

ATTACHMENT TO LETTER TO C. AUER DATED MAY 4, 2000: ONGOING ENVIRONMENTAL STUDIES ON PERFLUOROOCTANESULFONATES

Physical/Chemical Properties

Potential Fluorochemical Combustion By-Products (involves review of results of literature search regarding potential for formation of fluorinated dioxins and furans), 3M Environmental Laboratory. Expected completion: Sept. 2000. Study paper in progress.

Fluorochemical Decomposition Process: Quantification and Assessment (involves computational chemistry calculations of bond-breaking strengths of sulfonated perfluorochemicals), Battelle Memorial Institute. Expected completion: Aug. 2000. Study paper in progress.

Environmental Fate and Transport

Abiotic Degradation Studies (hydrolysis and indirect photolysis), 3M Environmental Laboratory. Expected completion: June 2000 (hydrolysis); Aug. 2000 (indirect photolysis). (Summary study plan and screening results summary being provided to EPA)

Missing 2a - Biodegradation Studies (aerobic acclimated closed bottle biodegradation, aerobic soil/sediment biodegradation, pure culture aerobic, and fluorochemical decomposition process, stability in water, photodegradation), Springborn Laboratories, Inc. Expected completion: Aug. 2000. (Summary study plan being provided to EPA)

2b - Study Design - 3M Microbial Metabolism Program
Ecotoxicity Elements

3 - PFOS: A 96-Hour Toxicity Test with the Freshwater Alga (*Anabaena flos-aquae*), Wildlife International, Ltd. Expected completion: July 2000. (Protocol being provided to EPA)

4 - PFOS: A 96-Hour Toxicity Test with the Freshwater Diatom (*Navicula pelliculosa*), Wildlife International, Ltd. Expected completion: July 2000. (Protocol being provided to EPA)

5 - PFOS: A 96-Hour Toxicity Test with the Marine Diatom (*Skeletonema costatum*), Wildlife International, Ltd. Expected completion: July 2000. (Protocol being provided to EPA)

6 - PFOS: A 7-Day Toxicity Test with Duckweed (*Lemna gibba*), Wildlife International, Ltd. Expected completion: July 2000. (Protocol being provided to EPA)

Missing 7 - Phytotoxicity - Seedling Emergence, Wildlife International, Ltd. Expected completion: July 2000. Protocol in progress.

Environmental Monitoring

Missing 8 - Global Environmental Sampling Plan, Michigan State University. Expected completion: Dec. 2000. (Summary being provided to EPA)

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9 - Determination of PFOS, PFOSA, and POAA in water by Liquid-Solid Extraction and High-Performance Liquid Chromatography/Tandem Mass Spectrometry (no date) 17 pp

10 - Compound-Specific Quantitative Characterization of Organic Fluorochemicals in Biological Matrices, K.J. Hanson et al. (no date), 22 pp

Abiotic Degradation Studies of Perfluorooctane Sulfonate

Purpose of Study:

The purpose of this investigation is to determine the abiotic degradation reactions, rates and products of the potassium salt of perfluorooctane sulfonate (PFOS or FC-95). These results will be used to aid in the determination of the environmental fate of this compound.

Significance of Study

When assessing environmental fate of production chemistries, there are four main factors taken into account. The first factor, environmental entry, considers the rate and media into which the substance enters the environment. The second factor, transport of the compound, concerns its physical and chemical properties such as solubility, vapor pressure and sorption to soil and sediments. These factors, when taken together, determine its movement in the environment. Third, the rate of transformation due to environmental degradation via biotic and abiotic processes are taken into account, and last sinks, places in the environment where the compound or its transformed product collects, are considered. Computer models then combine the information and are used to trace the rates of movement, transformation and distribution among the media of the environment as a function of time. Real world measurements of the degradation products and manufactured chemistries are conducted and correlated with models. Only with *all* of the above information can a full environmental assessment be conducted. The present study will provide information on abiotic degradation reactions, rates and products so that the assessment will have increased reliability and exposure issues will be more completely resolved.

