United States
Environmental Protection
Agency

Environmental Research
Laboratory
Athens GA 30613-7799

Research and Development

EPA/600/M-89/009 Aug. 1990

EPA

ENVIRONMENTAL RESEARCH BRIEF

REVISED

Pathway Analysis of Chemical Hydrolysis for 14 RCRA Chemicals

Heinz P. Kollig, J. Jackson Ellington, Eric J. Weber, and N. Lee Wolfe

The probable pathways of transformation by chemical hydrolysis in an aqueous environment were postulated for 14 chemicals. Acid, base, and neutral half-lives at pH 7 are given for the chemicals and their products. A structural formula is provided for each chemical.

Introduction

Assessment of potential risk posed to humans by man-made chemicals in the environment requires the prediction of environmental concentrations of those chemicals under various scenarios. Whether mathematical models or other assessment techniques are employed, knowledge of equilibrium and kinetic constants (fate constants) is required to predict the transport and transformation of these chemicals.

Under section 301 of the Resource Conservation and Recovery Act (RCRA), EPA's Office of solid Waste (OSW) has identified wastes that may pose a substantial hazard to human health and the environment. RCRA requires that EPA develop and promulgate criteria for identifying and listing hazardous wastes, taking into account, among other factors, persistence and degradability in the environment.

In 1986, OSW proposed additions to the list of chemicals regulated under the Toxicity Characteristic section of RCRA. A land disposal decision model developed at the Environmental Research Laboratory in Athens, Georgia (ERL-Athens) was applied to determine maximum permissible leachate concentrations resulting from the Toxicity Characteristic Leachate procedure for the additional chemicals. ERL-Athens had provided hydrolysis rates and sorption data for these chemicals. Response to the *Federal Register* proposals for regulated concentrations prompted OSW to (1) change some transport functions in the model and (2) remove from the list 15 chemicals that hydrolyze in order to evaluate these chemicals in more depth.

OSW requested that ERL-Athens postulate the probable pathways of transformation in an aqueous environment by chemical hydrolysis for the 15 chemicals. The chemicals were acrylonitrile, carbon tetrachloride, chlordane, *bis*(2-chloroethyl)ether, chloroform, 1,2-dichloroethane, heptachlor, lindane, methoxychlor, methylene chloride, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, 1,1,2,2-tetrachloroethane, and toxaphene. Toxaphene was not addressed in the pathway analysis,

however, because it is a mixture of more than 600 polychlorinated terpenes.

Pathway Analysis

A team of scientists met to discuss the hydrolysis rates and probable pathways of transformation. The methods used to arrive at the reaction products were based primarily on the team's experience with similar compounds, their knowledge of the hydrolysis theory, and their understanding of structure activity relationships. The final stable products were identified as containing either no hydrolyzable functional group (NHFG) or non-labile functional group (NLFG). Although the molecule with a non-labile functional group contains one or more heteroatoms, they are so unreactive towards hydrolysis that they will not hydrolyze. (Over the pH range of 5 to 9 and at 15°C, half-lives will be greater than 50 years if they react at all.)

Literature searches were conducted afterwards to find needed fate data for the intermediate products of hydrolysis. If the literature failed to provide the required data, they were determined in the laboratory if possible. All half-lives were calculated at pH 7. The values were arrived at by adding the acid and/or base portion of the rate constant at pH 7 to the neutral rate constant and calculating the half-life according to: $t^{1/2}$ = (ln 2)/rate constant.

Acrylonitrile (Figure 1) hydrolyzes through the intermediate product acrylamide to acrylic acid, a compound that has no hydrolyzable functional group. Ammonia is formed along with acrylic acid.

