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Exploring the limitations of the Hantzsch method used for quantification of hydroxyl radicals in systems of relevance for interfacial radiation chemistry

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HIGHLIGHTS

- Hydroxyl radicals can be indirectly quantified by quantifying CH_2O.
- The Hantzsch method using acetoacetanilide is used to determine CH_2O.
- H_2O_2 negatively interferes with the detection of CH_2O.
- Interference depends on $[H_2O_2]_0/[CH_2O]_0$.
- Interference is caused by the coupled equilibria.

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ABSTRACT

In the presence of Tris or methanol, hydroxyl radicals in systems of relevance for interfacial radiation chemistry can be quantified indirectly via the Hantzsch method by determining the amount of the scavenging product formaldehyde formed. In this work, the influence of the presence of H_2O_2 on the Hantzsch method using acetoacetanilide (AAA) as derivatization reagent is studied. The experiments show that the measured CH_2O concentration deviates from the actual concentration in the presence of H_2O_2 and the deviation increases with increasing $[H_2O_2]_0/[CH_2O]_0$. The deviation is negative, i.e., the measured formaldehyde concentration is lower than the actual concentration. This leads to an underestimation of the hydroxyl radical production in systems containing significant amount of H_2O_2. The main reason for the deviation is found to be three coupled equilibria involving H_2O_2, CH_2O and the derivative produced in the Hantzsch method.

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1. Introduction

The hydroxyl radical is of utmost importance in many fields, like radiation chemistry (Spinks and Woods, 1990), heterogeneous catalysis (Hiroki and Laverne, 2005; Lousada and Jonsson, 2010), Fenton chemistry (Nichela et al., 2008; De Laat and Gallard, 1999), corrosion science (Lee et al., 2014) and photocatalysis (Fujishima and Honda, 1972; Jaeger and Bard, 1979). Hydroxyl radicals cannot be detected or quantified directly mainly due to the high reactivity. There are some indirect means of detection of hydroxyl radicals, e.g. spectrophotometry is employed to measure the oxidized product (formaldehyde) of Tris(hydroxymethyl) aminomethane (Tris) (Lousada and Jonsson, 2010; Yang et al., 2015a) and methanol (Yang et al., 2015b) by hydroxyl radical; high performance liquid chromatography (HPLC) is used to detect the hydroxylated derivatives by using benzoic acid (Haseloff et al., 1990) and 4-chlorophenol (Chen et al., 2015); spin trapping and electron spin resonance (ESR) observation are utilized when using α-phenyl-N-tert-butyl nitrone and α-(4-pyridyl N-oxide) N-tert-butyl nitrone as spin traps. Jaeger and Bard (1979) The amount of hydroxyl radical can also be measured when using Tris and methanol based on the stable relationship between oxidized product formaldehyde and accumulated hydroxyl radicals under a given condition (solution pH and dissolved O_2 concentration) (Lousada and Jonsson, 2010; Yang and Jonsson, 2014). In order to be able to determine the production of hydroxyl radicals in different systems, a simple, highly sensitive and accurate method for the determination of formaldehyde is crucial.

A modified version of the Hantzsch method using acetoacetanilide (AAA) as derivatization reagent (Nash, 1953; Li et al.,

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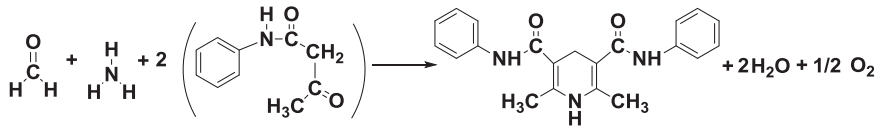

Scheme 1. The Hantzsch reaction using AAA as derivatization reagent.

2007) has been applied to quantify CH_2O in a number of studies (Lousada and Jonsson, 2010; Li et al., 2007; Matsuno and Suzuki, 2008; Pagadala et al., 2014; Cloteaux et al., 2014). The mechanism is depicted in Scheme 1 (Li et al., 2007).

The yield (Y) of CH_2O in the reaction between $HO^\bullet$ and the probe (e.g. Tris and methanol) is defined (equation (1)) as the ratio between the concentration of formaldehyde produced [CH_2O] and the accumulated concentration of hydroxyl radicals formed during the radiolysis of water ($C(HO^\bullet)_{acc}$). $C(HO^\bullet)_{acc}$ can be calculated from Eq. (2).

$$Y = [CH_2O]/C(HO^\bullet)_{acc} \quad (1)$$

$$C(HO^\bullet)_{acc} = \dot{C}(HO^\bullet) \times t = \dot{D} \times G(HO^\bullet) \times \rho t \quad (2)$$

where $\dot{C}(HO^\bullet)$ is the production rate in mol dm^{-3} s^{-1}, $G(HO^\bullet)$ is the G-value (radiation chemical yield) for hydroxyl radical which is equal to 2.8×10^{-7} mol J^{-1} after 10^{-7} s in neutral water. Draganic and Draganic (1971), $\dot{D}$ is the dose rate in Gy s^{-1} and ρ is the density of the solvent. According to the previous work (Yang and Jonsson, 2014), the formaldehyde yield increases significantly for both Tris (16% to 29%) and methanol (14% to 68%) in the presence of O_2. The pH only affects the formaldehyde yield in the Tris case. Specifically, the yield is doubled by increasing pH from 7.0 to 9.0.