Objectives

There are three primary abiotic degradation process in the environment: hydrolysis, photolysis and oxidation/reduction. Each process will be studied individually in controlled experiments to identify decomposition products and to evaluate the kinetics. The results of these experiments, when taken as a whole, will lead to a more complete picture of the abiotic degradation of PFOS in the environment.

Proposed Degradation Route and Products

It is proposed that abiotic degradation may lead to direct cleavage of the C-S bond to produce a C_8F_{17} radical, followed by subsequent rearrangements to produce a variety of compounds. Thus, the expected degradation products may include perfluorooctanoic acid (PFOA), perfluorinated C_8 olefins, and mixed C_8 hydrides. This type of mechanism is unknown in the scientific literature.

Alternatively there may be production of SO₂ via a sulfonite intermediate. This type of mechanism is known in the literature for both hydrocarbon based sulfonamide and sulfanate chemistries.¹⁻² This suggests that PFOS may undergo abiotic degradation.

Protocol

GLP Status

One goal of this study is to give fast, accurate and reliable data to select members of the 3M community and to those individuals performing environmental fate and assessment determinations. A second goal is to present the results in peer-reviewed journals for broader distribution and review of study integrity. Further, this data will be viewed by various government entities. However, these studies are research and an all-inclusive protocol cannot be written. With this notable exception, the studies will be conducted in compliance with GLP-type regulations.

Adsorption/Desorption Characteristics and Recoveries

A "preliminary " adsorption/desorption study, demonstrating acceptable analyte recovery for both PFOS and PFOA will be conducted per OECD Method 106, "Adsorption/Desorption."³ A report of the findings will be included in the final report. Homologues of C₈ materials will be assumed to behave in a similar manner to the C₈ compounds. It is assumed that possible volatile degradation compounds (e.g. olefins, hydrides etc.) will show little adsorption to the matrix or the container. Degradation products not herein predicted will not be assessed for adsorption/desorption properties if mass balance for that portion of the study is in excess of 85%.

Analytical Method(s) Validation

Analytical methods will be validated for each specific target material on each piece of analytical instrumentation. The methodology for method validation will be included in the final report.

Data Analysis

An analyst trained on software specific to that instrument on which the data will be collected will perform data work-up. Kinetic determinations, quantum yields, efficiency calculations and mechanistic elucidation will be performed by the lead investigator at the 3M Environmental Laboratory. All data will be reviewed internally in the environmental lab, externally by Dr. Robert Voyksner at the Research Triangle Institute and by Dr. Don Crosby at the Univ. of California – Davis.

Quality Control

An analysis will be deemed acceptable when the following quality control criteria are met: The standard deviation of triplicate analysis is less than 8%. Spiked samples show greater than 80% recovery for all target analytes. Instrument blanks and quality control blanks show less than 10% of the lowest quantitation level determined for each target in the analysis. Curves used for quantitation must have a correlation coefficient of 0.99 or greater. Residuals on the curve are less than 20%. Internal standard response must show less than an 8% standard deviation.

Sample Purity

NMR, GC\MS, HPLC\ITMS, HPLC\MS\TOFMS, IC\CD and ICP\MS will be used to analyze the PFOS used in this investigation for purity prior to use. Impurities contained in the production chemistry will be monitored for degradation. All chemicals used in the study will be logged into the environmental laboratory chemical tracking database.

Hydrolysis Studies

A study of hydrolytic reactions leads to information on the persistence of the parent compound as well as information on the stability of possible reaction products. In order to be representative, hydrolysis studies should be carried out at pH values normally found in the environment (pH 4 to 9), and under physiological conditions (pH 1 to 2). A pH 11.0 buffer will be added in the present study to better understand the behavior of FC-95 in basic solutions. Two types of solutions will be studied. The first study will be conducted in homogeneous solutions which contain only the fully solvated species in a buffer. The methodology for this portion of the study is based on that used by the 3M Environmental Laboratory and the U.S. Environmental Protection Agency⁴ with the exception that a total of eight separate time points will be collected over a seven-week period. The second series of tests will be conducted in buffered slurries (three types of soil corresponding to those used in adsorption/desorption studies³, each in 5:1 water soil mixtures). Both series will be run at elevated temperatures (50-70 °C).