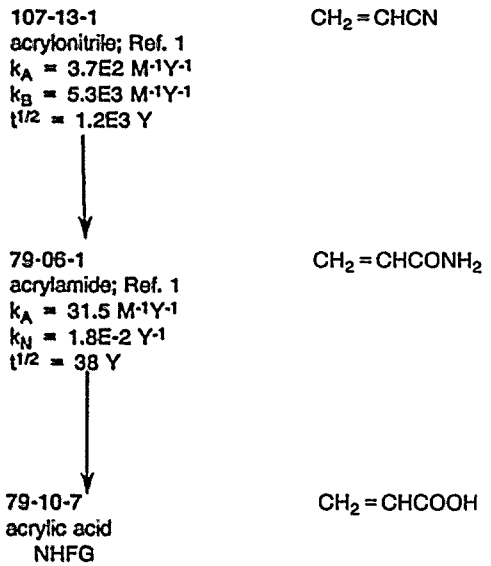

Figure 1. Acrylonitrile, hydrolysis pathway.

Carbon tetrachloride (Figure 2) hydrolyzes to inorganic products, carbon dioxide and hydrogen chloride, with no detectable intermediates.

Chlordane (Figure 3) hydrolyzes to the final stable product, 2,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methano-1H-indene. Hydrogen chloride is formed in the process. No other products have been observed. (Only the *cis*-isomer, CAS #5103-74-2, undergoes hydrolysis due to the 1-exo, 2-exo orientation of the chlorine.)

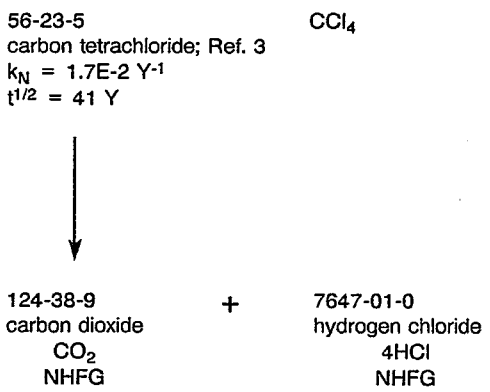

Figure 2. Carbon tetrachloride, hydrolysis pathway.

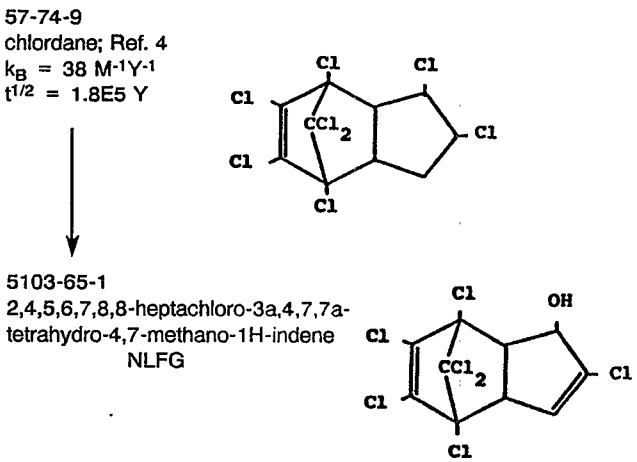

Figure 3. Chlordane, hydrolysis pathway.

bis(2-Chloroethyl)ether (Figure 4) hydrolyzes through the intermediate product, 2-(2-chloroethoxy)ethanol, to the final stable products, *bis*(2-hydroxyethyl)ether and para-dioxane. The 2-(2-chloroethoxy)ethanol will build to a significant steady state concentration. Hydrogen chloride is formed in the process.

Chloroform (Figure 5) hydrolyzes to inorganic products, carbon dioxide and hydrogen chloride.

