

Hydrolysis of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea in aquatic system*

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Abstract. The degradation of the insect growth regulator 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) was studied both in distilled water and in buffer solution. The experimental results indicated that CCU is not stable in aqueous solution and easily decomposes in alkaline water. At pH 6 and pH 10, the half lives ($T_{1/2}$) of hydrolysis are about 9 days and 2 days, respectively. The rate of hydrolysis increases as either the concentration of alkalinity or temperature increases. At $[\text{NaOH}] = 0.01865 \text{ mol/L}$, with every 10°C increase in temperature, the reaction rate increases about 3 times, the activation energy for hydrolysis is 71.56 kJ/mol . Basic catalyzed degradation of CCU at levels greatly above its solubility in water resulted in rapid degradation to as many as four identified products: (4-chlorophenyl)urea, 2-chlorobenzoic acid, 2-chlorobenzamide, and 4-chloroaniline. The major products were (4-chlorophenyl) urea and 2-chlorobenzoic acid.

Keywords: hydrolysis; degradation; pesticide; 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea.

INTRODUCTION

1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea (CCU) is an insect growth regulator of which affect mechanism is obviously different from organochlorine, organophosphorous, carbamate, pyrethroid pesticides and so on. It is an insecticide-larvicide which inhibits the synthesis of cuticle chitin, thus disrupts the normal growth and development processes of developing insects (Xiao, 1975; Wu, 1989). Insecticide CCU is a broad spectrum insecticide-larvicide with very low mammalian toxicity (actual oral LD_{50} for mice $> 20000 \text{ mg/kg}$). The compound is particularly toxic to the larval stages of Lepidoptera (Granett, 1975).

Since CCU is only put into use as a commercial larvicide here in China, there were only few references which deal with the analysis of the compound residues (Wu, 1986).

With a widespread use of pesticides, residues poison has already come into being in the environment. The degradation of pesticide in aquatic system is of significance which clarify residue

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poison. The study on the hydrolysis of pesticide in aquatic system is one of the main aspect on clarifying residue poison. The behavior of pesticide in laboratory conditions do not reflect the complexity found in the environment, however, there are several examples where rate of hydrolysis have been measured in both pure and natural waters and which showed good agreement between the two kinds of measurements for a variety of chemical structures (Zepp, 1975; Mabey, 1978) providing that both pH and temperature were measured.

Insecticide-larvicide is a urea substitutional phenyl benzamide. It is also called inhibiting agent of chitin synthesis enzyme. CCU is the new one which is of highly efficiency and low toxicity. Its oral LD_{50} for mouse, male or female, is greater than 20000 mg/kg weight body. Through 90 days feeding, the ultimate no effect dose is 125 mg/kg weight. ADI is 1.25 mg/kg body weight. Mammal experiment indicated that CCU is neither carcinogenic, nor teratogenic and mutagenic.

The rate law for hydrolysis is pseudo-first-order rate for most hydrolysis reactions. The half life of hydrolysis is independent on concentration of the compound. The purpose of this investigation was to obtain more information on the behavior of CCU in water at laboratory conditions.

MATERIALS AND METHODS

Chemicals

CCU was provided by Tonghua Pesticide Plant, Jilin Province. It was recrystallized three times in toluene. 99% of purity was obtained.

Extraction of CCU from water

Double distilled water were fortified with 0.1, 0.5 and 1.0 mg CCU/L. Less than 2 ml methanol solution of CCU was added in each case. Duplicate 10 ml samples of each were pipetted out and then added 2 ml 5% NaCl solution and partitioned against 3×10 ml aliquots of dichloromethane, these were dried over anhydrous Na_2SO_4 and the combined aliquots were reduced nearly to dryness in a Kuderna-Danish concentrator. The residues were dissolved in 1 ml of anhydrous methanol and analyzed for CCU by HPLC.

High-pressure liquid chromatography equipment and operation condition.

A Shimadzu Model LC-3A HPLC with a UV photometer (254nm) was used for all quantitative analysis. A ZORBAX-ODS Column, 25 cm \times 4.6mm (i. d.) was used for reverse-phase chromatography. Mobile phase ($CH_3OH:H_2O=85:15$) flow rate was 1 ml/min at room temperature.

