KINETIC STUDY BY UV SPECTROPHOTOMETRY OF ISOPROCARB DEGRADATION IN AQUEOUS MEDIUM

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ABSTRACT: Anthropogenic compounds used as pesticides often persist in the environment and can cause toxicity to humans and wildlife. Some of them are easily degraded, whereas others are degraded very slowly or only partially, leading to accumulation of toxic products. This review examines the physico-chemical factors that affect the degradation of pesticides and the mechanisms by which new pathways emerge in nature. The present work deals with the degradation mechanism of an insecticide, Isoprocarb or 2-isopropylphenyl-N-methylcarbamate in aqueous media. It may result in the inhibition of the vital enzyme acetyl-cholinesterase. The reaction kinetics has been investigated using UV Spectrophotometry. The determination of 2-isopropylphénol, as the main degradation product of Isoprocarb hydrolysis gives evidence for the significant reactivity of this insecticide in alkaline solution. The rate constants were determined following a first order kinetic model. The obtained positive activation entropy $\Delta S^{\neq} = +21.78$ J mol^{-1} K^{-1} and the absence of basic general catalysis indicate an E1cB mechanism involving unimolecular collapse of the Isoprocarb via a methylisocyanate intermediate. This elimination process is confirmed by the position of the point corresponding to the Isoprocarb on the Brönsted and Hammett plots, determined for a serie of substituted N-methylcarbamate which the decomposition mechanism in aqueous media proceede via E1cB.

Key words: Isoprocarb, carbamate, kinetic, mechanism, spectrophotometric UV.

INTRODUCTION

Carbamates represent a large chemical family, which are derivatives of carbamic acid **[1]**. They are widely used for the control of insects and other pest organisms as a result of their relatively short life, their effectiveness and their broad spectrum of biological activity **[2,3]**.

Different methods of analysis have been described in the literature for the determination of N-methyl carbamates and their hydrolysis products in different environmental media **[4-7]**. Hydrolysis and hydroxylation reactions are the main modes of carbamates degradation as Isoprocarb among insecticide classes **[8,9]**. We therefore proposed to study the degradation of Isoprocarb or 2-isopropylphenyl-N-methylcarbamate in aqueous media.

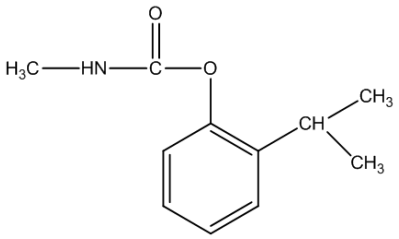

Figure-1: Chemical structure of Isoprocarb

Isoprocarb is considered as one of the most important carbamate insecticides **[10,11]**. It is used against various types of parasites in the treatment of plants of tropical and subtropical regions such as fulgorids rice and cotton leafhopper **[12,13]**. The detailed kinetic study of Isoprocarb

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alkaline hydrolysis reaction in aqueous medium was investigated by UV absorption spectrophotometry.

RESULTS AND DISCUSSION

Determination of 2-isopropyphenol obtained at the end of the hydrolysis reaction of Isoprocarb in aqueous medium

The determination of 2-isopropylphenol formed during the hydrolysis of Isoprocarb at pH = 10.94, at T = 25°C, and at μ = 1.00 was confirmed by the good superposition of the UV absorption spectrum of the species produced (spectrum b) with that of a reference (spectrum c) whose it was conducted under the same experimental conditions (Figure-2).

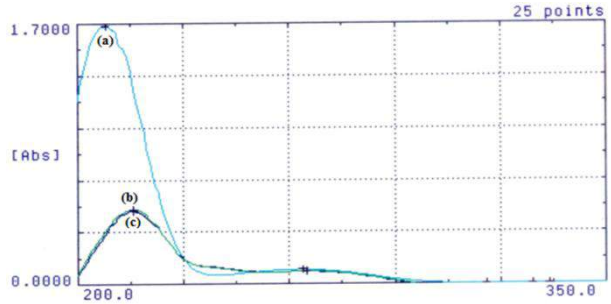

Figure-2: UV absorption spectra of 2-isopropylphenol (c), of the hydrolysis product of Isoprocarb (b) and of Isoprocarb (a) (510^{-5}M). [Isoprocarb] = [2-isopropylphenol] = 510^{-5}M; at pH = 10.94, T = 25°C, and μ = 1.00.