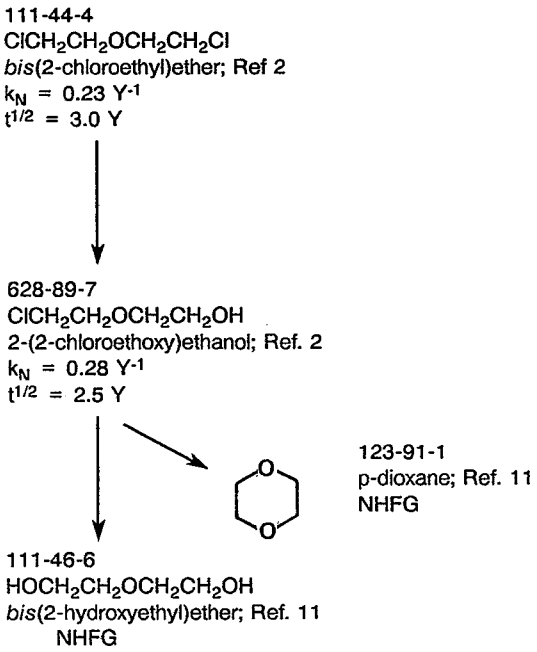

Figure 4. *bis*(2-Chloroethyl)ether, hydrolysis pathway.

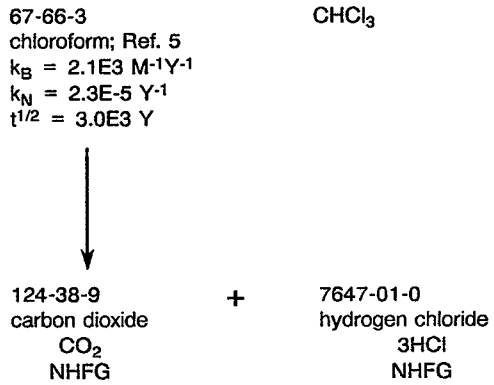

Figure 5. Chloroform, hydrolysis pathway.

1,2-Dichloroethane (Figure 6) hydrolyzes to the fairly stable product vinyl chloride and to the final stable product ethylene glycol through the intermediate product 2-chloroethanol. Vinyl chloride may further hydrolyze to acetylene at alkaline pHs or to acetaldehyde at near neutral pH. Ethylene glycol is the main product at near neutral pH, and the reaction shifts to give vinyl chloride as the pH increases. Hydrogen chloride is formed in the process.

Heptachlor (Figure 7) hydrolyzes to 1-hydroxychlordene, which has an estimated half-life of longer than 8 million years at pH 7. Hydrogen chloride is formed in the process.

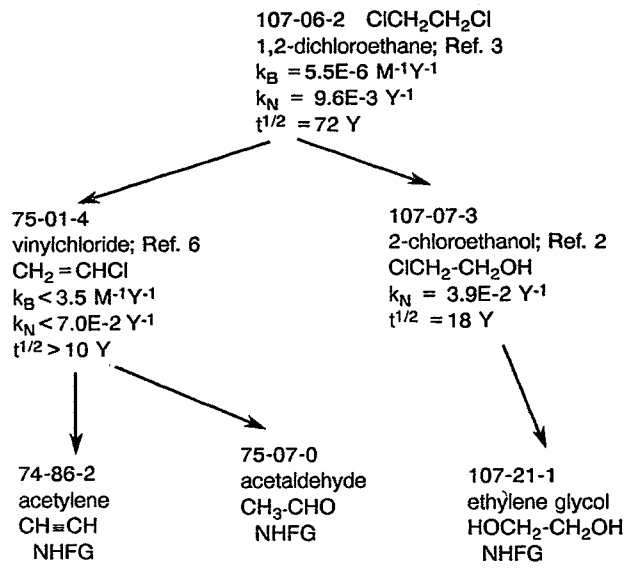

Figure 6. 1,2-Dichloroethane, hydrolysis pathway.

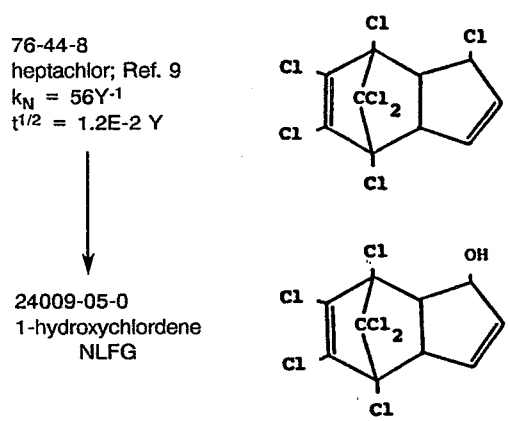

Figure 7. Heptachlor, hydrolysis pathway.

