R- 16492

Aventis CropScience

Aventis

C012614

Estimation of the Reaction with Photochemically Produced Hydroxyl Radicals in the Atmosphere

Code
Endosulfan, AE F002671

Author
Leo W. Buerkle

Completed On
18 April 2001

Institution

Aventis CropScience

Environmental Chemistry – Environmental Risk Assessment

D-65926 Frankfurt a. M.

Bundesrepublik Deutschland

Aventis CropScience

Aventis

C012614

CONFIDENTIALITY STATEMENT

Aventis CropScience

Aventis

C 0 1 2 6 1 4

APPROVALS PAGE

Author   _Leo W. Buerkle_   _18-April-2001_

Leo W. Buerkle   Date (ddMONyyyy)

C 0 1 2 6 1 4

TABLE OF CONTENTS

The last page of this report is number 10.

SUMMARY

C 0 1 2 6 1 4

Estimation of the Reaction with Photochemically Produced Hydroxyl Radicals in the Atmosphere
Endosulfan, AE F002671

This Atmospheric Oxidation Program (AOPWIN) estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals. It also estimates the rate constant for the gas-phase reaction between ozone and olefinic/acetylenic compounds. The rate constants estimated by the program are then used to calculate atmospheric half-lives for organic compounds based upon average atmospheric concentrations of hydroxyl radicals and ozone. AOPWIN requires only a chemical structure to make these predictions.

The AOPWIN program was developed by W. Meylan and P. Howard, Syracuse Research Corporation (SRC), Environmental Science Center, 6225 Running Ridge Road, North Syracuse, NY 13212-2510, USA

The estimation methods used by the AOPWIN are based primarily upon the structure-activity relationship (SAR) methods developed by Dr. **Roger Atkinson** and co-workers as cited below. This version of AOP, version 1.88 (January 1999), incorporates updated fragment and reaction values as cited in Kwok and Atkinson (1995); many of the updated values differ slightly from previously cited values. In addition, SRC has derived some new fragment and reaction values from new experimental data.

The overall OH rate constant and consequently the half-life in the atmosphere depend on the mean concentration of the hydroxyl radicals. The following results were calculated for Endosulfan with the standard OH concentrations used in Europe and USA:

Scenario used in	EU	USA
OH concentration [10^6 radicals/cm^3]	0.5	1.5
Time frame [hours/day]	24	12
OH rate constant [cm^3 molecule^{-1} sec^{-1}]	8.1671 x 10^{-12}	
Half-life [hours]	47.1	15.7
Half-life [days]	2.0	1.3

Based on both scenarios (EU and USA) there can be stated that Endosulfan is readily degradable the air due to a reaction with photolytically generated hydroxyl radicals resulting in an atmospheric half-life of approximately one to two days.

A reaction with ozone was also estimated and resulted in a half life of 320 days.

1. INTRODUCTION

C 0 1 2 6 1 4

Evaporated organic chemicals may be diluted in the air, deposed from the air by wet (e.g. rain wash out) and dry deposition (with dust) and/or degraded by direct and indirect photolysis. A very effective removal from the air is the reaction with photolytically formed, highly reactive intermediates, e.g. hydroxyl radicals, ozone, nitrosyl etc. In case of pesticides which are frequently semi- or low volatile the experimental determination of the reaction rate of that reactions often failed due to the unmeasurable low vapour concentration.

2. ESTIMATION METHOD FOR DETERMINATION OF THE REACTION WITH HYDROXYL RADICALS

Estimation methods based on structure-activity relationship (SAR) methods developed by Roger Atkinson and co-workers (Atkinson, 1985, 1986, 1987, 1991; Atkinson and Carter, 1984; Biermann et al., 1985; Kwok et al., 1992; Kwok and Atkinson, 1995, Kwok et al., 1996) proved to be a good approach for the evaluation of the reaction with hydroxyl radicals in the air. This estimation methods adds up the partial reaction rates of the hydroxyl reaction with subgroups of the test molecule (increments) resulting in the overall reaction rate. The following hydroxyl reactions are considered

- hydrogen abstraction
- addition to double bonds
- addition to triple bonds
- reaction with N, S and –OH
- addition to aromatic rings
- addition to fused rings

The listed increments (group rate constants for hydrogen abstraction, addition to double and triple bonds and reaction with heteroatoms) are compiled in a data base which additionally uses algorithms for consideration of adjacent groups (substituent factors) and the position of the attack to substituted aromatic rings (electrophilic substituent factors).

