

**DETERMINATION OF HYDROXYL RADICALS USING COUMARIN AND COUMARIN-3-CARBOXYLIC ACID DURING GAMMA RADIOLYSIS AND HETEROGENEOUS PHOTOCATALYSIS**

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**Abstract**

Coumarin and 3-carboxycoumarinic acid, two fluorescent probes commonly used for HO• detection has been used during gamma radiolysis and heterogeneous photocatalysis. The O<sub>2</sub> dependency and the radiation yield of their hydroxylated fluorescent products (7-hydroxycoumarin and 7-hydroxy-3-carboxycoumarinic acid) has been investigated during gamma radiolysis. The radiation yields were found to be 1.2(±0.2) % in O<sub>2</sub>-free solutions, while it was 2.9 (±0.06) % in the presence of O<sub>2</sub>, proving the importance of peroxy radicals in the formation of these products. The results obtained from radiolysis experiments, were employed during heterogeneous photocatalysis performed with commercial TiO<sub>2</sub> catalyst. The effect of dissolved O<sub>2</sub> was also investigated, as its electron scavenging role during photocatalysis is also important. The formation rate of HO• during photocatalysis was calculated from the formation rate of the fluorescent products, and were found to be 1.8×10<sup>-7</sup> mol dm<sup>-3</sup> s<sup>-1</sup>, while the quantum efficiency for its formation is 0.0038.

**Introduction**

Advanced oxidation processes (AOPs) have been investigated in the last few decades for their possible use as an additional wastewater purification method. During AOPs different reactive species form, the most important one is the hydroxyl radical (HO•), due to its high reaction rate with most organic pollutants. However several methods can be employed, like time-resolved spectroscopy, ESR, the determination of HO• formation rates is a complicated task. Fluorescent probes, like terephthalic acid or coumarines, have also been applied during heterogeneous photocatalysis to evaluate the formation rate of HO•. [1-5]

In this study coumarin (COU) and coumarin-3-carboxylic acid (3-CCA) have been used as a fluorescent probe for determination of the HO• formation rate. They are reported to form highly fluorescent hydroxylated products in their reaction with HO•, 7-hydroxycoumarin (7-HO-COU) and 7-hydroxy-3-carboxycoumarinic acid (7-HO-3-CCA), respectively. The formation rate of both hydroxylated products are reported to be dependant on dissolved O<sub>2</sub>. In the presence of O<sub>2</sub> they form via peroxy type radicals, while in the absence of O<sub>2</sub> they form via dismutation, significantly reducing their formation rate. [1-3]

The application of COU and 3-CCA for HO• detection was investigated during two, different AOPs. In the case of gamma radiolysis the formation rate of all reactive species (HO•, e<sub>aq</sub><sup>-</sup>, H•) is well determined, since the values of their radiation yields (G value) are well known. Heterogeneous photocatalysis is also a highly researched field of AOPs, but the reaction mechanisms are often not clear. The transformation of organic compounds is mostly related to the reactions with HO•. In addition, the reactions initiated directly by the photogenerated charges (h<sub>vb</sub><sup>+</sup> and e<sub>cb</sub><sup>-</sup>) has to be taken into consideration too. The reactions take place on the surface or close to the surface of photocatalyst, and consequently the interactions between the photocatalyst and substrate may have an important role.

The aim of this study is to determine the radiation yields of 7-HO-COU and 7HO-3-CCA, and investigate the effect of dissolved O<sub>2</sub> during gamma radiolysis. Based on these result, the formation rate of HO• and the quantum yield of the HO• formation ( $\Phi_{\text{HO}\cdot}$ ) may be determined during the heterogeneous photocatalysis. By comparing the transformation of the non-adsorbed COU, and the well adsorbed 3-CCA, we may investigate the importance of adsorption on the reactions of these substrates with HO•.

