

US EPA ARCHIVE DOCUMENT



## CONCLUSIONS

### Degradation - Photodegradation in Water

1. This study is scientifically valid and provides useful information on the photodegradation of acephate in pH 7 aqueous buffer solution. Acephate did not photodegrade in sterile aqueous solutions at pH 7 when exposed to natural sunlight; any degradation seen in the samples was due to hydrolysis. Acephate can be photodegraded in the presence of a photosensitizer (acetone); degradation products in photosensitized solutions are the same as in nonphotosensitized solutions.
2. This study meets Subdivision N Guidelines for the fulfillment of EPA data requirements on photodegradation in water.
3. The study was separated into two phases: the first phase determined the photodegradation of [S-<sup>14</sup>CH<sub>3</sub>]acephate in pH 7 aqueous buffer solution; the second phase determined the photodegradation of [S-<sup>14</sup>CH<sub>3</sub>]acephate in pH 7 aqueous buffer solution in the presence of a photosensitizer (1% acetone). In the first phase, [S-<sup>14</sup>CH<sub>3</sub>]acephate, at an actual concentration of 8.94 ppm, was photolytically stable in sterile pH 7 phosphate buffer solution that was irradiated under natural sunlight at 25.0 ± 1 °C for 35 days; based on HPLC analysis, 86.6% and 85.5% of the applied radioactivity was present as parent compound following 35 days of incubation in the irradiated and dark control samples, respectively. In the presence of 1% acetone, [S-<sup>14</sup>CH<sub>3</sub>]acephate, at 9.35 ppm, degraded with a reviewer-calculated (corrected for degradation in the dark control) half-life of 39.6 days in sterile pH 7 aqueous buffer solution that was irradiated under natural sunlight at 25.0 ± 1 °C for 31 days. At 31 days, the parent compound was present at 46.0% and 84.4% (HPLC data) of the applied radioactivity in irradiated and dark control solutions, respectively. Two of the three degradates detected in the irradiated and dark control samples without photosensitizer (DMPT, 3.6%; RE-17245, 4.6%; and methamidophos, 1.6% of the applied in the irradiated solutions) were observed in greater amounts in the irradiated solutions with photosensitizer (40.6%, 2.5% and 8.6% of the applied, respectively). In addition to the three degradates listed above, methyl disulfide was also detected only in the dark control solutions at 2.3% (at day 35) and ≤1.6% (at days 26 and 31) of the applied in the first and second phases, respectively.

## METHODOLOGY

Radiolabeled [S-<sup>14</sup>CH<sub>3</sub>]acephate [O,S-dimethyl acetylphosphoramidothioate (RE-12420); radiochemical purity 100%, specific activity 23.7 mCi/mmol] plus nonradiolabeled acephate (purity 99.7%), dissolved in water, was added at 8.94 ppm to pH 7 (potassium phosphate) 0.01 M aqueous buffer solution that was then filter-sterilized (0.2 µm). Solutions were transferred to autoclaved quartz glass flasks and maintained at 25.0 ± 1 °C

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by use of a constant temperature, circulating water bath connected to the flasks through a coil in the reaction vessels. The samples were irradiated with natural sunlight from August 2 to September 6 at Richmond, CA (38° latitude). The intensity of the sunlight was measured every two minutes with a photometer. Daily average light intensities were presented in Figure 2, and cloud pattern and weather conditions were reported in Appendices IIA and IIB. Dark control solutions were transferred to screw-capped amber bottles wrapped in foil, and were incubated at 25.0 °C in the constant temperature water bath. Duplicate aliquots of the irradiated and dark control samples were removed from the reaction vessels for analysis at 0, 3, 9, 16, 23, and 35 days posttreatment. Aliquots of each solution were analyzed by reverse-phase HPLC (Ultremex and Phenomenex columns) with a mobile phase gradient of acetonitrile:0.5 mM heptyltriethylammonium phosphate plus 1 mM  $\text{KH}_2\text{PO}_4$  (pH 7: NaOH):methanol (0:100:0 to 2:75:23 to 8:0:92; v:v:v) with both UV (230 nm) and radioactive flow detection. Aliquots of each solution were also analyzed by TLC using cellulose plates (with fluorescent  $\text{UV}_{254}$  indicator) developed with isopropyl alcohol:benzene:concentrated ammonium hydroxide (13:10:3, v:v:v). To identify degradates, samples were co-chromatographed with unlabeled reference standards visualized by exposure to iodine crystals followed by spraying with 1% (w:v) 2,6-dibromoquinone chlorimide in glacial acetic acid. Radiolabeled [ $^{14}\text{C}$ ]residues were located with autoradiography, scraped from the plates and analyzed by LSC; method detection limits were not reported.