It is known that the Hantzsch method using another derivatization reagent 1,3-cyclohexanedione (CHD) (Sawicki and Carnes, 1968) suffers positive interference from H_2O_2 at very high [H_2O_2] to [CH_2O] ratio (Li et al., 2005; de Serves, 1994; Staffelbach et al., 1997; Li et al., 2001). However, the possible interference from H_2O_2 on CH_2O determination using AAA as derivatization reagent has not been studied.

Formaldehyde can react with H_2O_2 forming hydroxymethyl hydroperoxide (HMP) in aqueous-phase. HMP reaches equilibrium with CH_2O producing bis-(hydroxymethyl) peroxide (BHMP) (Zhou and Lee, 1992). The reactions are as follows:

$$CH_2O + H_2O_2 \rightleftharpoons HOCH_2O_2H$$
Hydroxymethylhydroperoxide (HMP) (3)

$$HOCH_2O_2H + CH_2O \rightleftharpoons HOCH_2O_2CH_2OH$$
Bis(hydroxymethyl)hydroperoxide(BHMP) (4)

At room temperature, the equilibrium constants (K_3 and K_4) for reaction (3) and (4) are 149.6 M^{-1} and 11.7 M^{-1}, respectively (Zhou and Lee, 1992).

It should be noted that CH_2O denotes the total analytical formaldehyde, i.e., hydrated plus unhydrated. The equilibrium reaction between the unhydrated CH_2O and the hydrated form methanediol is presented in reaction (5) with equilibrium constant $K_5 = 4.9 \times 10^3$ (Bell, 1966). Both hydrated and unhydrated formaldehyde can undergo the equilibrium reactions reaction (3) and (4) (Zhou and Lee, 1992).

$$CH_2O + H_2O \rightleftharpoons CH_2(OH)_2 \quad (5)$$

In this work, we investigate the influence of H_2O_2 on CH_2O determination by the modified Hantzsch method using AAA as derivatization reagent. The ratio between $[H_2O_2]_0$ and $[CH_2O]_0$ is varied from 3 to 892.

2. Experimental section

2.1. Reagents and chemicals

All the solutions used in this study were prepared using Millipore Milli-Q water (18.2 MΩ cm).

Acetoacetanilide (AAA) (CAS[102-01-2], Aldrich, ≥ 98%) and ammonium acetate (AA) (CAS[631-61-8], Aldrich, ≥ 98%) were used for quantifying formaldehyde in the modified version of the Hantzsch method (Nash, 1953; Li et al., 2007). 1 mL AAA (0.2 M, dissolved in ethanol (99.5%)), 2.5 mL AA (4 M) and 1.5 mL sample are mixed into a test tube at 40 °C for 15 min to react completely to form the dihydropyridine derivative (Scheme 1). After the incubation, the solution is transferred to a quartz cuvette and moved to the UV–VIS spectrophotometer to measure the absorbance at 368 nm. A calibration curve plotting the absorbance of the derivative against formaldehyde concentration (in bulk) has previously been presented (Lousada and Jonsson, 2010), displaying a linear relationship between absorbance and formaldehyde concentration in the range from 0.15 μM to 1 mM. The reference formaldehyde solution was prepared from a stock solution (CAS[50-00-0], Aldrich 37 wt% in H_2O). As reported earlier, the uncertainty of this method is < 2% (Lousada and Jonsson, 2010).

The H_2O_2 solutions were prepared from a 30% standard solution (Merck). The Ghormley triiodide method (Ghormley and Stewart, 1956; Hochanadel, 1952) was adopted to determine the concentration of H_2O_2 using potassium iodide (KI) (VWR BDH Prolabo, 99.0%) and ammoniumdimolybdate (ADM) (Alfa Aesar, 4% w/v). The uncertainty associated with the determination of the concentration of H_2O_2 was < 2% (Lousada and Jonsson, 2010).

2.2. Procedures

To study the influence of H_2O_2 on the modified Hanztsch method (Lousada and Jonsson, 2010), concentrated H_2O_2 solution was added into CH_2O solution with known concentration. The mixed solution (H_2O_2+CH_2O) was analyzed according to the procedure described above.

Additional experiments were performed by adding concentrated H_2O_2 to the mixed solution (H_2O_2+CH_2O) after the incubation time (15 min).

3. Results and discussion

A series of experiments was performed to elucidate the influence of H_2O_2 on CH_2O detection at different $[H_2O_2]_0/[CH_2O]_0$ ratios. The experimental deviation (D_{exp}) is defined in Eq. (6)

$$D_{exp} = 100\% \times ([CH_2O]_0 - [CH_2O])/[CH_2O]_0 \quad (6)$$

K_4 is smaller than K_3 (Zhou and Lee, 1992) and therefore we consider equilibrium (3) to dominate the overall equilibrium while equilibrium (4) can be neglected as a first approximation. Thus, K_3 is defined as.

$$K_3 = [HMP]_{eq}/([H_2O_2]_{eq}[CH_2O]_{eq}) \quad (7)$$

where eq represents the equilibrium state. The amount of complexed CH_2O ($[CH_2O]_0 - [CH_2O]_{eq}$) is equal to $[HMP]_{eq}$, $[H_2O_2]_{eq} \approx$

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