## Experimental

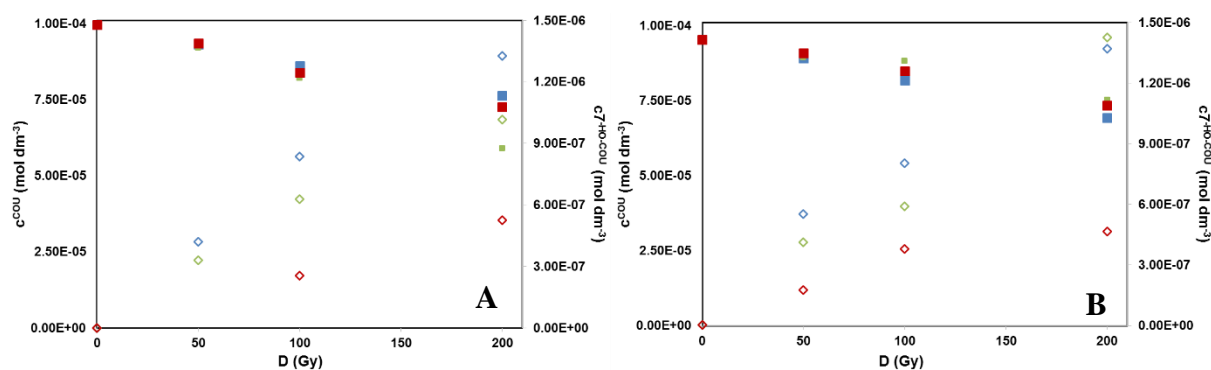
In the gamma-radiolysis experiments a <sup>60</sup>Co gamma source was used in a panoramic type irradiator, the dose rate was 1.48 Gy min<sup>-1</sup>. The solutions of COU and 3-CCA were irradiated in sealed ampoules, which were saturated with either O<sub>2</sub>, N<sub>2</sub>O or N<sub>2</sub>. All experiments were performed in 10<sup>-4</sup> mol dm<sup>-3</sup> solutions of COU and 3-CCA in pH = 7.0 (in 0.01 mol dm<sup>-3</sup> phosphate buffer).

Photocatalysis experiments were performed in a glass reactor. 1.0 g dm<sup>-3</sup> TiO<sub>2</sub> Aeroxide P25 (Acros Organics) was added to the 250 cm<sup>3</sup> solutions, and irradiated using a fluorescent UV light source (GCL303T5/UVA, Lighttech) emitting in the 300-400 nm range. The photon flux of the lamp was 1.20×10<sup>-5</sup> mol<sub>photon</sub> min<sup>-1</sup>, determined by ferrioxalate actinometry. Since 3-CCA adsorbed on the photocatalyst surface (≈30 % adsorbed on TiO<sub>2</sub>), NaF was added to the samples, for the desorption of the analytes. All samples were centrifuged at 15000 RPM, and filtered using 0.22 μm syringe filters (FilterBio PVDF-L).

The transformation of COU and 3-CCA ( $\lambda_{\text{max}}^{\text{COU}} = 277 \text{ nm}$ ,  $\lambda_{\text{max}}^{3\text{-CCA}} = 291 \text{ nm}$ ,  $\epsilon^{\text{COU}} = 10300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\epsilon^{3\text{-CCA}} = 12170 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) has been followed using UV-Vis spectrophotometry (Agilent 8453). The formation of 7-HO-COU and 7-HO-3-CCA were followed using fluorescence spectroscopy (Hitachi F4500) at 455 and 447 nm, respectively. The initial transformation rates of COU and 3-CCA were determined from linear regression fits to the actual concentration versus the duration of irradiation, up to 15 % conversion. The initial formation rates of 7-HO-COU and 7-HO-3-CCA were obtained from the linear regression fits to the actual concentration versus the duration of irradiation.

