], this species is not capable to oxidize luminol per se [9]. In an early report, Miller and Fridovich [22] demonstrated that the enzyme superoxide dismutase (SOD) decreased, but not completely abolished, hematin-catalyzed CL, and postulated that $O_2^{\bullet-}$ generated during the reaction resulted from the autooxidation of luminol radical anion (Fig. 9). To investigate the involvement of $O_2^{\bullet-}$ generation in CL detected under the current conditions, reactions were performed in the presence of increasing amounts of SOD (0.05–1 U). SOD effectively reduced the amount of CL detected, an effect that linearly depended on the concentration of the enzyme in the reaction media (Fig. 8(A)). Interestingly, at the maximal concentration of SOD assessed (1 U=0.30 μg protein), CL decreased only 30% (Fig. 8(A)). This finding is in agreement with that of Miller and Fridovich [22] showing that the amount of CL generated by

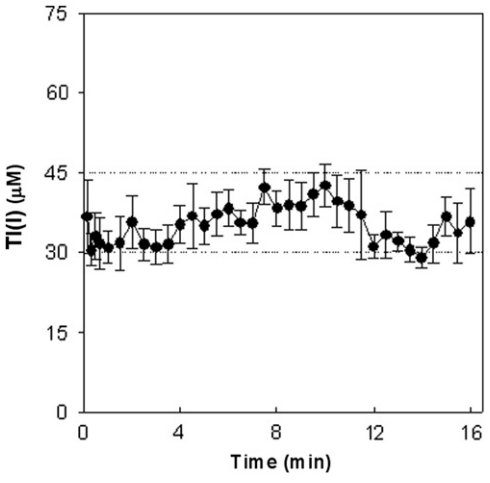

Fig. 6. Tl(I) concentration. Samples containing 0.25 mM luminol and 1 mM H_2O_2 in 20 mM Tris–HCl buffer (pH 7.4) were incubated at room temperature in the presence of 75 μM Tl(III). Every 30 s, aliquots were separated, and Tl(I) concentration was measured as indicated in Section 2.5. Results are shown as the mean ± SEM of six independent experiments.

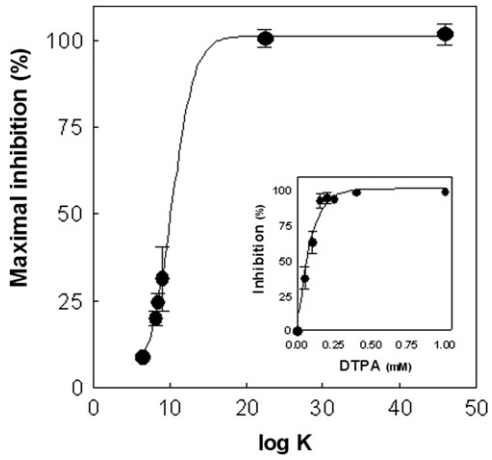

Fig. 7. Effects of Tl(III)-chelating agents. Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4), 1 mM H_2O_2 and 0.05–1 mM of the following Tl(III) chelators: DTPA, EDTA, Na_2SO_4, NaAc, NaCl, or NaF, were preincubated at room temperature and the reaction was started by the addition of 75 μM Tl(III). Maximal inhibition of CL was calculated for each chelating agent by adjusting results to a one-phase exponential association curve. Results are shown as the mean ± SEM of four independent experiments. Inset: Effect of DTPA (0.05–1 mM) on CL emission.

