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Title

Endosulfan, AE F002671

**Evaluation of Estimation and Experimental Methods on
Determination of the Half-Life in the Atmosphere**

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APPROVALS PAGE

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1 INTRODUCTION

The insecticide endosulfan could enter the environmental compartment air by volatilisation or adsorbed to air-borne particles and has therefore to be assessed for a potential persistence and long-range transport in this mobile compartment.

Degradation by direct photolysis is negligible due to the absence of a chromophor that is able to absorb natural sunlight with wavelengths above 290 nm. This was already indicated in an aqueous photolysis study in sterile water (Stumpf, K., Schink, C., 1988, Doc No.: 37588). However, indirect photolysis, particularly the photo-oxidative reaction with photo-induced hydroxyl radicals would efficiently reduce endosulfan residues in the air.

2 SAR-ESTIMATION OF THE PHOTO-OXIDATIVE DEGRADATION IN THE GASEOUS PHASE

Description of the method

An empirical method for the estimation of the rate of a reaction with hydroxyl radicals and consequently the half-life in the atmosphere was introduced by R. Atkinson (Chem. Rev. 1985: 69-201). It is based on a quantitative structure-activity relationship (QSAR) and comprises the six types of reaction between the test molecule and the hydroxyl radical: hydrogen abstraction, addition to double bonds, addition to triple bonds, addition to aromatic rings, addition to fused rings, and reaction with N, S and OH heteroatomic groups. Different parts of the molecule were individually evaluated in view of the mentioned reactions resulting in partial reaction rate constants (increments). The sum of all partial rate constants yields the overall rate constant k . The half-life DT50 can be calculated from that rate constant assuming pseudo-first order kinetics according to the following formula

$$DT50 = \frac{\ln 2}{k \times c(OH)}$$

with $c(OH)$ being the mean concentration of the hydroxyl radicals in the troposphere (long-term mean = $5 \times 10^5 \text{ cm}^{-3}$). The term pseudo-first order means that the concentration of one of the two reaction partners (test substance and hydroxyl radicals) must be kept constant.

First approach to use the method

A first Atkinson evaluation that was manually conducted in 1991. Several estimations for different parts of the endosulfan molecule have to be made, as a lot of currently measured increments were not available at that time (Palm, W.-U., Zetzsch, C., 1991, Doc. No.: A48681). This estimation yielded an atmospheric half-life of 8.5 days. However, the preliminary character of this result was appreciated in the report by an uncertainty factor of 10.



3 EXPERIMENTAL APPROACH FOR DETERMINATION OF THE PHOTO-OXIDATIVE DEGRADATION IN THE AIR

Following this first Atkinson application resulting in a very rough estimation for the atmospheric half-life (0.85 - 85 days) experimental methods were tried to apply in order to achieve an more exact half-life. Two different experimental approaches were used to meet this objective, one in the gaseous phase at an enhanced temperature and a second one in the liquid phase.

3.1 Flashlight photolysis – resonance fluorescence in the gaseous phase (Zetzsch, C., 1992, Doc. No.: A48146)

Description of the method

A constant stream of endosulfan vapour in an inert gas was passed through a reaction chamber at an elevated temperature (75°C). A gaseous precursor of hydroxyl radicals was admixed. In the reaction chamber, the reactive hydroxyl radicals were generated at an initially high concentration from the precursor by an ultra-short pulse of flashlight. These hydroxyl radicals react with the gaseous endosulfan resulting in a time-dependent decrease of their concentration. Additional UV-light caused fluorescence of the hydroxyl radicals, which in turn was used to quantify their concentration. The rate constant for the reaction between endosulfan and the hydroxyl radicals could now be determined from the decrease of the radicals with time assuming pseudo-first order reaction kinetics. This study yielded a half-life of 27 days at 75°C for alpha-endosulfan based on a radical concentration of $5 \times 10^5 \text{ cm}^{-3}$.