## Results and discussion

First the effect of O<sub>2</sub> on the formation of 7-HO-COU and 7-HO-3-CCA was investigated. In the case of radiolysis mainly HO• and e<sub>aq</sub><sup>-</sup> forms from water. In the presence of O<sub>2</sub> e<sub>aq</sub><sup>-</sup> transforms into O<sub>2</sub><sup>-•</sup>. Since both O<sub>2</sub><sup>-•</sup> and its protonated form, HO<sub>2</sub><sup>•</sup> have a low reactivity towards organic compounds, mainly HO• is responsible for the transformation of COU in this case. Moreover, from carbon centered radicals peroxy radicals form immediately. The formation of peroxy radicals opens a new pathway for the formation of hydroxylated products via unimolecular HO<sub>2</sub><sup>•</sup> elimination. In O<sub>2</sub>-free solutions both the HO• and the e<sub>aq</sub><sup>-</sup> are able to initiate the transformation of COU. Without O<sub>2</sub>, the formation of 7-HO-COU happens via bimolecular dismutation. The formation rate of HO• in the presence of O<sub>2</sub>, air or N<sub>2</sub> can be calculated ( $r_0^{\text{HO}\cdot} = 6.91 \times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ ). In N<sub>2</sub>O saturated solutions e<sub>aq</sub><sup>-</sup> transforms into HO•, and doubling the HO• yield ( $r_0^{\text{HO}\cdot} = 1.33 \times 10^{-8} \text{ mol dm}^{-3} \text{ s}^{-1}$ ).



**Figure 1.** Concentration of COU (A) and 3-CCA (B) as a function of dose in O<sub>2</sub> (■), N<sub>2</sub>O (■) and N<sub>2</sub> (■) saturated solutions, and the formation of 7-HO-COU during gamma radiolysis in O<sub>2</sub> (◇), N<sub>2</sub>O (◇) and N<sub>2</sub> (◇) saturated solutions.

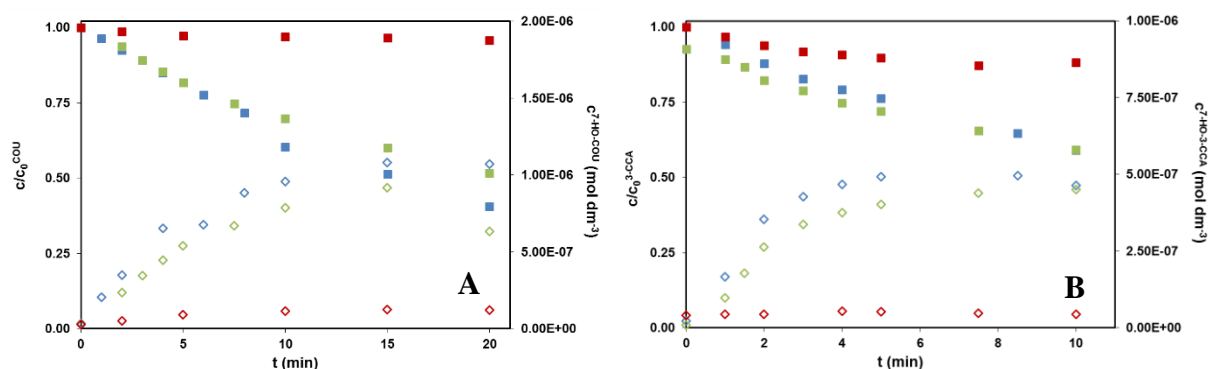
The effect of the different gases on the transformation rate of COU and 3-CCA were negligible. Despite the similar transformation rates, the formation rate of the hydroxylated products show significant differences. The lowest formation rate can be observed in O<sub>2</sub>-free solution, due to the lack of the possibility of peroxy radical formation, and probably because of the significant contribution of  $e_{aq}^-$  to the transformation of COU/3-CCA, which do not result in hydroxylated products. The formation rates in N<sub>2</sub>O saturated solutions are greatly increased, due to the increased HO• formation rate. The formation rates are even higher in the presence of O<sub>2</sub>, despite the lower HO• formation, proving the importance of peroxy radicals in the formation of the hydroxylated products. (Figure 1. and Table 1)

From the formation rates of the hydroxylated products and the formation rate of HO•, the radiation yield for both fluorescent product can be calculated. In N<sub>2</sub> saturated solutions 0.94 and 1.35 %, in N<sub>2</sub>O saturated solutions 1.16 and 1.29 %, while in O<sub>2</sub> saturated solutions 2.99 and 2.86% of HO• produces 7-HO-COU from COU and 7-HO-3-CCA from 3-CCA, respectively.