In dilute solutions, the rate law for a hydrolysis reaction is shown by the following equations. It is important to note that the equations must be modified in solutions that are not dilute.

$$\frac{-d(\text{PFOS})}{d(t)} = k_{\text{hyd}}(\text{PFOS})$$

or

$$\ln \frac{(\text{PFOS})_t}{(\text{PFOS})_0} = -k_{\text{hyd}}t$$

The half-life of the compound at a specific pH is related to the rate of hydrolysis by:

$$t_{1/2} = \frac{(0.693)}{k}$$

Using the equations above, the concentration of PFOS in the aqueous buffers will be monitored to calculate the hydrolysis rate constant and half-life. If any loss of FC-95 is observed the degradation products will be determined. If the calculated half-life is less than five years, a second study will be initiated over multiple temperatures and multiple pH's to determine the kinetic order and rate of reaction.

Aqueous samples will be prepared in buffer solutions of pH = 1.5, 5.0, 7.0, 9.0, and 11.0 according to published EPA guidelines. The buffers selected will be those published by EPA method, or used because they are acceptable buffers for HPLC/MS analysis. Five-ml aliquots of PFOS at ca. 2.00 µg/ml in aqueous buffer will be added to 40 ml VOA vials. One set of samples for each time point and each pH will be placed inside an orbital shaker held at a constant temperature of 50°C. These will be prepared in triplicate with one additional replicate for spike recovery data. One set of blanks, containing only the buffer at each pH and for time point, but without PFOS, will also be included for quality control. At selected time intervals, a set of sample vials will be pulled for analysis. The samples will be diluted with either isopropyl alcohol or methanol containing a suitable internal standard, and analyzed by HPLC/MS for PFOS concentration.

Slurry samples will be prepared by first wetting each of the three dried and characterized soils with 0.01 M CaCl₂ (1:10 soil to CaCl₂) in 40 ml VOA vials for at least 24 hours at room temperature. Following this, the liquid will be pored off and a volume of buffer (pH = 1.5, 5.0, 7.0, 9.0, and 11.0) equal to the amount of CaCl₂ removed will be added. A 10 µL spike of PFOS will then be added at a predetermined concentration sufficient to give a ca. 2.00 µg/ml concentration in aqueous buffer. One set of samples for each time point and each pH will be placed inside an orbital shaker held at a constant temperature of 50°C. These will be prepared in triplicate with one additional replicate for spike recovery data. One set of blanks, containing only the buffered slurry at each pH and for time point, but without PFOS, will also be included for quality control. At selected time intervals, a set of sample vials will be pulled for analysis. The samples will be diluted with either isopropyl alcohol or methanol containing a suitable internal standard, centrifuged and analyzed by HPLC/MS for PFOS concentration.

The solvents chosen for dilution and preparation of reagents (IPA and methanol, respectively) are water-soluble solvents in which the subject material being analyzed is soluble. Solutions will be degassed prior to sample preparation. Biodegradation of the analyte by microbial growth in the buffered media should be excluded because of the study being conducted at 50°C, a

temperature that is forbidding for most mesophilic microorganisms (the type found in laboratory settings).

Indirect Photolysis Studies

Due to minimal light absorption in the UV/vis region by many 3M fluorochemicals, the indirect mechanism of photolytic decomposition will be studied.⁵⁻⁸ The indirect mechanism can be defined as a chemical or electronic excitation transfer from a light absorbing species to the target species which induces some type of chemical change.⁹ In these studies, photons from the light source will be used to induced the formation of radicals from hydrogen peroxide contained in the solution.¹⁰⁻¹⁶ These radicals in turn reacted with the fluorochemicals to produce the chemical changes discussed below.