Hydrolysis of CCU in buffer solution

A certain amount of buffer solution was pipetted into a 250 ml brown-flask and 1 ml of CCU standard solution (0.5 mg in 1.0 ml methanol) was added. The reaction mixture was shaken thoroughly and kept in the thermostat at 25°C. At intervals, 10 ml duplicate samples were drawn out and extracted with 10 ml portions of dichloromethane three times. The following

processes were carried out as described above.

Hydrolysis of CCU in sodium hydroxide solution

Sodium hydroxide solution was pipetted into a 200 ml Brown-flask and then kept in the thermostat at 25°C for half an hour and then 0.5 ml of standard solution of CCU was added. The following processes were carried out as described above. In order to retard the further reaction before analysis, a small amount of 3 mol/L HCl was added rapidly in each case.

Effect of temperature on hydrolysis of CCU in water

Choose 0.01865 mol/L sodium hydroxide solution as reaction medium. The temperature of thermostat was kept at 25, 35, 45, 55 and 65°C, respectively.

Separation of degradation products

Three aliquot of CCU in sodium hydroxide were kept for some time at room temperature, the solution were acidified with dilute HCl, extracted with 4×50 ml ethyl acetate, the organic phase was dried over anhydrous Na₂SO₄, concentrated and subjected to thin-layer chromatographic (TLC) analysis and gas chromatography-mass spectrum analysis.

RESULTS AND DISCUSSION

The 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea, m. p. 199–200°C, has a water solubility of about 0.2 ppm at 25°C, and an octanol/water partition coefficient of appropriately 1600 (Yang, 1990).

Recovery of CCU from water

Table 1 shows the recovery of CCU from water.

Table 1 Recovery of CCU from water

Fortified Con., ppm	0.1	0.5	1.0	Average
Recovery, %	90.7±1.9	91.5±2.1	97.2±2.2	93.2±3.5

Degradation in buffer solution

The results of hydrolysis of CCU in buffer solution are shown in Fig.1. At pH 10, 9, 8, 7, 6 and 5, the half lives of hydrolysis are 1.90, 3.53, 4.65, 5.69, 8.78 and 35.5 days, respectively. It is apparent that hydrolysis rate increases with the pH increase of reaction medium, at the same time, the half life decreases, as shown in Fig.2. In terms of Fig.2 CCU is not stable in high pH solution and easily decomposes, e.g. at pH 8, half life is less than 5 days. Therefore CCU is not suitable to be used in alkaline conditions, whereas it is somewhat stable when pH is low.

Degradation in sodium hydroxide solution

Experimental data under the condition of basic solution are presented in Fig.3. Plot pseudo-first-order rate constants k against concentration of hydroxide, the slope K resulted from regression analysis is the rate constant Kb of that temperature. The linearity between its

hydrolysis rate and concentration of sodium hydroxide was maintained (Fig.4).