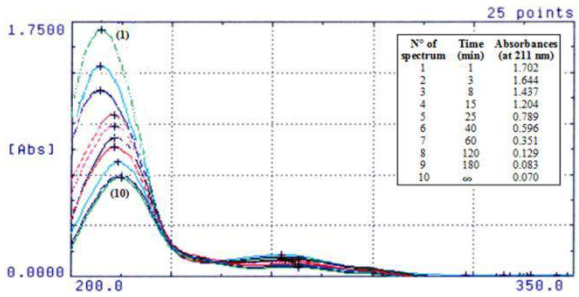

Figure-3: UV spectra of the Isoprocarb hydrolysis (510^{-5} M) in function of time; in alkaline solution at pH = 10.94, T = 25°C, and μ = 1.00.

Based on our previous works of laboratory on insecticides from the same family of carbamates, we can use other techniques for the determination of 2-isopropylphenol formed during the hydrolysis of Isoprocarb at the above experimental conditions such as HPLC coupled to mass spectrometry **[9]** and ^{1}H NMR spectroscopy **[14]**.

Determination of the rate constant k_{obs} of Isoprocarb hydrolysis reaction

UV spectra show an isosbestic point at 228 nm, indicating that there is no intermediate storage and the constant rate of Isoprocarb hydrolysis followed the pseudo-first order kinetics model (Figure-3).

The absorption evolution of Isoprocarb solution contained in a thermo regulated tank, corresponds to the disappearance of the substrate (λ = 211 and 241 nm) in function of time (Figure-4).

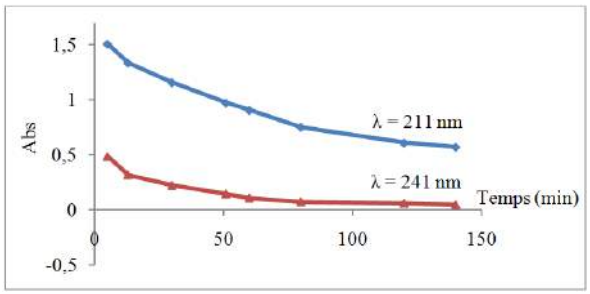

Figure-4: Absorption evolution in function of time at wavelengths 211 nm and 241 nm

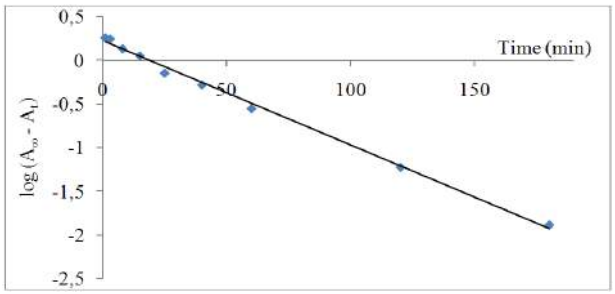

Figure-5: Determination of the observed rate constant k_{obs} of Isoprocarb hydrolysis reaction at λ = 211 nm in a buffer solution of sodium bicarbonate at pH = 10.94, T = 25°C and μ = 1.00.

The rate constant k_{obs} = 2.69 10^{-2} min^{-1} was determined graphically from the slope of the linear equation log (A_∞-A_t) = - k_{obs}/2.303 t + log (A_∞-A_0) where A_0, A_∞ and A_t represent respectively the initial absorptions, final and at time t of the reaction mixture (Figure-5).

Effect of ionic strength μ on rate constant of Isoprocarb hydrolysis reaction

Debye-Huckel-Bronsted relation shows the influence of ionic strength on the rate constant of an ionic reaction **[15]**:

$\log k = \log k^0 + 1.02\, z_A\, z_B\, \sqrt{\mu}$. Where k is the specific rate constant, k^0 is the specific rate constant at zero ionic strength and z_A and z_B are the charges of ions A and B respectively. This equation is valid for dilute solutions. It predicts that the plot of log k versus the square root of ionic strength I should be a straight line.

The first-order rate constants of the hydrolysis reaction of Isoprocarb k_{obs} were investigated at 211 nm in aqueous buffers at pH = 10.94, at T = 25°C and at different ionic strengths values (from 0.2 to 1.0).

The obtained results are shown in Table-1

Table-1: Rate constants k_{obs} of pseudo first-order of Isoprocarb hydrolysis reaction versus $\sqrt{\mu}$ at T = 25°C and at pH = 10.94.

Ionic strength μ	1	0.8	0.6	0.4	0.2
k_{obs} 10^2 (min^{-1})	2.69	2.07	1.41	0.91	0.61
$\sqrt{\mu}$	1	0.89	0.77	0.63	0.44
log k_{obs}	-1.57	-1.68	-1.85	-2.04	-2.21

The relationship of the reaction rate with changes in the ionic strength was determined by plotting log k_{obs} against $\sqrt{\mu}$ (Figure-6).