PFOS will be exposed to simulated sunlight in increasingly more "dirty" or complex environments [water spiked with hydrogen peroxide, synthetic humic water, natural lake water and soil slurries (three types of soil)]. These exposures will test how each environment affects the photolytic mechanism. Achieving near mass balance by accounting for all parent and product species is a necessary goal, so that meaningful comparisons between the results of each photolytic exposure can be assessed. It is expected that adsorption of both parent and product species to particulates and organic materials will induce changes in the photolytic behavior over the pure water system. However, what these effects will be is highly speculative.

Samples for the pure water portion of this investigation will be prepared as follows. Five to twenty ml aliquots of PFOS in water at a concentration of ca. 2.0 µg/ml will be added to 40 ml VOA vials and spiked with 10 µL of a 30% H₂O₂ solution in water. Four sets of samples for each time point will be prepared in triplicate with two additional replicates for spike recovery data. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. Four sets of blanks, containing only the analyte but without the H₂O₂ will be set up for each time point. Again, two sets will be exposed to the light source; the two other will be kept dark but held at the same temperature. Four sets of blanks, containing the H₂O₂ but without the analyte will be set up for each time point. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. The vials will be inverted and placed in a custom designed liquid cooling bath contained in the test chamber of an Atlas Suntest CPS Plus light stability chamber. A xenon-arc lamp (simulated sunlight) with a 330 nm – 800 nm notch filter will be turned on for an exposure time of 68 -72 hours with the H₂O₂ solution being spiked in each appropriate vial at 24 hour intervals. Light intensity will be recorded using a commercial radiometer interfaced to a personal computer. Samples will then removed and divided for analysis by dynamic purge and trap gas chromatography/mass spectrometry (GC/MS) for volatile degradation products. High performance liquid chromatography/mass spectrometry (HPLC/MS) will be used for non-volatile and

semi-volatile analysis. Ion chromatography/conductivity detection (IC/CD) will be used for sulfite, sulfate, sulfonamidic acid, trifluoroacetic acid and free fluoride analysis.

Samples will be prepared as follows for the synthetic humic water portion of the investigation. Synthetic humic water will be prepared as per EPA procedure.¹⁷ Five to twenty ml aliquots of PFOS in synthetic humic water at a concentration of ca. 2.0 µg/ml will be added to 40 ml VOA. Four sets of samples for each time point will be prepared in triplicate with two additional replicates for spike recovery data. Two sets will be exposed to the light source while the other two will be kept dark but held at the same temperature. Four sets of blanks, containing only the analyte but without the synthetic humic water will be set up for each time point. Again, two sets will be exposed to the light source; the two other will be kept dark but held at the same temperature. Four sets of blanks, containing only the synthetic humic water but without the analyte will be set up for each time point. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. The vials will be inverted and placed in a custom designed liquid cooling bath contained in the test chamber of a Atlas Suntest CPS Plus light stability chamber. A xenon-arc lamp (simulated sunlight) with a 330 nm – 800 nm notch filter will be turned on for an exposure time of 68 -71 hours. Light intensity will be recorded using a commercially built radiometer interfaced to a personal computer. Samples will then removed and analyzed by dynamic purge and trap gas chromatography /mass spectrometry (GC/MS) for volatile degradation products. High performance liquid chromatography/mass spectrometry (HPLC/MS) will be used for non-volatile and semi-volatile analysis. Ion chromatography/conductivity detection (IC/CD) will be used for sulfite, sulfate, sulfonamidic acid, trifluoroacetic acid and free fluoride analysis.

