

Fate of Acrolein, an Agricultural Biocide, Overtime.

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ABSTRACT: Acrolein is an efficient agricultural herbicide within irrigation canal ditches and a biocide within oilfield water-flood systems. The fate of acrolein is typically attributed to evaporation, however, it is found that acrolein also dimerizes in water. This hetero-Diels-Alder product is stable over an extended period of time, thus losing its original function as an effective biocide and herbicide. Various 1D/2D NMR and GC-EIMS techniques were used to elucidate the structure of said dimerization product, found to be 5,6-dihydro-2H-pyran-3-carbaldehyde.

Acrolein, an herbicidal and biocidal agent, is commonly used within both the agricultural and petroleum industries. As the simplest unsaturated aldehyde, other uses include aiding in the building of the amino acid methionine, as well as fixation chemical within histology.¹ As an herbicide, this colorless liquid is used within water irrigation canal systems in the Western U.S., controlling the excessive growth of plants, algae, fungi, and other microorganisms.³ After direct application into the irrigation canals, the water is then transferred onto cropland. Baker Petrolite Corporation was the first to utilize Magnacide H, the herbicide with acrolein as the 95% active ingredient, in November 1975. It is reported that the chemical's mechanism of action is to degrade the cellular structure of organic material by cross-linking proteins. As a biocide, Magnacide B, established in 1959, is injected into water within oil well drilling equipment, preventing slime producing organisms within drilling muds. It occurs via the same mechanism of action. A single application of acrolein is 15 ppm, and application number limits do not currently exist, with Magnacide H at times being applied up to 26 times per year. There are no registered food related dietary assessments, as well as no drinking water risk assessments of acrolein herbicides and biocides.²

Two metabolites of acrolein are known and recorded. 3-hydroxypropanal has been found in treated water, however, due to being formed spontaneously in equilibrium, acrolein is reformed. There is not registered risk due to dissipation by other processes. Glycidol, a metabolite of acrolein found within fish, has potential human carcinogenic properties, thus posing a significant risk. Studies have been performed on said metabolite.²

Collaborator Dr. Charles L. Kissel, an industrial chemist with expertise in acrolein chemistry, possessed a gallon-sized, glass container of pure acrolein in water in which he held onto for over twenty-five years. After weighing the material, the

mass balance did not add up the mass of the initial contents: acrolein in H₂O. Initially, it was thought to have polymerized, but after analysis, it was a surprise to discover dimerization of the acrolein had occurred. Determining the organic structure of the new compound is essential in assuring efficacy and safety of the product within agricultural and petroleum industries.

Acrolein in aqueous media is thought to become biologically inactive via hydrolysis after a period of time, however discovery of dimerization sheds light on the hetero-Diels-Alder reaction occurring (Figure 1).

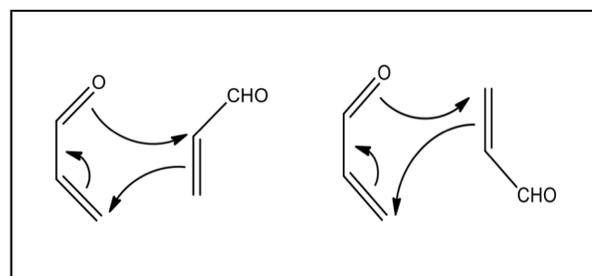


Figure 1. Hetero-Diels-Alder reaction of acrolein in H₂O.

Said reaction is propagated by the environmental heat within the irrigation canal systems. When the dimer is produced, the material changes from a colorless liquid to a dark yellow liquid (Figure 2).

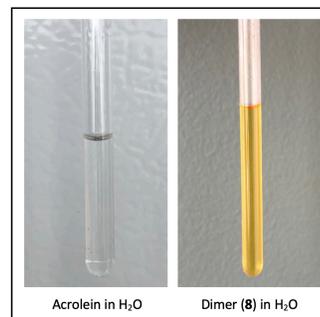


Figure 2. Physical appearance of acrolein in H₂O and dimerization product (**8**) in H₂O, post reaction.

