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Captan Hydrolysis

N. Lee Wolfe,* Richard G. Zepp, James C. Doster, and Reginald C. Hollis

Captan [N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide] undergoes hydrolysis readily in water with a maximum half-life of 710 min. Over the pH range 2–6, the reaction is pH independent and the pseudo-first-order rate constant is $(1.8 \pm 0.1) \times 10^{-5}$ s^{-1}. Above pH 7 the reaction is pH dependent and the second-order rate constant for alkaline hydrolysis is $(5.7 \pm 0.4) \times 10^2$ M^{-1} s^{-1}. The products are 4-cyclohexene-1,2-dicarboximide, carbon dioxide, hydrochloric acid, and sulfur. Folpet [N-(trichloromethylthio)phthalimide] and captafol [N-(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarboximide] hydrolyze at pH 7 with rates similar to that of captan. It is very likely that hydrolysis will be an important degradative pathway for these fungicides in the aquatic environment.

Captan [N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide] is a widely used surface fungicide (18 million lb, 1971) (U.S. Environmental Protection Agency, 1972) for control of scabs, blotches, rots, mildew, and other diseases on fruits, vegetables, and flowers. It is also used in general purpose pesticide mixes. With widespread usage, therefore, captan may be expected to have an impact on the aquatic environment.

A few studies are reported in the literature concerning the effects of the fungicide on aquatic life. One of the most recent reports (Hermanutz et al., 1973) presents data on the toxic effects of captan on survival, growth, and reproduction of fathead minnows. They also investigated the survival of blue gills and brook trout in the presence of captan breakdown products.

The literature contains several reports concerning the hydrolysis of sulfenimide fungicides, but the available data are inconsistent and are not helpful in delineating the degradative pathway in water. Kinetics and products of the hydrolysis of captan are reported and compared with those of folpet [N-(trichloromethylthio)phthalimide] and captafol [N-(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarboximide]. In addition, hydrolysis data are compared with some of the findings of biologists concerned with the reaction of captan with thiols.

EXPERIMENTAL SECTION

Equipment. All melting points (mp) were obtained on a Fisher Johns melting point apparatus and are uncorrected. Infrared spectra (ir) were obtained with a Perkin-Elmer 621 grating infrared spectrophotometer, and ultraviolet spectra were recorded on a Perkin-Elmer 602

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CAPTAN

FOLPET

CAPTAFOL
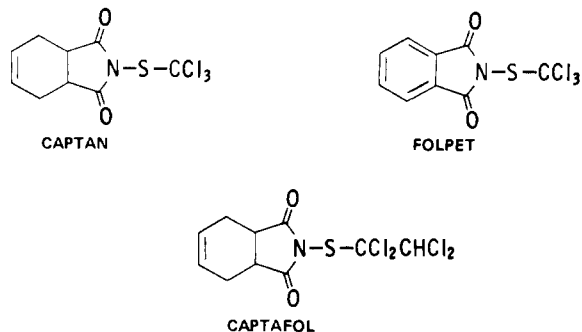
recording spectrophotometer. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained on a Varian Associates HA-100 spectrometer in the frequency sweep mode with a probe temperature of 30 °C. Tetramethylsilane (Me$_4$Si) was used as an internal standard and lock source.

Gas chromatography (GC) was carried out on a Tracor MT-220 gas chromatograph equipped with a ^{63}Ni electron capture detector and fitted with a 0.6 mm × 3.5 m i.d. column packed with 3% SE-30 on 50–100 mesh Chromosorb W. Gas chromatographic–mass spectrometric (GC–MS) analyses were performed with a Varian Aerograph Model 1532-B gas chromatograph interfaced with a Finnigan 1015 SL quadrupole mass spectrometer having a Gohlke glass separator and a Systems Industries System/150 digital computer.

Chemicals. Captan, obtained from Matheson Coleman and Bell, was purified by recrystallization from carbon tetrachloride (mp 175–176 °C). Captafol and folpet were obtained from Chevron Chemical Company and were purified by recrystallization from carbon tetrachloride: captafol, mp 161–162 °C; folpet, mp 180–182 °C.

In kinetic studies hydrochloric acid was used for low pH runs. For higher pH values the following buffer systems were employed: acetic acid–sodium acetate, sodium dihydrogen phosphate–disodium hydrogen phosphate, and boric acid–sodium hydroxide. These chemicals were commercially available and were used as received.