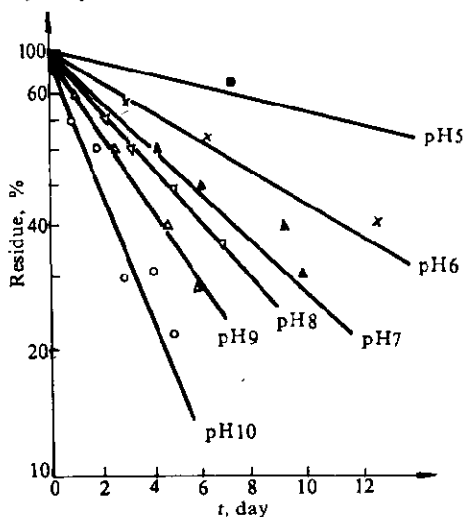


Fig.1 Hydrolysis of CCU in buffer solution

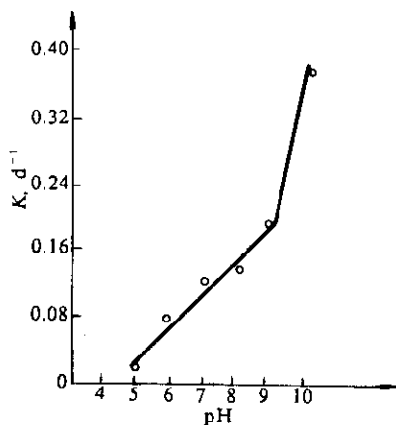


Fig.2 Relationship between pH value and rate constant

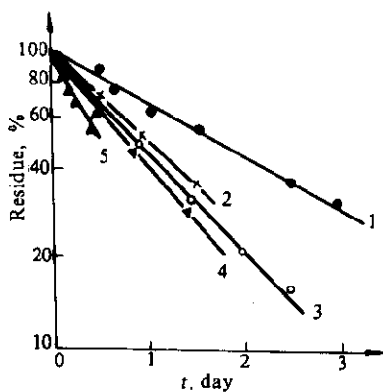


Fig.3 Hydrolysis of CCU in alkaline solution

1. 9.362×10^{-3} mol/L NaOH; 2. 5.141×10^{-3} mol/L NaOH;
3. 9.326×10^{-3} mol/L NaOH; 4. 1.408×10^{-2} mol/L NaOH;
5. 2.448×10^{-2} mol/L NaOH.

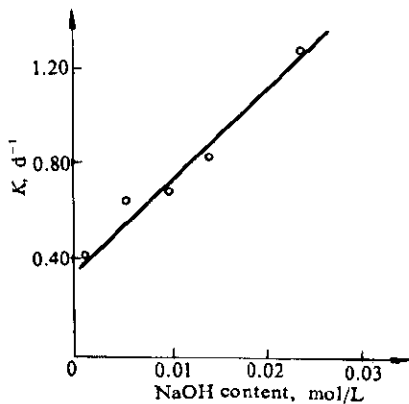


Fig.4 Effect of concentration of sodium hydroxide on rate of hydrolysis

Effect of temperature on hydrolysis of CCU

It is obvious that hydrolysis rate increases with the increase of the reaction temperature (Table 2 and Fig.5). For instance, when $t=65^{\circ}\text{C}$, the half life is only 26 min. The temperature coefficient is about 2.5. This is responsible to the Van't Hoff's Law.

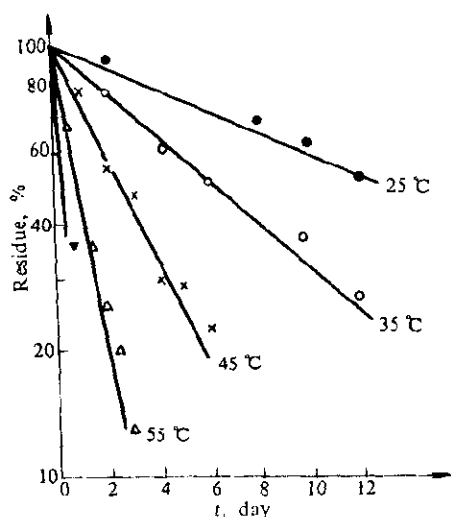


Fig. 5 Hydrolysis of CClU in different temperature
[NaOH] = 0.01865 mol/L

In terms of Arrhenius equation, plot $\ln Kb$ vs $1/T$, a good linearity between them is obtained (Fig. 6). The active energy E equals to $-2.303 RK$ where K is the slope of the straight line.

Identification of degradation products

The plate used (10×20 cm) to thin-layer chromatography were precoated silica gel with fluorescent indicator. The ethyl acetate extract and authentic samples were spotted on thin-layer plates and developed in appropriate solvent system. The compound were visualized under shortwave ultraviolet light. The R_f values of each compound were measured and compared with that of the authentic samples and are listed in Table 3.

Table 2 Effect of temperature on rate of hydrolysis

[NaOH] = 0.01865 mol/L

Temperature, °C	k , 1/h	Kb , L/h. mol	R	q^*	E , kJ/mol
25	0.0563	3.02	-0.993	2.5	71.6
35	0.102	5.45	-0.986		
45	0.256	13.7	-0.985		
55	0.669	35.9	-0.994		
65	1.60	85.6	-0.992		

$$*q = \frac{Kb(t+10)}{Kb(t)}$$

GC-MS analysis

High-resolution mass spectral studies were done with a VG7070E-HF mass spectrometer. Ionization energy: 70 eV, EI source, source temperature 300°C.