The product is extremely stable, thus the re-formation of acrolein does not occur. Dimerization of acrolein not only inhibits the intended use of the chemical, but also poses a threat due to the lack of information and research present on the new product. Determining the specific structure of the dimer aids in gaining understanding of what is occurring within systems, possibly having toxic, undesired effects on croplands short thereafter.

RESULTS AND DISCUSSION

Ten structures were determined to be possible for the unknown dimer as products of the hetero-Diels-alder reaction and isomerization of said products (Figure 3).

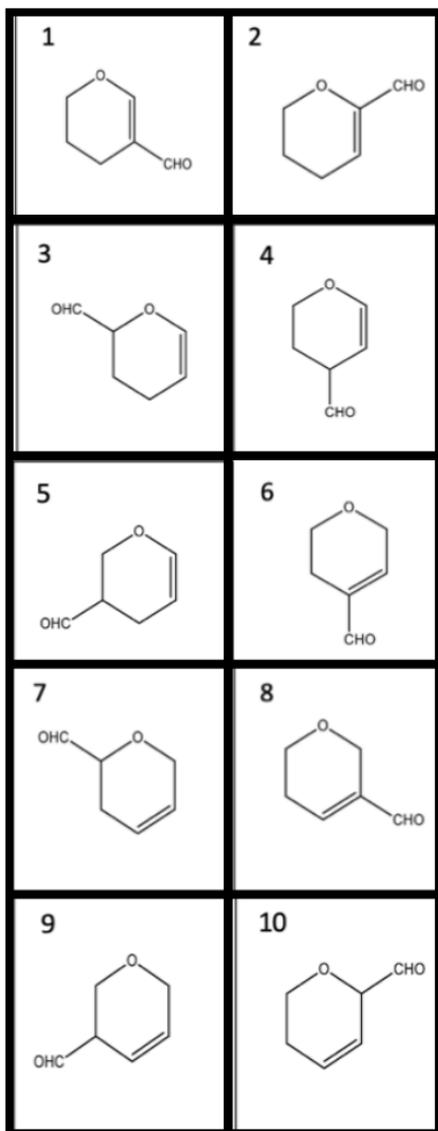


Figure 3. Possible dimerization products of acrolein hetero-Diels-alder reaction and isomerization.

Specific structure of unknown was carried out by 1D and 2D NMR experiments and GC-EIMS. Spectra obtained (Supporting Information) aided in the characterization as **8**.

¹H 1D NMR spectroscopy of **8** gave five signals, confirming five unique types of hydrogens. ¹³C 1D NMR spectroscopy of **8** alluded to the presence of six unique carbons. This data supports the molecular formula of C₆H₈O₂, thus confirming the presence of the dimer within the sample. NMR data is summarized in Table 1.

Table 1. Summary of NMR Data (in CDCl₃) for 5,6-dihydro-2H-pyran-3-carbaldehyde (**8**).

Position	δ_c , type	δ_H	HMBC
1	63.23, CH ₂	4.35, m, 2H	1, 2, 3, 4, 5, 6
2	140.47, C	-	-
3	191.94, CH	9.41, s, 1H	1, 2, 6
4	147.04, CH	6.95, m, 1H	6
5	26.36, CH ₂	2.46, m, 2H	-
6	63.65, CH ₂	3.81, t, 2H	3, 4, 5

The signal at 9.41 singlet peak suggests the presence of an aldehyde hydrogen. The triplet at 3.81 and the multiplet at 4.35 suggests the presence of hydrogens next to an oxygen (H-C-O). The signal at 2.46 suggests hydrogens attached to a carbon one bond away from a carbon-carbon double bond. Due to impurities within the sample as well as low concentration, a sufficient COSY spectra was not obtained.

One quaternary carbonyl is seen at 140.47 ppm, an expected chemical shift. Both signals at 63.23 ppm and 63.65 ppm are de-shielded due to their close proximity to the oxygen atom, correlating to 4.35 and 3.81 by HMQC, respectively. The aldehyde carbon is seen at 191.94 ppm and is correlated with the single hydrogen at 9.41, as expected. HMQC data correlates the carbon at 26.36 ppm with 2.46, and the carbon at 147.04 ppm with 6.95.