To test the behavior of acephate in the presence of a photosensitizer, [ $\text{S-}^{14}\text{CH}_3$ ]acephate (radiochemical purity 99.47%, specific activity 23.7 mCi/mmol) plus nonradiolabeled acephate, dissolved in water, was added at 9.35 ppm to pH 7 (0.01 M  $\text{KH}_2\text{PO}_4$ ) aqueous buffer solution; 1% acetone was added as a photosensitizer, and the solution was filter-sterilized (0.2- $\mu\text{m}$ ). Solutions were transferred to flasks and maintained at  $25.0 \pm 1$  °C as described above. Samples were irradiated with natural sunlight from August 12 to September 12 at Richmond, CA, and conditions were monitored as described previously. Dark control solutions were incubated as described previously. Duplicate aliquots of irradiated samples and dark controls were removed from the reaction vessels for analysis at 0, 3, 9, 14, 26, and 31 days posttreatment. Aliquots of each solution were analyzed by reverse-phase HPLC and TLC as described above for the solutions without the acetone addition.

## DATA SUMMARY

Radiolabeled [ $\text{S-}^{14}\text{CH}_3$ ]acephate (radiochemical purity 100%), at 8.94 ppm, was photolytically stable in sterile pH 7 aqueous buffer solution that was irradiated under natural sunlight at  $25.0 \pm 1$  °C for 35 days at Richmond, CA; based on HPLC analysis, 86.6% and 85.5% of the applied radioactivity was present as parent compound following 35 days of incubation in the irradiated and dark control samples, respectively (Tables III, IV). The minor degradates O,S-dimethyl phosphorothioate (DMPT, RE-18421), S-methyl

N-acetylphosphoramidothioate (RE-17245) and O,S-dimethyl phosphoramidothioate (methamidophos, RE-9006) were detected in irradiated solutions at maximums of 3.6%, 4.6% and 1.6% of the applied, respectively (HPLC data); in dark control solutions, the three degradates were detected at maximums of 4.7%, 5.8%, and 1.7% of the applied, respectively. The minor degradate methyl disulfide accounted for 2.3% of the applied radioactivity in dark control solutions at day 35.


In the presence of 1% acetone, [S-<sup>14</sup>CH<sub>3</sub>]acephate (radiochemical purity 99.47%), at 9.35 ppm, degraded with a reviewer-calculated (corrected for degradation in the dark control) first-order half-life of 39.6 days in sterile pH 7 aqueous buffer solution that was irradiated under natural sunlight at 25.0 ± 1 °C for 31 days at Richmond, CA. In the irradiated solutions, the parent compound decreased from an initial 100% to 89.6% of the applied radioactivity by 14 days, 66.6% by 26 days and 46.0% of the applied by 31 days posttreatment (HPLC data; Table V). In the dark control solutions at 31 days posttreatment, the parent compound was present at 84.4% (HPLC data) of the applied radioactivity (Table VI). Two of the three degradates (DMPT and methamidophos) detected in the irradiated and dark control samples in the first phase were observed in greater amounts in the irradiated solutions containing the photosensitizer (40.6% and 8.6% of the applied, respectively); the degradate RE-17245 was detected at 2.5% of the applied. In the dark control solutions, the three degradates were observed at 5.3% (DMPT), 5.3% (RE-17245) and 3.5% (methamidophos) of the applied radioactivity; methyl disulfide was detected at a maximum of 1.6% of the applied on days 26 and 31.