Assessment problems

- Only alpha-endosulfan could be investigated due to the lower volatility of beta-endosulfan, i.e. the concentration of beta-endosulfan was too low to cause a significant change of the radical concentration, even at 75°C.
- The measurement was performed close to the determination limit of the method. Therefore, small amounts of volatile impurities have a significant interference with endosulfan resulting in false rate constants.
- The result of this study was only valid for alpha-endosulfan under the specific test conditions, i.e. at 75°C. A measurement at lower temperatures was impossible due to a too low vapour concentration of endosulfan. Higher temperatures with higher vapour concentrations can cause thermic degradation resulting in an ambiguous correlation between the measured fluorescence signal and the radical concentration. Measurements at other temperatures are therefore not feasible.
- Numerical transformation of the high-temperature rate constant to lower temperatures is impossible due to two opposing effects: The hydrogen abstraction as the first of two occurring reactions with OH radicals is diffusion-controlled. Therefore the partial rate constant for this type of reaction decreases with lower temperatures resulting to an increase of the half-life. In contrast, the addition of hydroxyl radicals to the double bond of endosulfan has a negative activation energy resulting to an increase of this partial rate constant at lower temperatures, because the transition complex retreats at lower temperatures according to Le Chatelier's Principle of Least Restraint. As a consequence,



the half-life of the addition of OH to the double bond in the gaseous phase decreases with lower temperature. Both types of reaction occurred simultaneously between endosulfan and hydrogen radicals and their opposing effects to the overall rate constant at lower temperatures cannot be predicted from a measurement at a single temperature.

- As a consequence, the result of this method is only valid for the enhanced temperature used. Transfer to ambient conditions (approx. 20°C) is not possible due to mechanistic and technical reasons.

3.2 Freon-113 method in the condensed phase (Kloepffer, W., 1992b, Doc. No.: A49538)

Description of the method

Hydroxyl radicals were formed from a precursor by short-wave light in an unpolar, inert liquid in continuous two-phases-distribution process. Freon-113 (1,1,2-trifluoro-1,2,2-trichloroethane) proved to be one of the very rare liquids that fulfils both demanding properties of being unpolar representing unpolar "air molecules" and inert, i.e. being unable to react with the short-wave light, the hydroxyl radicals, its precursor and the test molecule. The decreasing concentrations of dissolved endosulfan and reference compounds with known reaction rates were simultaneously determined by residue analysis while reacting with the continuously generated hydroxyl radicals. By comparison of the decreasing concentration of test and reference compounds the rate constant of endosulfan can be determined assuming pseudo-first order kinetics. For beta-endosulfan only, this method resulted in a half-life of 15 days based on hydroxyl concentration of $5 \times 10^5 \text{ cm}^{-3}$.

Assessment problems:

- A half-life could only be determined for beta-endosulfan. Alpha-endosulfan and endosulfan sulfate were additionally investigated (Kloepffer, W., 1992a, Doc. No.: A49537, Kloepffer, W., 1992c, Doc. No.: A49536), but did not result in a measurable reaction rate (and consequently in a half-life), in spite of very similar molecular structures and the same initial concentration applied. The reason was that this method was not sufficient sensitive to result in a measurable effect, which may be due to the investigation in the liquid phase.
- The transfer of the reaction rate constants measured in the liquid phase to the gaseous phase is difficult due to different diffusion-controlled impacts for test and reference compounds particularly distinct for solutions in the liquid phase
- The transfer of the rate constants from the liquid to the gaseous phase is additionally be complicated by "compression effects to the transition complex of the addition reaction in the liquid phase" according to Le Chatelier's Principle of the Least Restraint. This effect may have a significant influence on the result, if the investigation is performed at the methodical limit as applied for this study.
- As a consequence, this method should be considered with great care, as there is no plausible reason for the inconsistent results obtained for the structurally closely related molecules alpha- and beta-endosulfan and endosulfan sulfate. In addition, variable diffusion dependencies of the rate constant for test and reference compounds in the liquid phase make the interpretation of the results even more difficult.