Kinetic Procedure. The rate of disappearance of captan was determined employing a GC procedure. The procedure described below for a single kinetic run is representative of the method used throughout the studies.

The buffered reaction solution was prepared by diluting 0.6 ml of 0.20 M Na$_2$HPO$_4$ and 0.4 ml of 0.20 M Na$_2$HPO$_4$ to 99 ml with distilled water, and followed by the addition of 1 ml of 1.02 × 10^{-3} M captan in acetonitrile. The pH of the solution was determined after calibrating the pH meter with standard buffers. The flask was placed in a constant temperature bath; after allowing for temperature equilibration, a 5-ml aliquot was removed, added to 5 ml of benzene, and shaken to quench the reaction. This sample was designated as 0 time. Subsequent samples were obtained at recorded time intervals through approximately two disappearance half-lives of captan hydrolysis. A sample obtained after approximately 10 half-lives was taken as 100% reaction.

The pseudo-first-order rate constant was calculated from the integrated form of the first-order rate expression:

$$k = \frac{1}{t} \ln \frac{C_0 - C_\infty}{C_t - C_\infty}$$

where t = time, C_0 = concentration of captan at zero time, C_∞ = concentration of captan at 10 half-lives, and C_t = captan concentration at time t (Frost and Pearson, 1961). The rate constant k was determined by a least-squares fit of the data.

Scheme I
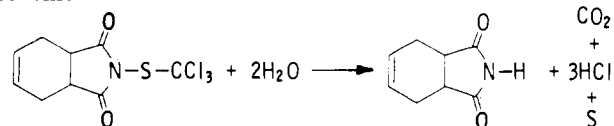
Product Studies. Product studies were carried out at 27 °C at 1 and 10 half-lives at both pH 9.0 and 3.5. Organic products were tentatively identified by GC retention times and confirmed by GC–MS, ir, and NMR. Chloride was qualitatively confirmed by extracting the 10 half-lives reaction solution with benzene and adding silver nitrate to the aqueous layer. Sulfide and thiols were qualitatively tested for with mercuric chloride. The change in hydrogen ion concentration throughout the reaction in a nonbuffered solution was determined with a pH meter. Sulfur was qualitatively confirmed as a product by solid probe MS.

DISCUSSION OF RESULTS

A literature survey disclosed several reports dealing with captan degradation in water and the products of hydrolysis. Melnikov (1971) reported that captan was hydrolyzed by moisture and the reaction was accelerated by alkali. The products of hydrolysis were reported to be 4-cyclohexene-1,2-dicarboximide, carbon dioxide, hydrochloric acid, and sulfur (Scheme I).

Daines et al. (1957) reported similar hydrolysis products, the only difference being the oxidation state of sulfur. Instead of elemental sulfur, hydrogen sulfide was reported as a product. von Rumker and Horay (1972) presented data showing that the half-life of captan decreased with increasing pH at 20 °C: pH 4, 4 h; pH 10, <2 min. The half-lives also decreased when the temperature was increased to 40 °C. Hermanutz et al. (1973) reported half-life data for captan in Lake Superior water: pH 7.6, 12 °C, 7 h; pH 7.6, 25 °C, 1 h; pH 6.7, 12 °C, 40 h; pH 6.7, 23 °C, 8 h.

In our laboratory, kinetic studies were carried out employing a GC method to determine the concentration of captan at various time intervals. With column temperatures above 200 °C, a second peak with a shorter retention time appeared in the chromatogram in addition to the captan peak. Since both peak sizes varied with each sample injection, captan was assumed to be decomposing. With a short column (2 ft) and a column temperature of 160 °C, the anomalous peak was eliminated, and the response was linear under these conditions over the concentration range of 1.2 × 10^{-5} to 1.2 × 10^{-6} M.

It was necessary to add captan to the aqueous solution with a carrier solvent (acetonitrile) because the rate of solution in water was slow compared to the rate of hydrolysis. In a separate kinetic experiment the concentration of acetonitrile was reduced to 0.1% with no detectable effect on the rate constant. Thus, the 1% organic solvent was not expected to have a pronounced effect on the rate constant when compared with pure water.

Kinetic Studies. Captan (1 × 10^{-4} M) was first hydrolyzed in an open beaker in nonbuffered water (5% acetonitrile), and captan concentration and pH were followed as a function of time. The results are shown graphically in Figure 1. As captan hydrolyzes the pH of the solution decreases, indicating acidic product formation. Also, the decrease in pH apparently retards the rate of captan degradation. Because acidic products altered the pH of the reaction solution, kinetic studies were done under pH buffered reaction conditions.