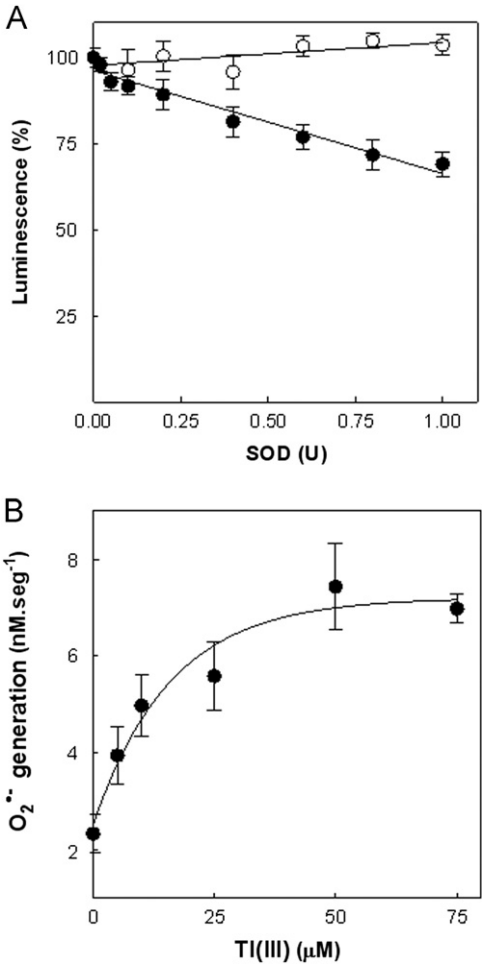

Fig. 8. Superoxide anion ($O_2^{\bullet-}$) generation. (A) Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4), 1 mM H_2O_2, and variable amounts of either native (●) or heat-denaturated (○) SOD (0.025–1 U) were preincubated at room temperature. Reaction was started by the addition of 75 μM Tl(III) and CL was recorded for 16 min. Results are shown as the percentage of the value measured in the absence of SOD, and are the mean ± SEM of four independent experiments. (B) Samples containing 0.25 mM luminol in 20 mM Tris–HCl buffer (pH 7.4), 100 μM cytochrome c and 1 mM H_2O_2 were preincubated at room temperature. Reaction was started by the addition of Tl(III) (5–75 μM). $O_2^{\bullet-}$-dependent cytochrome c reduction was followed at 550 nm as described in Section 2.6. Results are shown as the mean ± SEM of three independent experiments.

the hematin/luminol system negatively related to SOD concentration in the media, and that required a concentration of the enzyme as high as 30 μg ml^{-1} to fully inhibit the reaction. In the current experimental model, the specificity of SOD-mediated impairment of CL generation was verified by previously denaturing SOD for 10 min at 90 °C. When reactions were carried out in the presence of heat-denatured SOD, CL generation remained unaffected (Fig. 8(A)). The relevance of this finding is two-fold. First, it demonstrates that in this system, the generation of $O_2^{\bullet-}$ accounts for total CL generation. And second, it demonstrates that the lower CL observed was due to SOD activity instead of a decrease in the amount of Tl(III) available to react with luminol as a consequence of the interaction between Tl(III) and the protein. Supporting that, $O_2^{\bullet-}$ was quantified in the current system and the generation rate attained depended on Tl(III) concentration in a non-linear manner (Fig. 8(B)).

Based on the above discussed findings, we postulate the following mechanisms to explain the dependence of Tl(III)-luminol reaction on H_2O_2 presence, and on the species of Tl(III) that interact with luminol (Fig. 9). In a media with a pH close to neutrality, luminol is ionized (pK 6.7). Luminol anion binds to $Tl(OH)_2^+$, which is the predominant Tl(III) species at neutral pH. Supporting that, it has been reported that Tl(III) coordinates with N-containing compounds such as heme [23,24], iminophenolate [25], and a triamino-derivative of inositol [7], among others. In all these cases the average distance between Tl(III) and N atoms (2.1–2.7 Å) confers this interaction a covalent rather than ionic character. Upon binding to luminol anion, Tl(III) oxidizes it by a two-electron reaction, rendering diazaquinone. The reaction of diazaquinone with H_2O_2, followed by an internal rearrangement of the bonds, generates luminol dioxetane, which decomposes liberating molecular nitrogen. Thus, singlet-excited state of 3-aminophthalate anion is formed that emits CL with a maximum at 431 nm in water solutions [9].

The second mechanism (Fig. 9(B)) may occur simultaneously with the former one, and involves the participation of $Tl(OH)^{2+}$, the second most abundant Tl(III)-species at neutral pH. $Tl(OH)^{2+}$ would interact simultaneously with two molecules of luminol anion. The possibility that Tl(III) could form a 1:2 complex with another nitrogen-containing molecule, the spin probe DMPO has been previously suggested [13]. Once the complex is formed, luminol molecules are oxidized by Tl(III) rendering luminol radical (Fig. 9(B)) which is ionized at neutral pH. The reaction of the latter with molecular oxygen renders diazaquinone that will react with H_2O_2 through the mechanism described above (Fig. 9(A)). During this process $O_2^{\bullet-}$ is generated that, after reacting with luminol radical, will produce dioxetane and contribute to total CL emission in a H_2O_2-independent manner [22].