Material balances based on LSC analysis were 99.41-100.99% of the applied radioactivity for irradiated solutions without photosensitizer and 97.27-100.00% for dark control solutions without photosensitizer (Table VII). In solutions with 1% acetone, material balances were 96.54-102.13% for irradiated solutions and 94.14-100.00% for dark control solutions.

## COMMENTS

1. The registrant calculated a first-order half-life for acephate in the irradiated solutions of 173 days ( $r^2 = 0.98$ ); the half-life for the dark controls was 163 days ( $r^2 = 0.99$ ). Because of the similarity in the calculated half-lives, it can be concluded that acephate did not photodegrade; any degradation was due to hydrolysis. This stability is consistent with acephate's UV spectrum, which shows that acephate in deionized water does not absorb light at wavelengths greater than 260 nm (Figure 3). In the presence of 1% acetone, acephate degraded with a first-order half-life of 30 days ( $r^2 = 0.87$ ; overall rate constant 0.02274/day); in the dark control solutions, the half-life was 132 days ( $r^2 = 0.995$ ; hydrolysis rate constant 0.00524/day). To determine the photolysis rate (correct for hydrolysis), the hydrolysis rate constant was subtracted from the overall rate constant to give a rate constant due to photolysis alone of 0.0175/day, which converts to a half-life due to photolysis of 39.6 days.

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2. The pH chosen for the photolysis study was not the most hydrolytically stable pH for acephate in aqueous buffer solutions. An acephate hydrolysis study (MRID 41081604) determined that the half-lives of acephate in sterile pH 5, 7, and 9 aqueous buffer solutions were 325, 169, and 18 days, respectively. The study author stated that pH 7 was chosen for the photolysis study because it was representative of the pH of natural ponds and lakes. In addition, the hydrolysis half-life at pH 7 is consistent with the degradation half-life in the dark control (169 days vs. 163 days).
  3. The sterility of the sample solutions was not determined following the incubation period; therefore the sterility of the samples throughout the study could not be confirmed. Although the solutions were filter-sterilized ( $<0.2 \mu\text{m}$ ) before the incubation, an independent determination of sterility (i.e., plate counts) was not conducted. However, because the parent compound was photolytically stable in the absence of a photosensitizer, this does not adversely affect the acceptability of the study.
  4. Test solutions were not prepared in duplicate, although duplicate aliquots were removed for analyses. The use of single samples is generally not considered to be good laboratory practice. At a minimum, the use of duplicate samples is necessary for the valid determination of half-lives. However, because the parent compound was photolytically stable (in the absence of a photosensitizer), it is unlikely that a new study would provide additional information.
  5. Method detection limits for LSC and HPLC were not reported. It is necessary that method detection limits be reported in order to assure that the analytical method is appropriate for the quantification of the parent compound and its degradates.
  6. A phosphate buffer solution was used; it is recommended that borate or acetate buffers be utilized to minimize buffer effects.
  7. The solubility for acephate in water or pH 7 buffer was not reported.
  8. The study author stated that the pH of the test solutions remained relatively constant throughout the study period; however, the pHs were not reported.
  9. The reviewer notes that the total percentages of radioactivity reported as material balances did not equal the sum of the reported individual percentages of the identified residues for specific sampling intervals. This discrepancy was not addressed by the study author.
  10. The study author stated in a footnote to Table V that HPLC and TLC results for days 26 and 31 for two degradates in the irradiated solutions with acetone "differed...by a large factor for an unknown reason." The reviewer notes that only HPLC data were discussed in this review.
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