Plots of log concentration vs. time are shown in Figure 2 for captan, folpet, and captafol in the buffered pH range of 7.0–7.2. These plots are linear through at least one
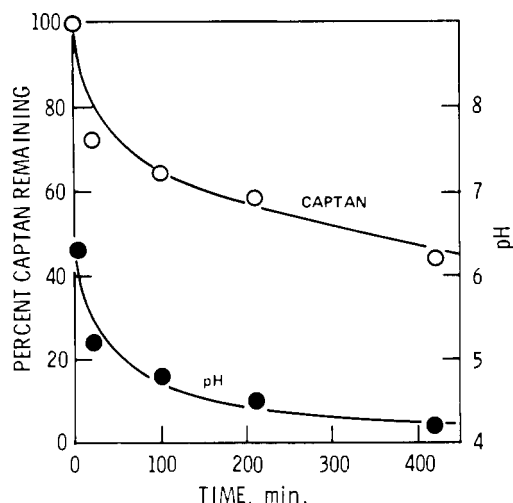
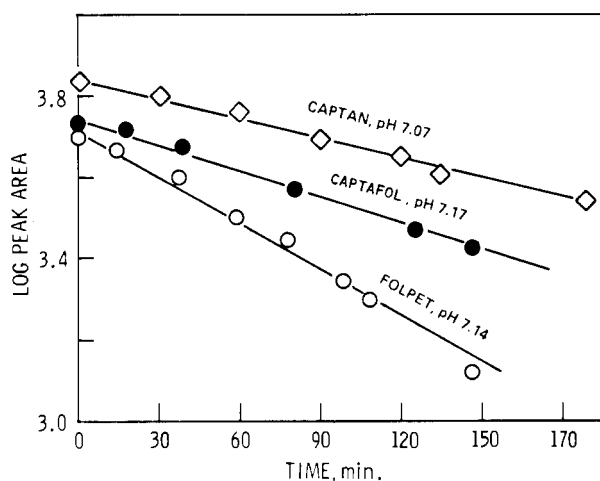Figure 1. Captan concentration and pH vs. time in nonbuffered water at 28 °C.

Figure 2. Pseudo-first-order plots for the hydrolysis of captan, folpet, and captafol.

Table I. Pseudo-First-Order Rate Constants for Captan Hydrolysis at Several pH Values and Temperatures

Temp, °C	pH	k, s^{-1}	Buffer or acid
8	8.39	$(1.49 \pm 0.03) \times 10^{-4}$ [a]	H_2BO_3/NaOH
28	1.97	$(1.79 \pm 0.06) \times 10^{-5}$	HCl
	2.48	$(1.67 \pm 0.08) \times 10^{-5}$	
	3.39	$(1.87 \pm 0.08) \times 10^{-5}$	
	4.83	$(1.97 \pm 0.08) \times 10^{-5}$	NaOAc/HOAc
	5.16	$(1.87 \pm 0.09) \times 10^{-5}$	
	6.10	$(4.6 \pm 0.3) \times 10^{-5}$	Na_2HPO_4/ NaHPO_4
	7.07	$(6.5 \pm 0.5) \times 10^{-5}$	
	7.45	$(1.5 \pm 0.1) \times 10^{-4}$	
	7.66	$(2.81 \pm 0.2) \times 10^{-4}$	
	7.82	$(3.9 \pm 0.1) \times 10^{-4}$	H_2BO_3/NaOH
	7.93	$(4.8 \pm 0.2) \times 10^{-4}$	
	8.08	$(6.5 \pm 0.1) \times 10^{-4}$	
	8.25	$(1.1 \pm 0.1) \times 10^{-3}$	
48	3.3	$(3.57 \pm 0.09) \times 10^{-4}$ [a]	HCl

Acid	Base
$\Delta H^{\ddagger} = 28.8 \pm 0.7$ kcal/mol	$\Delta H^{\ddagger} = 22.8 \pm 1.6$ kcal/mol
$\Delta S^{\ddagger} = 13.0 \pm 2.5$ eu	$\Delta S^{\ddagger} = 2.2 \pm 5.4$ eu