4. Conclusions

Tl(III) is a highly oxidizing molecule that was previously demonstrated to generate CL from its reaction with the probe luminol in alkaline conditions. Even when the reaction between Tl(III) and luminol at neutral pH occurs, it does not produce CL. In the current work we demonstrated that it is possible to detect micromolar concentrations of Tl(III) through its reaction with luminol at neutral pH, using H_2O_2 as co-oxidant. Further experiments are required to verify if this approach may be applicable to Tl(III) detection in biological samples.

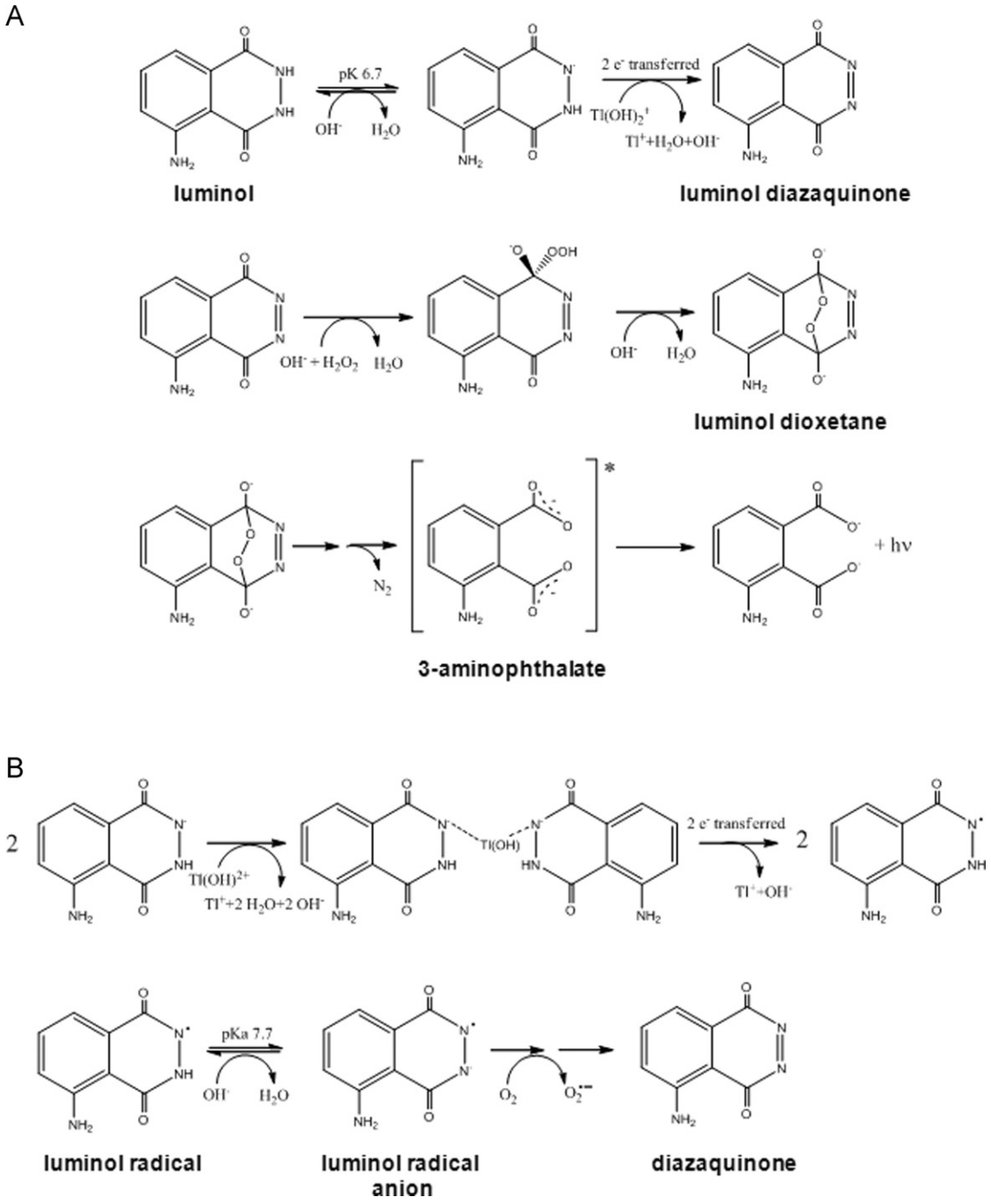

Fig. 9. Mechanisms proposed for the reactions between luminol and (A) $Tl(OH)_2^+$ or (B) $Tl(OH)^{2+}$ in the presence of H_2O_2 at neutral pH. For details see text.

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