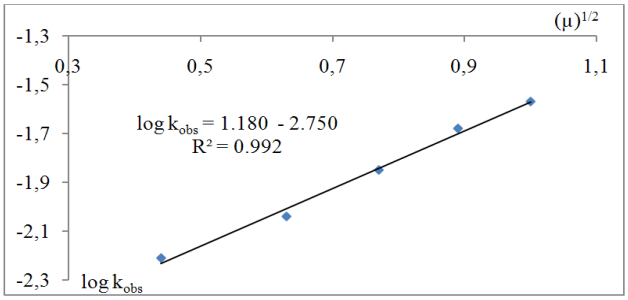

Figure-6: log k_{obs} versus $\sqrt{\mu}$ for Isoprocarb hydrolysis reaction

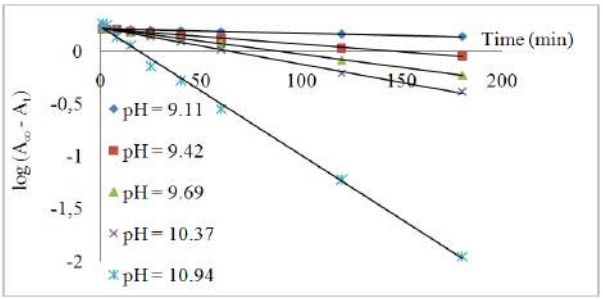

Figure-7: Effect of pH on the rate constant k_{obs} of Isoprocarb hydrolysis reaction (510^{-5} M) at 25°C and μ = 1.00.

The increase in the ionic strength from 0.2 to 1.0 using KCl resulted in an increase in the rate of the hydrolysis reaction of Isoprocarb (Table 1). Plot of log k_{obs} versus $\sqrt{\mu}$ gave a linear graph [Fig-5] with a slope of 1.18 (R^2 = 0.992) showing positive salt effect on Isoprocarb degradation.

Effect of pH on the rate constant of Isoprocarb hydrolysis reaction

The rate constants of pseudo first-order of Isoprocarb hydrolysis reaction in aqueous medium were determined at 211 nm in buffered solutions at different pH values (from 9.11 to 11.87); by measuring the evolution of UV absorption of 2-isopropylphenol versus time at 25°C and at a constant ionic strength I = 1 (Figure-7).

The obtained results are shown in Table-2:

Table-2: Rate constants k_{obs} of pseudo first-order of Isoprocarb hydrolysis reaction versus pH at 25°C and at ionic strength μ = 1.00.

pH	9.11	9.42	9.69	10.37	10.94
k_{obs} 10^2 (min^{-1})	0.04	0.09	0.15	0.79	2.69

The graphic representation of the logarithm of the observed rate constant k_{obs} of Isoprocarb hydrolysis reaction versus pH at 25°C, is a straight line which is represented by the following equation: $\log k_{obs} = 0.999\ pH - 12.48$ ($R^2 = 0.999$) (Figure-8).

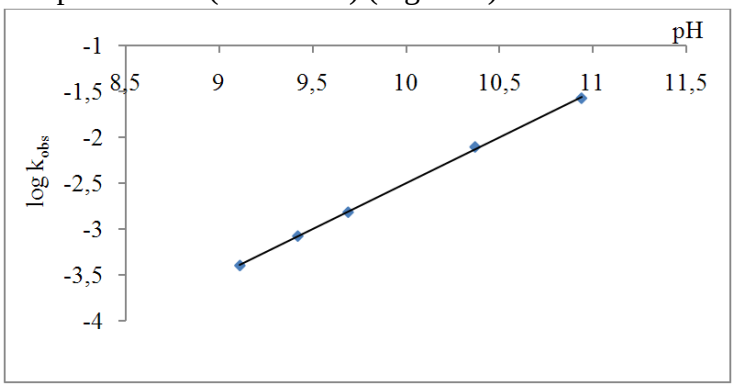

Figure-8: logarithmic Variation of the observed rate constant of Isoprocarb hydrolysis reaction versus pH at 25°C and at ionic strength μ = 1.00.

The value of the slope of this line is almost equal to unity. This is in perfect accordance with the limits forms of the rate laws: $k_{obs} = (k_1 K_a / a_H)$ and $k_{obs} = k_2 [OH^-]$ corresponding respectively to E1cB and $B_{AC}2$ hydrolysis mechanisms for N-monosubstituted carbamates (Figure-9).