Lindane (Figure 8) hydrolyzes through the intermediate product, 1,3,4,5,6-pentachlorocyclohexene, to the final stable products, 1,2,3-trichlorobenzene and 1,2,4-trichlorobenzene. Hydrogen chloride is formed in the process.

Methoxychlor (Figure 9) hydrolyzes to the final stable product, 2,2-bis(p-methoxyphenyl)-1,1-dichloroethylene under alkaline conditions, and to the final stable product anisil through the intermediate product anisoin under acidic or near neutral conditions. Hydrogen chloride is formed in the process. Anisoin oxidizes to anisil. A rate of oxidation was not available.

Methylene chloride (Figure 10) hydrolyzes with no detectable intermediates to the final stable products, formaldehyde and hydrogen chloride.

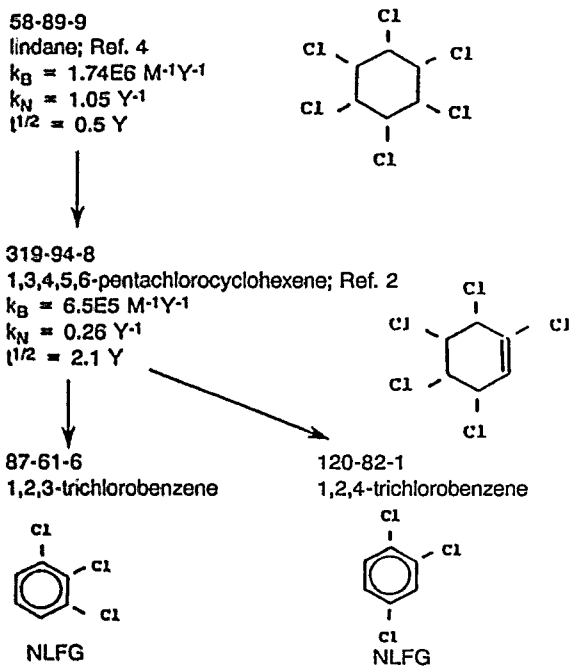

Figure 8. Lindane, hydrolysis pathway.

1,1,1-Trichloroethane (Figure 11) hydrolyzes to the two final stable products, acetic acid and 1,1-dichloroethene. Hydrogen chloride is formed in the process. The ratio of acetic acid to 1,1-dichloroethene is dependent on pH and temperature. Production of 1,1-dichloroethene increases directly with pH and temperature.

1,1,2-Trichloroethane (Figure 12) hydrolyzes to the final stable product hydroxyacetaldehyde through the intermediate product chloroacetaldehyde and to the final stable product 1,1-dichloroethene. Hydrogen chloride is formed the process.

1,1,1,2-Tetrachloroethane (Figure 13) hydrolyzes to the final product, 1,1,2-trichloroethylene. Hydrogen chloride is formed in the process.

1,1,2,2-Tetrachloroethane (Figure 14) hydrolyzes to the final product, 1,1,2-trichloroethylene. Hydrogen chloride is formed in the process.

