DATA EVALUATION RECORD

STUDY 2

CHEM 069601 Pyrazon §161-2

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41507914
Ellensen, J., J. Jordan, and V. Winkler. 1989. Degradation studies - Lab photodegradation/pyrazon. Photolysis of BAS 119H in pH 7 aqueous solution at 25 degrees Celsius. Report Number M8813. BASF Registration Document No. 89/5090. Unpublished study performed and submitted by BASF Corporation, Research Triangle Park, NC.

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CONCLUSIONS:

Degradation -Photodegradation in Water

1. This study cannot be used to fulfill data requirements at this time.

2. The reported results indicate degradation of pyrazon with a half-life equivalent to 150 hours of continuous irradiation in sterile aqueous pH 7 buffered solution exposed to a xenon light source.

3. This study is scientifically sound, but does not meet Subdivision N guidelines for the following reasons:

volatile degradates present at up to 17% of the applied radioactivity were not characterized; and

the electronic absorption spectrum of pyrazon in the photolysis buffer solution was not provided.

4. In order for this study to fulfill the photodegradation in water data requirement, the registrant must characterize all degradates present at >10% of the applied, and the electronic absorption spectrum (UV-VIS) of pyrazon in the photolysis buffer must be provided. The spectrum must be expressed in terms of molar absorptivities rather than in terms of absorbance.

METHODOLOGY:

Pyrazon (purity >99%, BASF) was spiked (50:1, w:w) with pyradiazinone ring-labeled [^{14}C]pyrazon (labeled in the 4- and 5-C positions; radiochemical purity 99%, specific activity 429.7 uCi/mg, BASF), then added at 50 ppm to an aqueous buffered solution (0.1 M sodium phosphate) adjusted to pH 7. The buffered test solution was filter-sterilized (0.45 um) while being transferred into a sterile glass photolysis chamber (Figure 5). The photolysis chamber was covered with a quartz plate, which was affixed with silicon sealant. The temperature in the chambers was maintained at 25 C by circulating cooling water through the water jacket, and the solution was constantly stirred using a magnetic stirrer. Filter-sterilized, CO_2-free air was drawn through the chamber; the exhaust air was vented through a scintillation cocktail (Harvey) to trap volatiles (Figure 4). The treated solution was irradiated for 9- to 12-hour intervals over a 3-week period using a filtered xenon lamp (Hanau Suntest) that had an intensity of 2100 uE/m^2·sec (Figures 2, 3, and 4); the light intensity was measured within the reaction chamber with a radiometer/photometer positioned "at a height corresponding to the liquid level in the reaction vessels". Aliquots of the test solution were withdrawn after 0, 15, 42, 89, 152, 213, 260 and 343 hours of irradiation. At the termination of the study, the photolysis chamber was rinsed, and the rinsate was saved for later analysis.

Aliquots of the samples and the rinsate were analyzed for total radioactivity using LSC and for degradates using reverse-phase HPLC. The HPLC column was eluted with methanol:water (60:40, v:v) and was equipped with UV detection (287 nm). Additional aliquots were analyzed using either reverse-phase TLC plates (Whatman Linear K LK5F) developed in methanol:water (6:4, v:v) or methanol:2% sodium chloride, or using silica gel TLC plates developed in n-hexane:-acetone (6:4, v:v). [^{14}C]Residues on the plates were located and quantified using radioscanning. In "selected cases", radioactive areas were scraped from the plates and quantified using LSC following combustion. In other "selected cases", radioactive areas were scrapped from the plates, extracted with methanol, filtered, re-concentrated, and re-chromatographed with an unspecified solvent system (method of quantification not reported). The trapping solution was analyzed for total radioactivity using LSC.

Additional attempts were made to identify specific degradates using MS performed under ammonia gas.

DATA SUMMARY:

Pyrazon (purity >99.5%) plus pyradiazinone ring-labeled [^{14}C]pyrazon (labeled in the 4- and 5-C positions; radiochemical purity 99%), at 50 ppm, photodegraded with a registrant-calculated half-life of 150 hours of continuous irradiation in a sterile aqueous pH 7 buffered solution that was irradiated at 25 C using a xenon lamp that had an intensity of 2100 uE/m^2·sec. In contrast, pyrazon did not degrade in the dark control during the 3-week study.

In the irradiated samples, pyrazon comprised 100% of the total recovered radioactivity immediately posttreatment, 50.1-57.02% after 152 hours, 40.21-41.47% after 213.2 hours, and 23.81-28.86% after 342 hours (Table IV). Three uncharacterized radioactive zones on the TLC plates, PP3, PP4, and PP6, were each present at ≤8.64-9.64% of the total recovered radioactivity. One zone, PP8, was present at a maximum of 13.4-14.13%. This zone was further resolved into several unidentified components, each present at 1-7% of the recovered. Three additional zones, PP1, PP2, and PP7, were each present at ≤6.15% of the total recovered radioactivity. Uncharacterized volatile [^{14}C]residues totalled 17.31-17.49% of the applied radioactivity after 343 hours posttreatment (Table V).

During the study, the mass balances for the photolysis solutions were 93.66-94.10% (Table II, III).

COMMENTS:

1. Volatile degradates present at up to 17% of the applied radioactivity were trapped but not characterized. The study authors assumed that the trapped [^{14}C]residues were carbon dioxide, but did not confirm the identity of the radioactivity. Identity of volatile material(s) must be confirmed.

2. An electronic absorption spectrum of pyrazon in the photolysis buffer was not provided. The study authors reported that the optimum wavelength for the UV detector in the HPLC system was determined by a UV absorbance analysis of pyrazon. An absorbance spectrum of pyrazon in an unspecified solution that was included in Study 3 (MRID 41507915) indicated that pyrazon did not absorb wavelengths >360 nm. Therefore, the registrant must provide an adequate electronic absorption spectrum (UN-VIS) of the test material in the buffer system used in this experiment. Molar absorptivities rather than absorbance units must be used in spectrum.

3. It was not clear whether a dark control was conducted in conjunction with this study. For dark control data, the study authors referenced the hydrolysis study (41507913) that was reviewed as Study 1 in this report.

4. The reverse phase TLC system used to separate the PP8 band into a "complex mixture" was not characterized.

   Also, the TLC R_f values obtained for the components that were resolved from PP8 did not agree with the proposed degradates, so additional possible degradates were synthesized and compared with the uncharacterized degradates. The R_f values of the components of PP8 were not matched to any known degradates of pyrazon.

5. The study authors reported that the results obtained by the HPLC and TLC systems did not agree, and attributed this difference to the inclusion of minor degradates in the TLC zones which were resolved by HPLC.

6. The study authors did not state whether reference standards were cochromatographed with the test solutions.

7. MS analysis of PP3 did not aid in the identification of the degradate(s). The results of any MS analysis of the other degradates were not reported.

8. The preliminary study, which was not included in this report due to poor material balances, indicated that the inclusion of 0.5% (v:v) acetone as a photosensitizer did not affect the half-life of pyrazon.

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