This program was developed by W. Meylan and P. Howard, Syracuse Research Corporation, Environmental Science Center, 6225 Running Ridge Road, North Syracuse, NY 13212-2510, USA. It is described in the basic publication:

> Meylan, W. M. & Howard, P. H. "Computer Estimation of the Atmospheric Gas-Phase Reaction Rate of Organic Compounds with Hydroxyl Radicals and Ozone", Chemosphere 26 (12), 2293-9 (1993).

It is commercially available under the name "Atmospheric Oxidation Program" (AOPWIN). It estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced hydroxyl radicals and organic chemicals. It also estimates the rate constant for the gas-phase reaction between ozone and olefinic/acetylenic compounds. The rate constants estimated by the program are then used to calculate atmospheric half-lives for organic compounds based upon average atmospheric concentrations of hydroxyl radicals and ozone. AOPWIN requires only a chemical structure to make these predictions.

The accuracy of the method used by AOPWIN was examined by comparison of estimated and experimentally determined hydroxyl radical rate constants. Over 90 percent of the estimated rate constants for 667 different chemicals were within a factor of two of the experiment value. Over 95 percent of the estimates were within a factor of three of the experimental.

This version of AOP, version 1.88 (January 1999), incorporates updated fragment and reaction values as cited in Kwok and Atkinson (1995); many of the updated values differ slightly from previously cited values. In addition, SRC has derived some new fragment and reaction values from new experimental data.
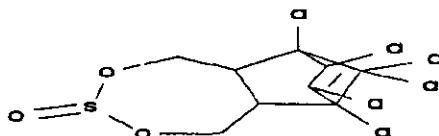
The half-life in the air can be calculated assuming a constant concentration of the hydroxyl radicals by the following formula:

Half-life = ln 2 / (OH rate constant * concentration of OH radicals)

3. RESULTS AS PRINT OUT FROM AOPWIN, VERSION 1.88

Test Substance

Structural formula of Endosulfan as constructed by the AOPWIN program from the smiles code:

Endosulfan

Atkinson-Calculation

Calculation of the Indirect Photolysis Reaction Using the Incremental Method of Atkinson and the Program AOPWIN, version 1.88 according to William Meylan, Philip Howard, Syracuse Research Corporation, Environmental Science Center, Merill Lane, Syracuse, NY 13212-2510, USA 1996:

SMILES : O=S1OCC2C(CL)(C3(CL)(CL))C(CL)=C(CL)C3(CL)C2CO1
or: S1(=O)OCC2C(CL)(C3(CL)(CL))C(CL)=C(CL)C3(CL)C2CO1
or: C13C(CL)(C2(CL)(CL))C(CL)=C(CL)C2(CL)C1COS(=O)OC3
CHEM   : Endosulfan
MOL FOR: C9 H6 CL6 O3 S1
MOL WT : 406.92

------------- SUMMARY (AOP v1.88): HYDROXYL RADICALS ----------------

Hydrogen Abstraction   =   5.3652 E-12 cm3/molecule-sec
Reaction with N, S and -OH =   0.0000 E-12 cm3/molecule-sec
Addition to Triple Bonds   =   0.0000 E-12 cm3/molecule-sec
Addition to Olefinic Bonds =   2.8019 E-12 cm3/molecule-sec
Addition to Aromatic Rings =   0.0000 E-12 cm3/molecule-sec
Addition to Fused Rings   =   0.0000 E-12 cm3/molecule-sec

OVERALL OH Rate Constant =   8.1671 E-12 cm3/molecule-sec
HALF-LIFE =   1.964 Days (24-hr day; 0.5E6 OH/cm3)
HALF-LIFE =   47.147 Hrs
HALF-LIFE =   1.310 Days (12-hr day; 1.5E6 OH/cm3)
HALF-LIFE =   15.716 Hrs

