Degradation of Monuron in Aqueous Solution by Ionizing Radiation

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Abstract

In this study ionizing radiation induced degradation of monuron was investigated by γ-radiolysis. γ-radiolysis is one of the Advanced Oxidation processes (AOPs) which is very effective method for the degradation of organic water pollutants. The end-products and transient intermediates were studied in order to describe the degradation mechanism. The main reaction is $OH^\bullet$ addition to the aromatic ring forming hydroxyl-cyclohexadienyl type radicals. In addition to this radical, aminyl and phenoxyl radicals have also some contribution to the degradation. Monuron as a halogenated compound is sensitive to the hydrated electron attack. Due to the oxidation, chemical oxygen demand and total organic carbon content decreases during irradiatin treatment. The efficiency of oxidation is high compared to other aromatics. Both, $OH^\bullet$ and e_{aq}^- take part in the dehalogenation reactions.

Introduction

Phenylurea herbicides are applied for the pre- and post-emergence control of weeds in agricultural and non-agricultural fields. They have a long lifetime [1] and because of their bioaccumulation and persistence they can be detected in the environment [2-4].

Our target of investigation, monuron (3-(4-chlorophenyl)-1,1-dimethylurea) is a phenylurea herbicide. Monuron is known to be carcinogenic on humans [5]. Its decomposition has already been studied by different AOP methods: the most effective method was found to be the photo–Fenton reaction [6].

In our laboratory decomposition of different phenylurea herbicides was investigated by high energy irradiation. This study is a sequence of our studies in which the degradation of a series of harmful organic pollutants was examined by γ-radiolysis [7-8].

Experimental

Monuron and other chemicals were purchased from Spectrum-3D or Carlo Erba and used without any purification. All solutions were prepared without any buffer addition and pH adjustment. The γ-irradiated samples were first examined by JASCO 550 UV-Vis spectrophotometer with a 1 cm cell applying appropriate dilutions before taking the spectra. The formation and decay of transient intermediates were followed up by pulse radiolysis to investigate the reactions between monuron and $^\bullet OH$, as well as monuron and e_{aq}^-.

In irradiated samples other comprehensive characteristics of the solution, such as Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Nitrogen (TN) contents were also measured using Behrotest TRS 200 COD system and Shimadzu TOC-VCSN equipment, respectively.

The concentration of adsorbable organic halides (AOX) and free chloride ions in solutions were monitored by an AOX equipment and perfectION[TM] Combination Chloride Electrode. Finally, an Agilent Technologies 6410 Triple Quad LC/MS system was used for final products identification.

Water radiolysis

During water radiolysis reactive primer intermediates (hydrated electron, e_{aq}^- (0.28 µmol J^{-1}); hydroxyl radical, $^\bullet OH$ (0.28 µmol J^{-1}); and hydrogen atom, H$^\bullet$ (0.062 µmol J^{-1}) and molecular products (H$_2$ and H$_2$O$_2$) form. The G-values (yields) of reactive primer intermediates can be seen in the parentheses. These intermediates are responsible for the decomposition of organic substances. The reaction between monuron and individual species were studied under different conditions. In N$_2$O saturated solution the main reaction partner is $^\bullet OH$. In e_{aq}^- reaction 5 vol% tert-butanol containing solution was saturated by N$_2$ to scavenge $^\bullet OH$ radicals. In the absence of TBA, all 3 primer reactive intermediates have some contribution to the reactions. In aerated saturated solutions, e_{aq}^- and H$^\bullet$ can react with dissolved oxygen. In this case reaction agents are $^\bullet OH$ and the superoxide radical/perhydroxyl radical pair $(O_2^{-\bullet}/HO_2^\bullet)$ (pK_a $(O_2^{-\bullet}/HO_2^\bullet) = 4.8$).

Results and discussion

During spectrometric measurements the reactions of individual species with monuron was studied (Figure 1.). In the UV spectra of monuron there is a well-resolved absorption band at 245 nm. This band is the characteristic excitation band for aromatics. During γ-radiolysis, this band decreases with increasing dose. When $^\bullet OH$ reacts with monuron, a new band can be observed between 270 and 320 nm. This band may belong to the hydroxylated versions of monuron [7-8]. In both $^\bullet OH$ and the e_{aq}^- reactions, a slight shift of absorption band at 245 nm can be seen to shorter wavelength due to the dehalogenation.
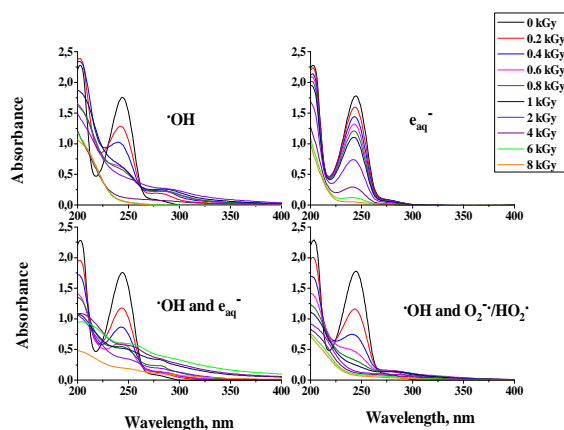

Figure 1. Absorption spectra of 1×10^{-4} mol dm^{-3} monuron irradiated with 0–8 kGy doses: (a) in N$_2$O saturated, (b) in N$_2$ saturated containing 5 vol. % TBA, (c) in N$_2$ saturated and (d) in aerated solutions.