Samples for the lake water portion of this investigation will be prepared as follows. Five to twenty ml aliquots of PFOS in lake water at a concentration of ca. 2.0 µg/ml will be added to 40 ml VOA vials. Four sets of samples for each time point will be prepared in triplicate with two additional replicates for spike recovery data. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. Four sets of blanks, containing only the analyte will be set up for each time point. Again, two sets will be exposed to the light source; the two other will be kept dark but held at the same temperature. Four sets of blanks, containing the lake water but without the analyte will be set up for each time point. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. The vials will be inverted and placed in a custom designed liquid cooling bath contained in the test chamber of a Atlas Suntest CPS Plus light stability chamber. A xenon-arc lamp (simulated sunlight) with a 330 nm – 800 nm notch filter will be turned on for an exposure time of 68 -72 hours. Light intensity will be recorded using a commercial radiometer interfaced to a personal computer. Samples will then removed and analyzed by dynamic purge and trap gas chromatography/mass

spectrometry (GC/MS) for volatile degradation products. High performance liquid chromatography/mass spectrometry (HPLC/MS) will be used for non-volatile and semi-volatile analysis. Ion chromatography/conductivity detection (IC/CD) will be used for sulfite, sulfate, sulfonamidic acid, trifluoroacetic acid and free fluoride analysis.

Slurry samples will be prepared by first wetting each of the three dried and characterized soils with 0.01 M CaCl_2 (1:10 soil to CaCl_2) in 40 ml VOA vials for at least 24 hours at room temperature. Following this, the liquid will be pored off and a volume of water equal to the amount of CaCl_2 removed will be added. A 10 μL spike of PFOS will then be added at a predetermined concentration sufficient to give a ca. 2.00 $\mu\text{g}/\text{ml}$ concentration in water. The vials will then be spiked with 10 μL of a 30% H_2O_2 solution in water. Four sets of samples for each time point will be prepared in triplicate with two additional replicates for spike recovery data. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. Four sets of blanks, containing only the analyte will be set up for each time point. Again, two sets will be exposed to the light source; the two other will be kept dark but held at the same temperature. Four sets of blanks, containing only the soils will be set up for each time point. Again, two sets will be exposed to the light source; the two other will be kept dark but held at the same temperature. Four sets of blanks, containing only water will be set up for each time point. Two sets will be exposed to the light source, the other two will be kept dark but held at the same temperature. The vials will be inverted and placed in a custom designed liquid cooling bath contained in the test chamber of a Atlas Suntest CPS Plus light stability chamber. A xenon-arc lamp (simulated sunlight) with a 330 nm – 800 nm notch filter will be turned on for an exposure time of 68 -72 hours. Samples, blanks and controls will be spiked with an additional 10 μL aliquot of a 30% H_2O_2 solution in water where appropriate every 24 hours. Light intensity will be recorded using a commercial radiometer interfaced to a personal computer. Samples will then removed and analyzed by dynamic purge and trap gas chromatography/mass spectrometry (GC/MS) for volatile degradation products. The samples for non-volatile analysis will be diluted with either isopropyl alcohol or methanol containing a suitable internal standard, centrifuged and analyzed by high performance liquid chromatography/mass spectrometry (HPLC/MS). Ion chromatography/conductivity detection (IC/CD) will be used for sulfite, sulfate, sulfonamidic acid, trifluoroacetic acid and free fluoride analysis.

Oxidation/Reduction Studies

Oxidation/reduction mechanisms are well known to occur in the abiotic degradation of many classes of compounds.¹⁸⁻²¹ This investigation will focus on one specific type - oxidation by ferric oxide, a reaction well known to occur in natural systems. This reaction has been shown to occur in both the presence and absence of sunlight (catalytic oxidation and indirect photolysis).²²⁻²³ Observations from these experiments may help in elucidation of results from both

hydrolytic and photolytic slurry studies, as the various oxides may be present in differing concentrations in the soils. Oxidation by TiO_2 under the same conditions will serve as a control experiment.²⁴⁻²⁷