HP5790 gas chromatography, capillary glass column packed with OV-1 (25m×0.33 mm i. d.) and Helium carrier were used. Column temperature: initial temperature 60°C, increase to 220°C in rate of 4°C/min, and then increase to 300°C in rate of 10°C/min, 300°C temperature maintained 9 min.

Based on TLC behavior and GC-MS behavior (Table 4), it was confirmed that the products were: 4-chlorophenyl urea, 2-chlorobenzoic acid, 4-chloroaniline and 2-chlorobenzamide and

undegraded CCU. The possible degradation pathway is shown in Fig.7

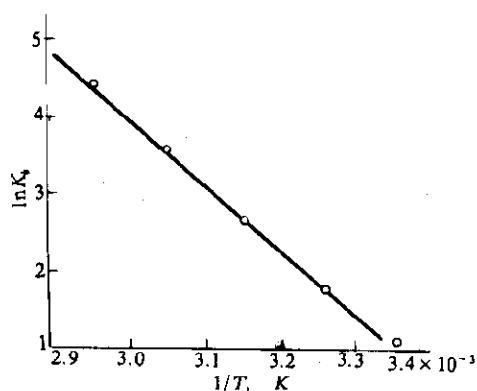


Fig.6 Effect of temperature on rate of hydrolysis of CCU,
[NaOH] = 0.01865 mol/L

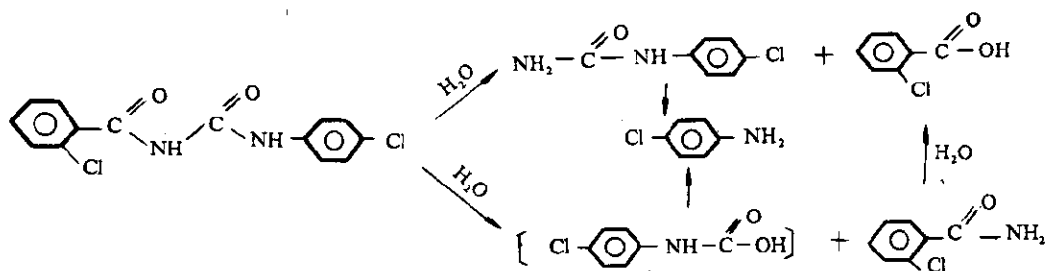


Fig.7 Degradation pathways of CCU (in basic solution)

Table 3 Thin-layer chromatographic behavior of CCU and
its water degradation products

Compound	R_f in indicated solvent system*			
	1	2	3	4
CCU	0.88 (0.87)**	0.55 (0.55)	0.69 (0.69)	0.78 (0.78)
4-chlorophenyl urea	0.56 (0.56)	0.18 (0.19)	0.26 (0.25)	0.60 (0.61)
2-chlorobenzoic acid	0.81 (0.80)	0.36 (0.37)	0.39 (0.40)	0.49 (0.48)
4-chloroaniline	0.77 (0.77)	0.42 (0.42)	0.56 (0.56)	0.71 (0.71)
Unidentified	0.62	0.29	0.82	0.39
Unidentified	—	0	0.44	—

* Solvent systems are as follows: (1) chloroform: ethanol: acetic acid = 85: 10: 5; (2) benzene: methanol = 5: 1; (3) benzene: ethanol = 9: 1; (4) n-hexane: ethyl acetate: methanol = 2: 2: 1

** R_f values in parentheses are from the authentic samples

Table 4 Mass fragmentation patterns of CCU degradation products

	Molecular ion	m/e	
		Base peak	Other ions
CCU	308	153 (4-chlorophenyl) isocyanate	139 (chlorobenzoyl)
2-chlorobenzoic acid	156	139 (chlorobenzoyl)	111.75
4-chloroaniline	127	127	92
2-chlorobenzamide	155	139 (chlorobenzoyl)	111.75

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