4 COMPUTER-ASSISTED SAR-ESTIMATION OF THE ATMOSPHERIC HALF-LIFE USING THE AOPWIN™ PROGRAMME

The Atkinson evaluation can now be performed with computer assistance using the AOPWIN™ programme (Atmospheric Oxidation Program, Window Version), that is owned by the U.S. Environmental Protection Agency (US EPA), who gave world-wide permission to use it. The programme was available from W. Meylan and P. Howard, Syracuse Research Corp., NY, USA and can now directly be downloaded from the EPA website within a set of other SAR programmes (EPISUITE). AOPWIN™ calculates the rate constant for the reaction with hydroxyl (OH) radicals and, in addition, the reaction rate for the addition of ozone to double bonds if feasible, following the input of the structure of the test molecule in form of the smiles code.

The AOPWIN™ programme has been repeatedly upgraded by inclusion of new structural increments (partial rate constants for parts of a molecule). Using the current version, AOPWIN™ Version 1.88 (January 1999) the programme calculated an OH reaction rate constant of $8.1671 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (Buerkle, L.W, 2001, Doc. No.: C012614). This rate constant resulted in an

atmospheric half-life of 47.1 hours (just below the 2-day trigger)

assuming a constant diurnal OH concentration of $5 \times 10^5 \text{ cm}^{-3}$ (long-term standard scenario).

Assuming the short-term OH concentration of $1.5 \times 10^6 \text{ cm}^{-3}$ for 12 hours per day, the calculation resulted in an even shorter half-life of 15.7 hours (for a sunlight period and appearance interval for hydroxyl radicals of 12 hours per day) corresponding to an overall half-life of 1.3 days.

The new programme version 1.90 is now available. It yielded the same results as version 1.88.

Quality check of the method and the results

An IUPAC Technical Report (Freudenberg et al., 2001) evaluated the Atkinson's method as "very accurate that can be applied to a large and diverse range of chemical classes." The report continued with the limitation: "However, Atkinson's method should not be used to estimate tropospheric degradation of haloalkenes and halolalkanes with $-CX_3$ (X = F, Cl, Br) groups, perhalogenated compounds, and ethers (especially polyethers, cycloethers, and halogenated ethers)." Endosulfan does not belong to any to the chemical classes for those Atkinson is not recommended. Therefore, the atmospheric half-life determined for endosulfan by the Atkinson's method is assessed to be very reliable.

It is important to note that the determination of all of the partial rate constants (single increments) for endosulfan was exclusively based on measured data as shown in the details of the calculation. None of increment used in this Atkinson calculation was estimated, as frequently happened to pesticides with complicated structures. Therefore, this AOPWIN™



application to endosulfan even increases the reliability in the rate constant and, consequently, the tropospheric half-life of less than 2 days.

5 SUMMARY AND CONCLUSION

A SAR estimation based on the Atkinson method was conducted in 1991 for the reaction of endosulfan and hydroxyl radicals. It resulted in a high degree of uncertainty for the tropospheric half-life due to several unknown and therefore estimated structural increments.

Therefore, experimental approaches were performed. Two different methods resulted in rate constants and half-lives valid only for specific artificial test conditions. But these half-lives could not be transferred to reliable tropospheric half-lives under ambient environmental conditions. A gaseous phase method yielded a result for an enhanced temperature, but was limited by a minimal vapour concentration, that was too low for endosulfan at ambient temperatures. A numerical extrapolation to ambient temperatures was not possible due to two opposing temperature-controlled mechanistic effects. A second liquid-phase method is not applicable to yield reliable half-lives for the gaseous phase due to an inconsistency within structurally closely related molecules and due to the unpredictability of a transfer of the measured liquid-phase rate constant to the gaseous phase.

The rate constant and tropospheric half-life has now been calculated using an upgraded version of the AOPWINTM programme, which is based on the Atkinson method and contained measured data for all required structural components (increments) of the endosulfan molecule. This reliable calculation resulted in a half-life of below the 2-day trigger, which is often used to estimate a potential for the long-range transport in the atmosphere.



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