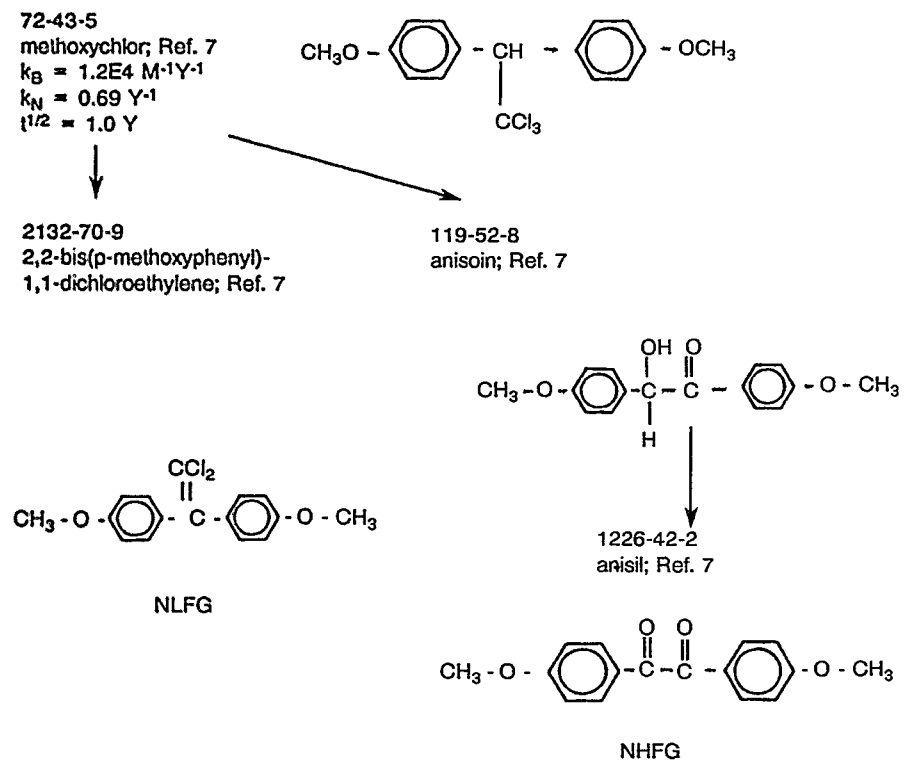

Figure 9. Methoxychlor, hydrolysis pathway.

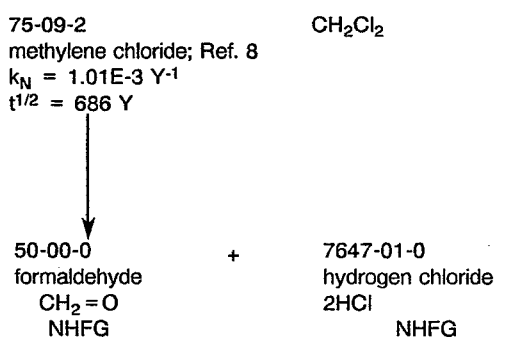

Figure 10. Methylene chloride, hydrolysis pathway.

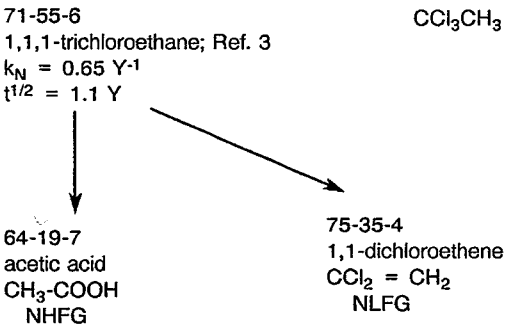

Figure 11. 1,1,1-Trichloroethane, hydrolysis pathway.

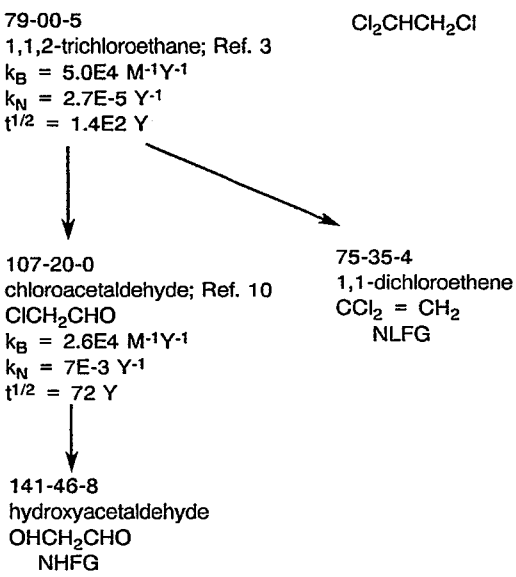

Figure 12. 1,1,2-Trichloroethane, hydrolysis pathway.