In pulse radiolysis experiments the reaction between monuron and $^\bullet OH$ was investigated (Figure 2.). In the transient spectra the absorption bands between 300-400 nm and above 400 nm showed time dependence. Based on this spectra, we assumed that there are least 2 intermediates in this reaction. The absorption band between 300 and 400 nm may belong to the hydroxycyclohexadienyl type radical. The measurements were also repeated in the presence of 1×10^{-4} mol dm^{-3} K$_3$Fe(CN)$_6$, Fe(CN)$_6^{3+}$ reacts OH adduct forming corresponding phenolic compound [9]. The spectra clearly indicated the peak at 350 nm belonging to the OH adduct. The band above 400 nm with a maximum at 450 nm may be due to the phenoxyl or aminyl type radicals. It will be show later phenoxyl radical formation is more probable than aminyl radical formation. The rate coefficients of the reaction between monuron and $^\bullet OH$, as well as monuron and e_{aq}^- were determined to be (Figure 2. Inset): 2.1 $\pm$

0.9×10^9 mol^{-1} dm^3 s^{-1} and $7.4 \pm 0.2 \times 10^9$ mol^{-1} dm^3 s^{-1}, respectively. Based on the rate coefficients, the electron withdrawing effect of chlorine atom increases the rate of nucleophile reaction and decreases that of electrophile reaction compared to other phenylureas [10].
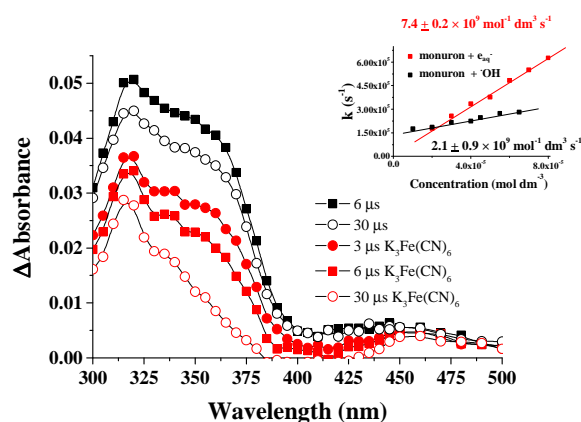

Figure 2. Transient absorption spectra of 1×10^{-4} mol dm^{-3} N$_2$O saturated monuron solution 6 and 30 µs after the electron pulse, and also with 1×10^{-4} mol dm^{-3} K$_3$Fe(CN)$_6$ added to the previous solution 3, 6 and 30 µs after the electron pulse. Inset: Concentration dependence of the pseudo-first-order rate coefficient of absorbance build-up

The rate of oxidation and mineralisation can be described by COD and TOC measurements (not shown). We can get some information on the fate of N-atoms in the molecule based on TN tests. In irradiated samples COD and TOC values decrease due to the oxidation (not shown). The efficiency of oxidation can be characterized by the ratio of rate of oxidation and the number of moles of $^\bullet$OH injected into 1 dm^3 solution [11]. Based on this, one-electron-oxidant $^\bullet$OH finally leads to ~4.4 electron oxidations. TN value changes just slighly with the absorbed dose which shows that the larger part of N-atoms remain in the solution as organic or inorganic nitrogen compounds during γ-radiolysis.

To follow up dechlorination processes, chloride release and the AOX content were measured (Figure 3.). Based on results, the most intense chloride release was observed in aerated solutions in the first stage of degradation. Above 4 kGy, chloride release was higher in $^\bullet$OH reactions. The chloride release in $^\bullet$OH reaction is assumed to be due to radical addition to the carbon atom with chlorine, and by HCl elimination from the adduct, in the reaction a phenoxyl radical also forms.
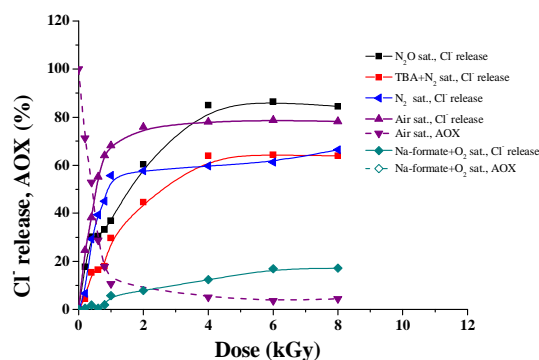

Figure 3. Chloride release in different solutions and AOX in air saturated solution (1.1×10^{-4} mol dm^{-3}) and in oxygen saturated Na-formate containing solution.

The presence of hydrated electron in the reaction mixture promotes dehalogenation processes. In addition to change of adsorbable organic chlorine content was measured in air saturated solutions because the highest in chloride release yield was observed under these conditions. The results showed that complete dehalogenation may take place during the reactions.

The identification of final products was carried out in aerated solution at 0.5 kGy dose. 10 end-products were identified. Particularly, hydroxylated versions of monuron form. During the decomposition of monuron, $^\bullet$OH may react with both aromatic ring and methyl group on the terminal N-atom. Based on the distribution of products, the main reaction takes place between $^\bullet$OH and aromatic ring. Dechlorination processes may occur through OH/Cl substitution or phenoxyl radical formation. Phenoxyl radical formation have some contribution to the phenol type products formation and ring fragmentation in the presence of dissolved oxygen.

Conclusion

γ-irradiation is a very effective method for the decomposition of monuron. During decomposition, hydroxylated molecules form through hydroxycyclohexadienyl type radical intermediates. In N_2O reactions phenoxyl and aminyl type radicals also take part in the degradation. The presence of chlorine atom in monuron increases the rate of oxidation and the efficiency of decomposition. During decomposition, dechlorination processes occur through phenoxyl radical formation and/or OH/Cl substitution.

Acknowledgements

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