Samples for this portion of the investigation will be prepared as follows. Five to twenty ml aliquots of PFOS in water at a concentration of ca. 10.0 $\mu\text{g/ml}$ and a metal oxide concentration of 100 $\mu\text{g/ml}$ will be added to 40 ml VOA vials. This gives approximately 50:1 molar excess of metal oxides to ensure sufficient concentration to induce any possible abiotic degradation. One-half of the vials will be spiked with 10 μL of a 30% H_2O_2 solution in water. Sixteen sets of samples for each time point will be prepared in triplicate with two additional replicates for spike recovery data (eight with the iron oxides, four of which will have H_2O_2 added and eight with TiO_2 , four of which will have H_2O_2 added). Eight sets will be exposed to the light source, the other eight will be kept dark but held at the same temperature. Sixteen sets of blanks, containing the H_2O_2 and metal oxide without the analyte will be set up for each time point (eight with the iron oxides, four of which will have H_2O_2 added and eight with TiO_2 , four of which will have H_2O_2 added). Eight sets will be exposed to the light source, the other eight will be kept dark but held at the same temperature. The vials will be inverted and placed in a custom designed liquid cooling bath contained in the test chamber of a Atlas Suntest CPS Plus light stability chamber. A xenon-arc lamp (simulated sunlight) with a 330 nm – 800 nm notch filter will be turned on for an exposure time of 160-168 hours with the H_2O_2 solution being spiked in the appropriate vials at 24 hour interval. Light intensity will be recorded using a commercial radiometer interfaced to a personal computer. Samples will then be removed and analyzed by dynamic purge and trap gas chromatography/mass spectrometry (GC/MS) for volatile degradation products. High performance liquid chromatography/mass spectrometry (HPLC/MS) will be used for non-volatile and semi-volatile analysis. Ion chromatography/conductivity detection (IC/CD) will be used for sulfite, sulfate, sulfonamidic acid, trifluoroacetic acid and free fluoride analysis.

Timeline

The study will be conducted in the 3M Environmental Laboratory. Select portions of this investigation have been carried out, although a complete data and kinetic work up has not been finished or reviewed. Each major portion of the investigation will have an individual preliminary report issued. A final report, which will tie the separate portions together, will be issued prior to September 1, 2000.

References:

1. Art, J.F.; Kestermont, J.P.; Soumillion, J.P. **Photodetosylation of Sulfonamides Initiated by Electron Transfer from an Anionic Sensitizer.** *Tetrahedron Letters*. Volume 32, Number 11, Pages 1425-1428, 1991.
2. Arnould, J.C.; Cossy, J.; Pète, J.P. **Photolysis of 2(N-Alkyl-Arylsulfonylamido) Cyclohexenone and Unusual and Useful Desulfonation Reaction.** *Tetrahedron Letters*. Number 43, Pages 3919-3922, 1976.
3. Organization for Economic and Cooperative Development (OECD) **Guideline for Testing of Chemicals, Number 106, Adsorption/Desorption, 1981.**
4. United States Environmental Protection Agency. **OPPTS 835.2110 Hydrolysis as a Function of pH.** *Prevention, Pesticides and Toxic Substances: Fate, Transport and Transformation Test Guidelines*. EPA 712-C-98-057, Pages 1-16, 1998.
5. Lunak, S.; Sedlak, P. **Photoinitiated Reactions of Hydrogen-Peroxide in the Liquid-Phase.** *Journal of Photochemistry and Photobiology A Chemistry*. Volume 68, Number 1, Pages 1-33, 1992.
6. Haag, W. R.; Hoigne, J. **Photo-Sensitized Oxidation in Natural-Water via OH· Radicals.** *Chemosphere*. Volume 14, Number 11-1, Pages 1659-1671, 1985.
7. Ruzo, L. O.; Casida, J. E. **Photochemistry of Thiocarbamate Herbicides-Oxidative and Free-Radical Processes of Thiobencarb and Diallate.** *Journal of Agricultural and Food Chemistry*. Volume 33, Number 2, Pages 272-276, 1989.
8. Draper, W.M.; Crosby, D.G. **Hydrogen-Peroxide and Hydroxyl Radical Intermediates in Indirect Photolysis Reactions in Water.** *Journal of Agricultural and Food Chemistry*. Volume 29, Number 4, Pages 699-702, 1981.
9. Lunak, S.; Sedlak, P. **Photoinitiated reactions of hydrogen peroxide in the liquid phase.** *J. Photochem. Photobiol. A: Chem.* Volume 68, Number 1, Pages 1-33, 1992.
10. Armbrust, K.L. **Photochemical Processes Influencing Pesticide Degradation in Rice Paddies.** *Journal of Pesticide Science*. Volume 24,