**Table 1.** Initial transformation rates of COU and 3-CCA and initial formation rates of 7-HO-COU and 7-HO-3-CCA during gamma radiolysis

	$r_0^{COU}$ ( $\times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ )	$r_0^{7-HO-COU}$ ( $\times 10^{-10} \text{ mol dm}^{-3} \text{ s}^{-1}$ )	$r_0^{3-CCA}$ ( $\times 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$ )	$r_0^{7-HO-3-CCA}$ ( $\times 10^{-10} \text{ mol dm}^{-3} \text{ s}^{-1}$ )
O <sub>2</sub>	3.35	2.06	3.23	1.98
Air	4.33	1.55	2.40	1.71
N <sub>2</sub>	3.38	0.64	2.73	0.93

During heterogeneous photocatalysis the main reactive species is the HO•. The photogenerated  $h_{\nu b}^+$  and  $e_{cb}^-$  pair may also react with organic compounds, especially when there is special interaction between the substrate and the catalyst surface. COU and 3-CCA have different adsorption properties, as COU do not adsorb on the catalyst surface, as opposed to 3-CCA, due to the strong interaction between its carboxyl groups and Ti=OH surface groups of photocatalyst.



**Figure 2.** Transformation of COU (A) and 3-CCA (B) as a function of time, in O<sub>2</sub> (■), air (■) and N<sub>2</sub> (■) saturated suspensions, and the formation of 7-HO-COU during heterogeneous photocatalysis in O<sub>2</sub> (◇), air (◇) and N<sub>2</sub> (◇) saturated suspensions.

O<sub>2</sub> plays a crucial role as an electron scavenger, hindering charge recombination, and helping HO• formation via O<sub>2</sub>•<sup>-</sup>. In the case of COU there was no difference in the transformation rates determined in O<sub>2</sub> saturated and airted suspensions. At the same time, the formation rate of 7-HO-COU is nearly 1.5 times greater in the case of higher dissolved O<sub>2</sub> concentration. In the case of 3-CCA the transformation rate is also higher with 25% in the case of O<sub>2</sub> saturated suspension, while the formation rate of 7-HO-3-CCA increased with 33%. In N<sub>2</sub> saturated suspensions the transformation of COU and the formation of 7-HO-COU is negligible. This suggests, that direct charge transfer reactions have a low probability, and HO• formation is negligible. The transformation rate of the well adsorbed 3-CCA is 47% of the value measured in O<sub>2</sub> saturated suspension, and there is no 7-HO-3-CCA formation. This suggest that, 3-CCA transformation can happen via direct charge transfer, but this way does not results in hydroxilated products.

**Table 2.** Initial transformation rates of COU and 3-CCA and initial formation rates of 7-HO-COU and 7-HO-3-CCA during heterogeneous photocatalysis

	$r_0^{\text{COU}} \times 10^{-8}$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	$r_0^{\text{7-HO-COU}} \times 10^{-9}$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	$r_0^{\text{3-CCA}} \times 10^{-8}$ (mol dm <sup>-3</sup> s <sup>-1</sup> )	$r_0^{\text{7-HO-3-CCA}} \times 10^{-9}$ (mol dm <sup>-3</sup> s <sup>-1</sup> )
<b>O<sub>2</sub></b>	6.15	2.55	8.98	2.77
<b>Air</b>	6.08	1.73	7.10	2.08
<b>N<sub>2</sub></b>	0.29	-	4.23	-

Using the results obtained from gamma radiolysis, the formation rate of HO• in the case of O<sub>2</sub> saturated TiO<sub>2</sub> suspension was found to be  $1.78 \times 10^{-7}$  and  $1.86 \times 10^{-7}$  mol dm<sup>-3</sup> in the case of COU and 3-CCA respectively. Assuming that, TiO<sub>2</sub> absorbs completely the emitted photons from the light source, the quantum yield for the formation of HO• is 0.0037 and 0.0039, respectively.

## **Conclusion**

- The formation of 7-HO-COU from COU and 7-HO-3-CCA from 3-CCA requires HO•, while dissolved O<sub>2</sub> highly enhances their formation rate.
- The radiation yield of 7-HO-COU from COU and 7-HO-3-CCA from 3-CCA were determined in the case of gamma-radiolysis
- Based on radiation yields of the hydroxylated products, and the photon flux of the light source, the formation rate of HO• and its quantum efficiency has been determined during heterogeneous photocatalysis, using TiO<sub>2</sub> as photocatalyst

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