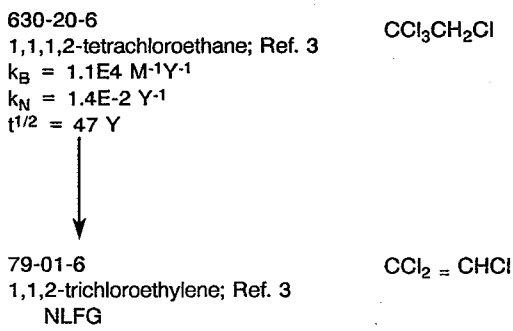

Figure 13. 1,1,1,2-Tetrachloroethane, hydrolysis pathway.

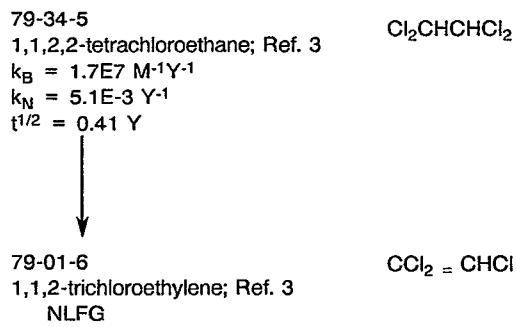

Figure 14. 1,1,2,2-Tetrachloroethane, hydrolysis pathway.

References

1. Ellington, J. J., F. E. Stancil, and W. D. Payne. 1986. Measurement of hydrolysis rate constants for evaluation of hazardous waste land disposal. Volume I. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-86/043.
2. Ellington, J. J., F. E. Stancil, W. D. Payne, and C. D. Trusty. 1988. Measurement of hydrolysis rate constants for evaluation of hazardous waste land disposal. Volume III. Data on 70 chemicals. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-88/028.
3. Jeffers, P. M., L. Ward, L. Woytowitch. and N. L. Wolfe. 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes and propanes. Environ. Sci. Technol. 23(8):965-969.
4. Ellington, J. J., F. E. Stancil, W. D. Payne, and C. D. Trusty. 1987. Measurement of hydrolysis rate constants for evaluation of hazardous waste land disposal. Volume II. Data on 54 chemicals. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-87/019.

5. Fells, I. and E. A. Moelwyn-Hughes. 1959. The kinetics of the hydrolysis of the chlorinated methanes. J. Chem. Soc., Part 1. No. 72:398-409.
6. Hill, J., H. P. Kollig, D. F. Paris, N. L. Wolfe, R. G. Zepp. 1976. Dynamic behavior of vinyl chloride in aquatic ecosystems. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-76/001.
7. Wolfe, N. L., R. G. Zepp, D. F. Paris, G. L. Baughman, R. C. Hollis. 1977. Methoxychlor and DDT degradation in water; Rates and products. Environ. Sci. Technol., 11:1077-1081.
8. Fells, I. and E. A. Moelwyn-Hughes. 1958. The kinetics of the hydrolysis of methylene dichloride. J. Chem. Soc., Part 2, No. 268:1326-1333.
9. Chapman, R. A. and C. M. Cole. 1982. Observations on the influence of water and soil pH on the persistence of insecticides. J. Environ. Sci. Health B17(5):487-504.
10. Osterman-Golkar, S. 1984. Reaction kinetics in water of chloroethylene oxide, chloroacetaldehyde, and chloroacetone. Hereditas, 101:65-68.
11. Payne, W. D. and T. W. Collette. 1989. Identification of bis(2-chloroethyl)ether hydrolysis products by direct aqueous injection GC/FT-IR. HRC 12:693-696.

United States
Environmental Protection
Agency

Center for Environmental Research
Information
Cincinnati OH 45268

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use $300

EPA/600/M-89/009