



PROCEEDINGS OF THE
22nd International Symposium
on Analytical and Environmental Problems

October 10, 2016

**University of Szeged, Department of Inorganic and
Analytical Chemistry**



Szeged
Hungary

Edited by:
Tünde Alapi
István Ilisz

Publisher:
University of Szeged, Department of Inorganic and Analytical
Chemistry, H-6720 Szeged, Dóm tér 7, Hungary

ISBN 978-963-306-507-5

2016.
Szeged, Hungary

***The 22nd International Symposium
on Analytical and Environmental Problems***

Organized by:

SZAB Kémiai Szakbizottság Analitikai és Környezetvédelmi Munkabizottsága

Supporting Organizations

*University of Szeged, Department of Inorganic and Analytical Chemistry
Hungarian Academy of Sciences*

Symposium Chairman:

István Ilisz, PhD

Honorary Chairman:

Zoltán Galbács, PhD

Organizing Committee:

István Ilisz, PhD

associate professor

University of Szeged Department of Inorganic and Analytical Chemistry

ilisz@chem.u-szeged.hu

Tünde Alapi, PhD

assistant professor

University of Szeged Department of Inorganic and Analytical Chemistry

alapi@chem.u-szeged.hu

TRANSFORMATION OF THIACTOPRID, A NEW INSECTICIDE, BY GAMMA RADIOLYSIS IN AQUEOUS SOLUTIONS

Georgina Rózsa^{1,2}, Zsuzsanna Kozmér^{1,2}, Tünde Alapi¹, Krisztina Schrantz¹, Erzsébet Takács², László Wojnárovits²

¹Department of Inorganic and Analytical Chemistry, University of Szeged,
H-6720 Szeged, Dómtér 7, Hungary

²Radiation Chemistry Department, Centre for Energy Research, Hungarian Academy of
Sciences, H-1121 Budapest, Konkoly-Thege Miklós út 29-33, Hungary
e-mail: rozsa.georgina@chem.u-szeged.hu

Abstract

Degradation of organic pollutants in wastewater by ionizing radiation is an emerging technology. Using this method the transformation of thiacloprid takes place by reactions with free radicals (hydroxyl radical ($\cdot\text{OH}$), hydrated electron (e_{aq}^-), hydrogen radical ($\cdot\text{H}$), and hydroperoxyl radical/superoxide radical anion ($\text{HO}_2\cdot/\text{O}_2^{\cdot-}$). Gamma (γ) radiolysis is an appropriate method to investigate the role of primary radicals in the transformation and degradation of thiacloprid. In this study we examined different reaction conditions (solutions of thiacloprid saturated with dissolved oxygen or nitrogen or nitrous oxide), in order to investigate the effect of different radical sets formed.

Introduction

The traditional wastewater treatment processes are often not sufficiently effective in fully removing certain contaminants. The advanced oxidation processes (AOPs), including the γ radiolysis, represent an up-to-date technology [1]. Radiation chemistry is nowadays a well-established field of science, because it makes possible to isolate reactions of various radicals with the chemicals of interest. γ radiolysis is suitable for the study of the primary radical induced transformations, as described above.

The present study deals with thiacloprid, an insecticide within the family of neonicotinoids. This compound is widely used for protection of different crops, such as rapeseed, potatoes, sunflower, apple and corn seed dressing. Unfortunately, some representatives of the family of neonicotinoids weaken the immune system of bees. Another problem is their high stability and good solubility in water (e.g. for thiacloprid: 184mgL^{-1} at 20°C) [2]. It consists of a chloronicotiny ring, thiazole ring and cyanoimino group.

During the γ radiolysis, the excited atomic nuclei's energy of excitation gets into ground state by photon emission. The emitted photons are mono-energetic and their energy are similar to the atomic nuclei. During radiolysis, the distribution of radicals in the solution is homogeneous, since they are forming in the whole solution. γ photons with 1.17 and 1.33 MeV energy, which are used in practice, are released from γ sources (eg. ^{60}Co) by neutron capturing.

In aqueous solutions irradiated by γ photons the decomposition of water molecules results $\cdot\text{OH}$, e_{aq}^- and (in the lower yield) $\cdot\text{H}$, as primary species. These reactive species are surrounded by water molecules in a small volume part, called Spur [3]. The primary radicals are generated (Eq. 1) with yields (G-values) of 0.280, 0.280 and $0.062\ \mu\text{mol J}^{-1}$, respectively [4, 5].