------------- SUMMARY (AOP v1.88): OZONE REACTION ----------------

OVERALL OZONE Rate Constant =   0.003579 E-17 cm3/molecule-sec
HALF-LIFE =   320.239 Days (at 7E11 mol/cm3)

Experimental Database Structure Match:

Chem Name : Endosulfan
CAS Number: 00115-29-7
Exper OH rate constant : <10 E-12 cm3/molecule-sec
Exper Ozone rate constant: --- cm3/molecule-sec
Exper NO3 rate constant : --- cm3/molecule-sec

Details of OH-Reactivity: Individual Increments

Hydrogen Abstraction Calculation:
Ksec = 0.934 F(>CH-)F(-OS(=O))=0.934(1.230)(0.700)= 0.804
Ktert = 1.94 F(>CH-)F(-C-1Halogen)F(-CH2-)(RS5)
    = 1.94(1.230)(1.000)(1.230)(0.64000) = 1.878
Ktert = 1.94 F(>CH-)F(-CH2-)F(-C-1Halogen)(RS5)
    = 1.94(1.230)(1.230)(1.000)(0.64000) = 1.878
Ksec = 0.934 F(-OS(=O))F(>CH-)=0.934(0.700)(1.230)= 0.804
H Abstraction TOTAL = 5.365 E-12 cm3/molecule-sec

OH Addition to Olefinic Bonds Calculation:
Kd = K(>C=C<)C(-CL)C(-C-Halogen)C(-CL)C(-C-Halogen)
    = 110.000(0.21)(0.76)(0.21)(0.76) = 2.802 E-12 cm3/molecule-sec

Ozone Reaction with Olefins Calculation:
Ko = K(R2-C=C-R2)Ox(-CL)Ox(-Tert C **)Ox(-CL)Ox(-Tert C **)
    = 0.175000(0.143)(1.000)(0.143)(1.000) = 0.003579 E-17 cm3/molecule-sec
    ....ASSUMED Values designated by: **

4. REFERENCES

Atkinson, R. 1985. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds under atmospheric conditions. Chem. Rev. 85: 69-201.

Atkinson, R. 1986. Estimations of OH radical rate constants from H-atom abstraction from C-H and O-H bonds over the temperature range 250-1000 K. Intern. J. Chem. Kinet. 18: 555-568.

Atkinson, R. 1987. A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. Intern. J. Chem. Kinet. 19: 799-828, Doc. No. A57325.

Atkinson, R. 1988. Estimation of gas-phase hydroxyl radical rate constants for organic chemicals. Environ. Toxicol. Chem. 7: 435-442, Doc. No. A47123.

Atkinson, R. 1989. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. J. Phys. Chem. Ref. Data Monograph No. 1. NY: Amer. Inst. Physics & Amer. Chem Soc.

Atkinson, R. 1991. Kinetics of the gas-phase reactions of a series of organosilicon compounds with OH and NO3 radicals and O3 at 297 ± 2K. Environ. Sci. Technol. 25: 863-6.

Atkinson, R. and Carter, W.P.L. 1984. Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. Chem. Rev. 84: 437-470.

Biermann, H.W., MacLeod, H., Atkinson,R., Winer,A.M., and Pitts,Jr. J.N. 1985. Kinetics of the gas-phase reactions of the hydroxyl radical with naphthalene, phenanthrene, and anthracene. Environ. Sci. Technol. 19: 244-248.

Kwok, E.S.C., Atkinson, R. and Arey, J . 1992. Gas-phase atmospheric chemistry of selected thiocarbamates. Environ. Sci. Technol. 26: 1798-1807.

Kwok, E.S.C. and Atkinson, R. 1995. Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update. Atmospheric Environment (29: 1685-95). [from Final Report to CMA Contract No. ARC-8.0-OR, Statewide Air Pollution Research Center, Univ. of CA, Riverside, CA 92521].

Kwok, E.S.C., S.M. Aschmann and Atkinson, R. 1996. Rate constants for the gas-phase reactions of the OH radical with selected carbamates and lactates. Environ. Sci. Technol. 30: 329-34.