[a] Average of two values.
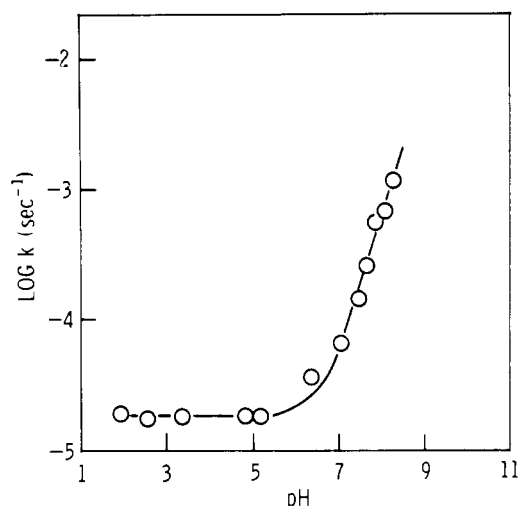
Figure 3. Plot of log k vs. pH for captan hydrolysis at 28 °C in buffered aqueous solution.

pesticide degradation half-life indicating pseudo-first-order reaction conditions. An examination of the chemical structures of these three pesticides suggests that the rates of hydrolysis would be similar. The pseudo-first-order rate constants at 28 °C are as follows: captan, 6.5×10^{-5} s^{-1} (pH 7.07); folpet, 1.4×10^{-4} s^{-1} (pH 7.14); captafol, 7.7×10^{-5} s^{-1} (pH 7.17).

The hydrolysis studies for captan were extended to other pH values to determine the contribution of acid and alkaline degradation and to evaluate the contribution of water. Table I lists the pseudo-first-order rate constants at the various pH values studied, along with the buffers employed. A pH–rate profile for the reaction is shown in Figure 3 as log k vs. pH. The plot shows that between pH 2 and 5, there is no change in the pseudo-first-order rate constant with pH since the slope of the line is essentially zero. Above pH 7 the pseudo-first-order rate constant increases with increasing pH and the slope of the line is +1. The nonlinearity of the plot between pH 6 and 7 is interpreted as resulting from competing reactions of captan with water and hydroxide.

Based on this interpretation of hydrolysis, the rate of disappearance of captan under buffered reaction conditions is given by:

$$-\frac{d[\text{captan}]}{dt} = k_{H_2O}[\text{captan}] + k_{OH}[\text{captan}][\text{hydroxide}]$$

where [captan] is the captan concentration, [hydroxide] is the hydroxide ion concentration, k_{H_2O} is the pseudo-first-order rate constant for reaction with water, and k_{OH} is the second-order rate constant for reaction with hydroxide ion. The average pseudo-first-order constant (k_{H_2O}) for the reaction of captan with water in the pH range 2–6 is $(1.8 \pm 0.1) \times 10^{-5}$ s^{-1}. The average second-order-rate constant (k_{OH}) for alkaline hydrolysis in the pH range 7–9 is $(5.7 \pm 0.4) \times 10^2$ M^{-1} s^{-1}.

A convenient way to express the chemical persistence of a pesticide is by the use of a half-life–pH diagram where half-life is given by:

$$t_{1/2} = 0.693/(k_{H_2O} + k_{OH}[\text{OH}])$$

where k_{H_2O} is the pseudo-first-order rate constant for reaction with water, k_{OH} is the second-order rate constant for alkaline hydrolysis, and [OH] is the hydroxide ion concentration.

Using this expression and the above rate constants, Figure 4 was constructed. It is apparent from this diagram that the maximum hydrolysis half-life for captan is about half a day. Although folpet and captafol were not included in these detailed pH studies, they would be expected to
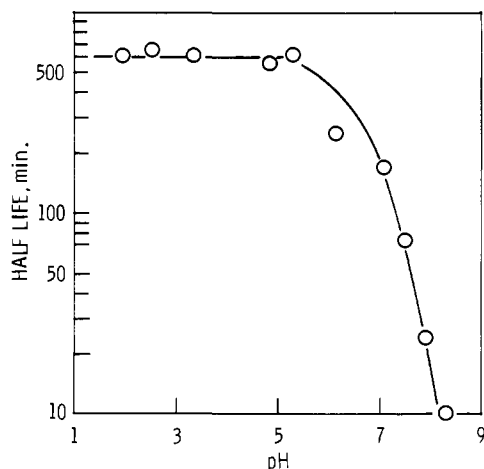
Figure 4. pH–half-life profile for captan hydrolysis in water at 28 °C.