Using various dissolved gases the radical set formed in solutions could be affected and therefore the effect of different species on the transformation or degradation of thiacloprid could be investigated.

In the presence of dissolved oxygen (DO) the reductive primary species ($\cdot\text{H}/e_{\text{aq}}^-$) transform to less reactive $\text{HO}_2\cdot/\text{O}_2^{\cdot-}$ (Eqs. 2 and 3).



The reaction of thiacloprid with e_{aq}^- could be examined in the presence of nitrogen (N_2). In nitrous oxide (N_2O) saturated solutions N_2O reacts with the e_{aq}^- and transforms it to $\cdot\text{OH}$, and therefore in this case the examination of $\cdot\text{OH}$ induced reaction mechanism of thiacloprid can be studied.



Experimental

2.1 Materials and equipment

During our experiments $10^{-4} \text{ mol L}^{-1}$ thiacloprid solutions were irradiated by γ -rays of a ^{60}Co source in the presence of different gases (DO, N_2 and N_2O). Thiacloprid was purchased from Sigma-Aldrich (99.9% purity). In γ radiolysis experiments the 5 mL ampoules with thiacloprid solution were placed to equal distance from the ^{60}Co - γ source of an SSL-01 panoramic type irradiator, to have a dose rate of 0.7 kGy h^{-1} ($700 \text{ J kg}^{-1} \text{ h}^{-1}$). The solutions were irradiated in open ampoules or in sealed ampoules saturated with N_2 or N_2O .

2.2 Analytical methods

Thiacloprid transformation was followed at 242 nm wavelength with UV-Vis spectrophotometry (Agilent 8453 or Agilent 1200) in a 0.5 cm cuvette, as well as by high performance liquid chromatography (Agilent 1100 HPLC equipment using a LiChroCART® C18 reverse-phase column) with diode array detector (DAD). A mixture of methanol (70%) and water (30%) was used as eluent, at a flow rate of 0.6 ml min^{-1} . 20 μL samples were analysed.

Results and discussion

In Figure 1 the transformation kinetic curves of thiacloprid ($c_0 = 1.0 \times 10^{-4} \text{ mol L}^{-1}$) are shown in the presence of DO, N_2 and N_2O .

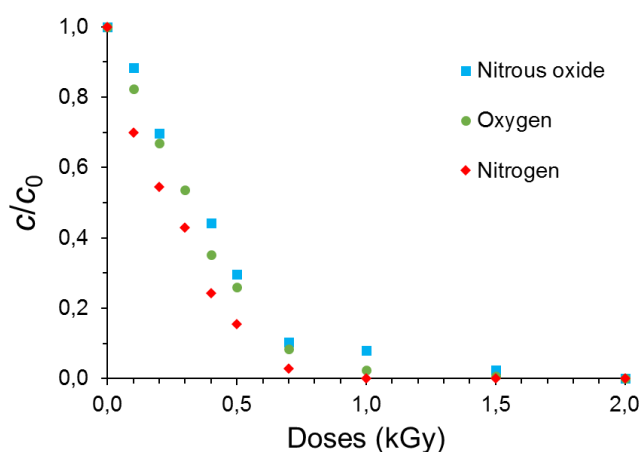


Figure 1. Kinetic curves of thiacloprid ($c_0 = 1.0 \times 10^{-4} \text{ mol L}^{-1}$) transformation during γ radiolysis in the presence DO, N_2 and N_2O

The results show slightly increased transformation rate observed in presence of N_2 . The initial rates of transformation (r_0) are $3.1 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ in the presence DO, $4.3 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ in the presence N_2 and $2.9 \times 10^{-8} \text{ mol L}^{-1} \text{ s}^{-1}$ in the presence N_2O . Since the reactions of e_{aq}^- with thiacloprid were suppressed by using DO and N_2O , and in these two cases the transformation rates of thiacloprid were lower than in the solution that did not contain any reactive dissolved gas (N_2 saturated samples), these results suggest that beside the $\cdot OH$, e_{aq}^- also contributes to the transformation of thiacloprid.

Furthermore, under all three experimental conditions (DO, N_2O and N_2 saturated solutions) complete transformation of thiacloprid could be achieved with 1.5 kGy absorbed dose.