Number 1, Pages 69-73, 1999.

11. Draper, W.M.; Crosby, D.G. **Photochemistry and Volatility of Drepamon in Water.** *Journal of Agricultural and Food Chemistry*. Volume 32, Number 4, Pages 728-733, 1984.
12. Draper, W.M.; Crosby, D.G. **Solar Photooxidation of Pesticides in Dilute Hydrogen Peroxide.** *Journal of Agricultural and Food Chemistry*. Volume 32, Number 2, Pages 231-237, 1984.
13. Draper, W.M.; Crosby, D.G. **Pesticide Photodecomposition in Dilute Hydrogen Peroxide Solution.** *175th American Chemical Society National Meeting*, 1978.
14. Benitez, F. J.; Beltranheredia, J.; Gonzalez, T.; Real, F. **Photooxidation of Carbofuran by a Polychromatic UV Irradiation without and with Hydrogen-Peroxide.** *Industrial and Engineering Chemistry Research*. Volume 34, Number 11, Pages 4099-4105, 1995.
15. Mabury, S. A.; Crosby, D.G. **Pesticide Reactivity Toward Hydroxyl and its Relationship to Field Persistence.** *Journal of Agricultural and Food Chemistry*. Volume 44, Number 7, Pages 1920-1924, 1996.
16. Aires, P.; Gal, E.; Chamarro, E.; Esplugas, S. **Photochemical Degradation of Malathion in Aqueous-Solutions.** *Journal of Photochemistry and Photobiology A-Chemistry*. Volume 68, Number 1, Pages 121-129, 1992.
17. United States Environmental Protection Agency. **OPPTS 835.5170 Indirect Photolysis Screening Test.** *Prevention, Pesticides and Toxic Substances: Fate, Transport and Transformation Test Guidelines*. EPA 712-C-98-099, Pages 1-16, 1998.
18. Pankratov, A. *Khim. Vys. Energ.* Volume 4, Pages 126- , 1970.
19. Shub, D.; Tyurikov, G.; Veselovskii, V. *Zh. Fiz. Khim.* Volume 34, Pages 2245- , 1960.
20. Sviridov, V.; Schevchenko, G. *Vestn. Beloruss. Univ.* Volume 2, Pages 13- , 1969.
21. Chang, I.; Zaleiko, N. *Proc. 36th Industrial Waste Conf., Purdue, IN.* Pages 814- , 1981.
22. Behar, B; Stein, G. *Science*. Volume 154, Pages 1012- , 1966.

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23. Kozlov, J.; Nadhezdin, A.; Purmal, A. *Int. J. Chem. Kinet.* Volume 6, Pages 383- , **1974.**
24. Augugliaro, V.; Davi, E.; Palmisano, L; Schiavello, M; Sclafani, A. *Appl. Catal.* Volume 65, Pages 101- , **1990.**
25. Salvader, P.; Gutierrez, C. *J. Phys. Chem.* Volume 88, Pages 3696- , **1988.**
26. Salvader, P. *J. Phys. Chem.* Volume 89, Pages 3863- , **1989.**
27. Gutierrez, C; Salvader, P. *J. Electrochem. Soc.* Volume 133, Pages 924- , **1986.**