Figure 5. Pseudo-first-order plot for the hydrolysis of captan in a Tombigbee River water sample (pH 7.0) at 28 °C.

give similar pH–rate profiles.

The temperature effect was determined for both the neutral and alkaline reactions. The activation parameters are included in Table I. For low pH studies the reaction rate was investigated at 48 °C and for high pH studies at 8 °C. As anticipated, rates of both reactions increase with increasing temperature.

It was not possible to determine the solubility of captan in water even at low pH values, because the rate of hydrolysis is fast enough over the pH range investigated to compete with the rate of solution. When 10 mg of finely divided captan was stirred (magnetic stirrer) in 100 ml of water for 16 h at room temperature, no captan could be detected in the water down to 10^{-6} M concentration. Thus, the persistence of captan in aquatic systems appears to be influenced by its rate of solution.

Hydrolysis was also studied in the presence of thioethanol at 1.02×10^{-5} M captan, 1×10^{-3} thiol, and pH 3.64. The reaction followed first-order kinetics through at least one half-life, but then deviated from first-order kinetics as shown by an increase in the rate constants during the second half-life. The effect of the thioalcohol was not investigated further and has not been interpreted. It does not appear likely that thiols will compete with water in the aqueous environment.

Natural Water Study. To determine if any species in the aquatic environment would alter the kinetics of reaction the hydrolysis was conducted in a natural water sample obtained from the Tombigbee River, South Carolina (pH 7.0). Degradation follows pseudo-first-order kinetics, as shown by a plot of the data (Figure 5). The half-life was determined to be 170 min, in good agreement with the calculated half-life of 155 min. Although this is only one natural water sample, the results are in agreement with the laboratory data.

Product Studies. Product studies were carried out at the end of 10 half-lives. To facilitate analysis the concentration of captan was increased to 2×10^{-4} M, using 10% acetonitrile–water as the solvent at pH 9.0. At the end of 10 half-lives, an aliquot of the reaction solution was qualitatively analyzed for chloride. The formation of a white precipitate, assumed to be silver chloride, upon addition of silver nitrate indicated the presence of chloride as a reaction product. Since the addition of mercuric chloride solution to a separate aliquot did not produce a precipitate, sulfide or thiols are not products. Also, hydrogen sulfide and carbon disulfide could not be detected in the reaction solution by GC–MS analysis of the toluene extracts of a separate aliquot.
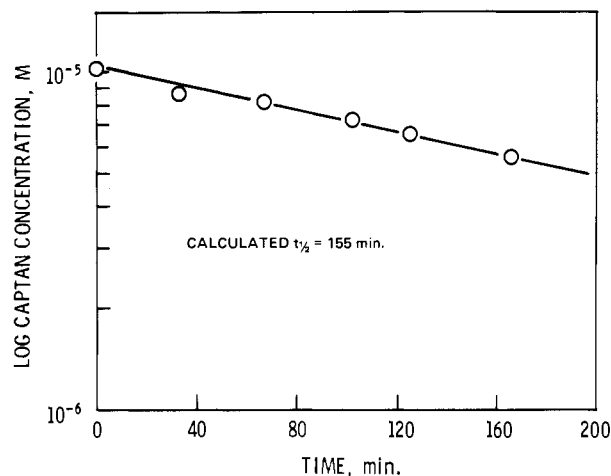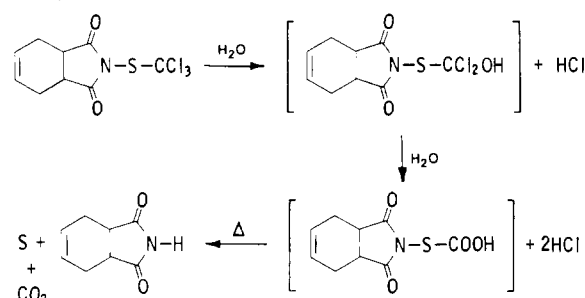
Scheme II

Extraction at pH 9.0 with chloroform gave upon work-up a small quantity of 4-cyclohexene-1,2-dicarboximide, as identified by GC retention time, melting point, ir spectra, and mass spectra data. Subsequent acidification (pH 2.5) and extraction of the reaction mixture with chloroform gave a residue that resisted crystallization. The ir spectra of this residue did not compare with that of the imide, but the solid probe mass spectra were compatible with a mixture of elemental sulfur and imide. However, the GC–MS gave two peaks; the mass spectrum of the first was interpreted to be that of 4-cyclohexene-1,2-anhydride, which may have been formed from the thermal decomposition of an intermediate compound, and the mass spectrum of the second was identical with that of the imide.