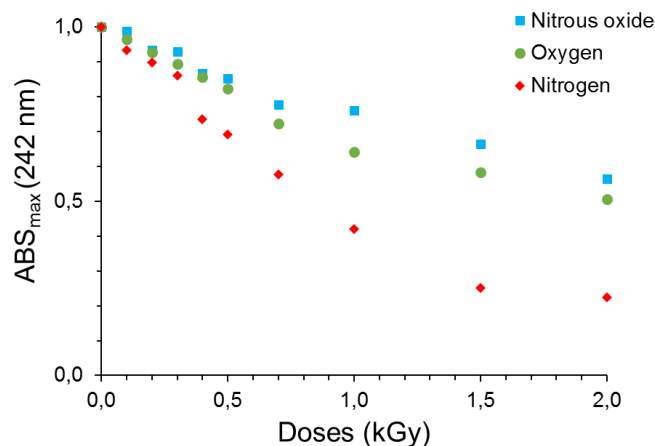


Figure 2. Absorption maxima of $1.0 \times 10^{-4} \text{ mol L}^{-1}$ thiacloprid solutions during γ radiolysis in the presence of DO, N_2 and N_2O

UV-absorption of the thiacloprid solutions during radiolysis were followed by UV-spectrophotometry between 200 and 350 nm. In the UV spectrum of thiacloprid there is an absorption maximum at 242 nm, and two shoulders around 220 and 270 nm. Based on literature data the strong absorption band with centre at 242 nm ($\epsilon_{\text{max}} = 18800 \text{ mol L}^{-1} \text{ cm}^{-1}$) belongs to the 2-thiazolidinecyanamide part of the molecule.

The absorbance maximum changes of the solutions versus absorbed doses are presented in Figure 2. The results show that DO and N_2O saturated solutions contained various intermediates in higher concentration than in N_2 saturated solution. After the total decomposition of thiacloprid (1.5 kGy), the absorbance of the nitrogen saturated solutions was less than half of that of the initial solutions. This results show also that the transformation of the thiacloprid and its intermediates was the most effective in presence of both $\cdot OH$ and e_{aq}^- (in N_2 saturated solution).

The rate constants for the primary radical-induced transformation of thiacloprid will be examined with linear electron accelerator (Linac) in the future. The identification of the main intermediates of thiacloprid transformation will be investigated by HPLC equipped with a quadrupole mass spectrometric detector.

Conclusion

In the present study the effect of dissolved O_2 or N_2O , affecting the radical set formed, were investigated on the radiolysis of thiacloprid. Based on the results the dissolved O_2 and N_2O

reduced slightly the transformation rate of thiacloprid, presumably due to the decreased e_{aq}^- concentration. Consequently, beside $\cdot OH$, e_{aq}^- also contributes to the thiacloprid transformation.

Acknowledgements

The financial support of the Swiss Contribution (SH7/2/20) is highly appreciated.

References

- [1] E. Illés, E. Takács, A. Dombi, K. Gajda-Schranz, K. Gonter, L. Wojnárovits, Radiation induced degradation of ketoprofen in dilute aqueous solution, *Radiat. Phys. Chem.*, 81 (2012) 1479-1483.
- [2] C.A. Morrissey, P. Mineau, J.H. Devries, F. Sanchez-Bayo, M. Liess, M.C. Cavallaro, K. Liber, Neonicotinoid contamination of global surface waters and associated risk to aquatic invertebrates: a review, *Environment International*, 74 (2015) 291-303.
- [3] L. Wojnárovits, *Sugárkémia*, Akadémiai Kiadó, Budapest, 2007.
- [4] G.V. Buxton, The radiation chemistry of liquid water: Principles and applications., in: A. Mozumder, Y. Hatano (Eds.) *Charged particle and photon interaction with matter*, Marcel Dekker, New York, 2004, pp. 331-365.
- [5] J.W.T. Spinks, R.J. Woods, *An introduction to radiation chemistry* 3rd edition, Wiley-Interscience, New-York, 1990.
- [6] G.V. Buxton, C.L. Greenstock, W.P. Helman, B.A. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot OH/O^-$) in aqueous solution, in: *A.I.o.P.a.t.A.C. Society (Ed.) USA*, 1988, pp. 513-886.
- [7] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($\cdot OH/O^-$) in aqueous-solution, *J. Phys. Chem. Ref. Data.*, 17 (1988) 513-886.