HMBC data correlates a hydrogen at 4.35 to the carbon at 191.94 ppm, the hydrogen at 3.81 to the carbon at 147.04 ppm, and the hydrogen at 6.95 to the carbon at 63.65 ppm. There is lack of correlation between hydrogen at 2.46 with carbon at 191.94, determining that the aldehyde is more than three bonds away from the 2.47 hydrogen. Said connections further evidence the structure of said molecule. Long range coupling does occur at times due to the rigidity of the dimer, as well as homoallylic coupling present.

5,6-dihydro-2H-pyran-3-carbaldehyde (**8**): yellow, pungent, viscous liquid; 1H NMR (400 MHz,

CDCl₃) δ : 2.46 (m, 2H), 3.81 (t, 2H), 4.35 (m, 2H), 6.95 (m, 1H), 9.41 (s, 1H); ¹³C NMR (400 MHz, CDCl₃) δ : 26.36, 63.23, 63.65, 140.47, 147.04, 191.94; EIMS m/z (%): 53 (99), 55 (30), 66 (50), 88 (60), 112 (67).

The gas chromatography-electron ionization mass spectrometry of **8** gave the molecular ion at m/z 112. An M-29 (m/z 83) peak supports the loss of an aldehyde. A M-46 (m/z 66) peak and M-59 (m/z 53) were also prominent. The index of hydrogen deficiency is three, thus suggesting three double bonds or rings present within the molecule. Structure **8** fits this model with one ring and two double bonds. Given the molecular formula, C₆H₈O₂, the m/z of 112 is consistent with the dimer structure. A commercial sample of compound **8** gave identical data, accounting for minor impurities within experimental sample.

By these spectrometric experiments, the unknown was determined to be structure **8** 5,6-dihydro-2H-pyran-3-carbaldehyde. Its labeled chemical structure is given in Figure 4.

Toxicity studies on goldfish concluded compound (**8**) to be toxic and lethal in under 36 hours.

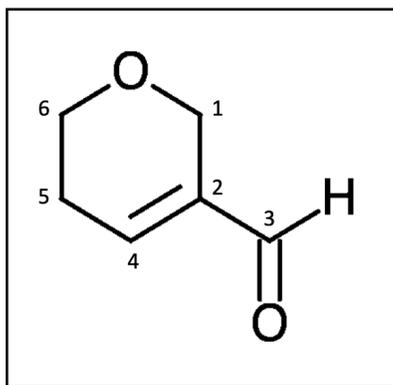


Figure 4. The chemical structure of 5,6-dihydro-2H-pyran-3-carbaldehyde (**8**), with carbon atoms labeled for reference in Table 1.

EXPERIMENTAL

Sample Collection

The samples were obtained from the gallon of aged acrolein in water from Dr. Charles Kissel (Anaheim, CA, USA). The dimer product was extracted from H₂O with CDCl₃.

NMR Analysis

The sample was analyzed by a Jeol 400 MHz nuclear magnetic resonance spectrometer (Jeol, Ltd., Akishima, Tokyo, Japan). The solvent used was CDCl₃.

GC-EIMS Analysis

The sample was prepared by diluting 1-2 drops of concentrated dimer product **8** in 1 mL of acetonitrile. The sample was analyzed by a PerkinElmer Clarus 500 gas chromatograph (PerkinElmer, Waltham, MA, USA) coupled to a PerkinElmer Clarus 560D electron impact mass spectrometer (PerkinElmer, Waltham, MA, USA). Mass/charge ratios (m/z) and relative abundances of the ions as percentages of the base peak intensity are reported.

Toxicity Study

Experiments were set up in four 2L tanks of DI water with 10 goldfish per tank. Three of the tanks were experimental with varying amounts of dimer **8** (15 ppm, 22.5 ppm, and 30 ppm) and one was used as a control with no dimer **8** added. Goldfish were left for 36 hours. 22.5 ppm showed to be the lowest concentration to be lethal to >90% of the population. Study was repeated twice more to conclude the same results. Concentrations below 22.5 ppm were also tested, but found to be less than 50% lethal. Fish in the control tank did not perish.

ASSOCIATED CONTENT

Supporting Information

Additional material as described in the text: NMR and GC-EIMS spectra for compound **8**. Available by contacting Dakota Brady*.

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