Pathway of Degradation. Captan has three different functional groups, the trichloromethyl, sulfenimide, and carboxyl groups, that are labile to hydrolysis, and the reactivity of these groups should be considered when invoking a degradative pathway. Based on hydrolysis data for phthalimide (Zerner and Bender, 1961), the carboxyl functional groups of captan would not react under our experimental conditions. On the other hand, the sulfenimide and trichloromethyl groups undergo hydrolysis readily and their reactions should therefore be scrutinized.

We have considered two reaction pathways for captan hydrolysis. The first is the heterolytic mechanism proposed by Owens and Blaak (1960) for the reaction of captan with thiols (Scheme II) and involves hydrolysis of the trichloromethyl moiety by nucleophilic substitution of chloride by water or hydroxide (March, 1968). Consideration of this pathway is based on literature hydrolytic data for similar readily hydrolyzed trichloromethyl compounds such as methyl trichloromethyl ether (Hine and Rosscup, 1960), trichloromethyl mercaptan (Bohme

Scheme III
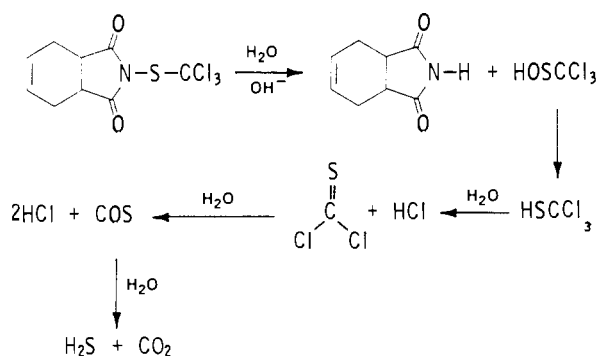
and Gran, 1953), and trichloromethylbenzene (Bensley and Kohnstam, 1957). In the case of captan, rapid nucleophilic substitution and subsequent decarboxylation with desulfurization (either concerted or stepwise) would give the imide and sulfur as products. The general reaction pathway is outlined in Scheme II where only the overall pathway is considered.

The second pathway (Scheme III) involves nucleophilic substitution at sulfur (Pryor, 1960). Sulfenimides are cleaved by acid and alkali to give the free imide and sulfenic acid (Kharasch et al., 1946; Riesz, 1966; Brown and Grayson, 1970; Behforouz and Kerwood, 1969; Heimer and Field, 1970). Reaction at the sulfenimide sulfur of captan with water or hydroxide would result in sulfur–nitrogen bond cleavage to give the imide and trichloromethyl-sulfenic acid. Bohme and Schneider (1943) have postulated trichloromethylsulfenic acid as an intermediate in the hydrolysis of trichloromethylsulfenyl chloride. This intermediate reacts rapidly to give hydrogen sulfide and carbon dioxide going through thiophosgene and carbonyl sulfide intermediates. Thus, hydrogen sulfide would be an anticipated detectable product of this pathway.

Based on our kinetic data, it is not possible to distinguish between the two schemes (II and III) outlined above. The reaction of water or hydroxide with either the trichloro-methyl or sulfenimide sulfur could be the rate-determining step for either pathway. Subsequent reaction in both schemes would be probably very rapid. The products are consistent with Scheme II and are the same as those reported by Melnikov (1971). However, we were not able to verify this pathway by isolating or spectrally identifying any of the proposed intermediates.

Any intermediates formed by the reaction with water or thiols are very reactive and would have short lifetimes in the aquatic environment. The end products of degradation with the exception of the imide are naturally occurring compounds and would have no impact on an ecosystem.

CONCLUSIONS

Captan undergoes degradation in water with a maximum hydrolysis half-life of half a day. The reaction is pH independent over the pH range 2–6 and pH dependent from pH 6 to 9. The products of the reaction were identified as sulfur, chloride, and 4-cyclohexene-1,2-dicarboximide. Captan, as well as folpet and captafol, is degraded very fast in water and hydrolysis is likely to be the predominating pathway of degradation in the aquatic environment.

ACKNOWLEDGMENT

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