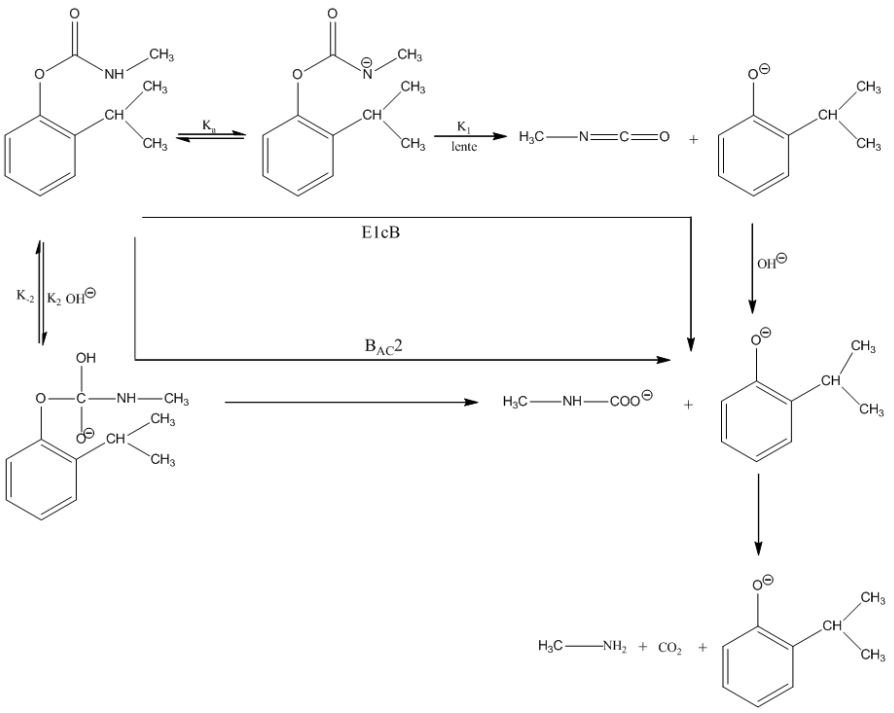

Figure-9: Hydrolysis of Isoprocarb according E1cB and $B_{AC}2$ mechanisms.

Both mechanisms E1cB and $B_{AC}2$ differ mainly by the formation of methylisocyanate, only formal proof of E1cB process. The identification of this intermediate in the reaction medium is very difficult because of its high chemical reactivity compared with the hydroxyl ion to form the N-methylcarbamic acid **[16]**.

Possibility of a bimolecular elimination reaction E2 – search for general basic catalysis

For hydrolyzing Isoprocarb, a bimolecular elimination mechanismn E2 in accordance with the formation of methylisocyanate, may be considered. This mechanism was mentioned by Homer and Bender **[17]** for the hydrolysis of p-nitrophenyl-N-methylcarbamate. The formation of the p-nitrophenyl-N-methylcarbamate anion then, is the limiting step.

In the case of Isoprocarb, the elimination E2 leads to 2-isopropylphenol anion during the slow step of the mechanism (Figure-10).

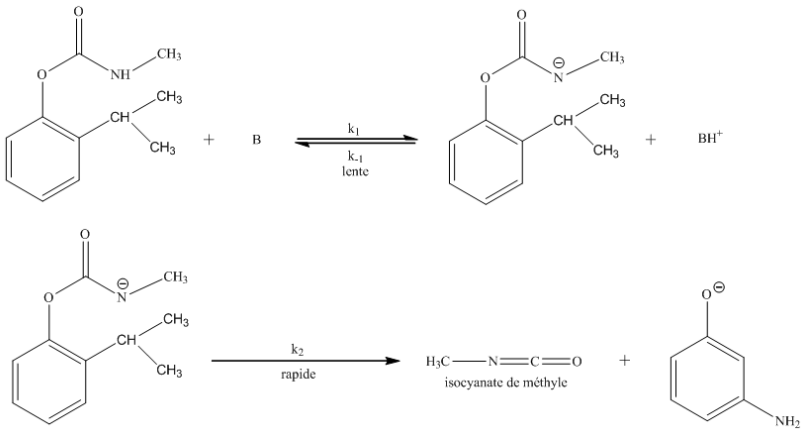

Figure-10: E2 elimination mechanism for Isoprocarb hydrolysis reaction.

E2 mechanism was investigated from the study of the effect of bicarbonate buffer concentration at pH = 10.94 on the rate of Isoprocarb hydrolysis reaction at temperature T = 25°C and at ionic strength μ = 1.00 (Table-3).

Table-3: Effect of the concentration of bicarbonate buffer solution at pH = 10.94 on the rate constant k_{obs} of Isoprocarb hydrolysis reaction at T = 25°C and μ = 1.00.

$[HCO_3^-]$ 10^2 mol L^{-1}	1	0.8	0.6	0.4	0.25
k_{obs} 10^2 min^{-1}	2.690	2.680	2.685	2.676	2.678

According to the found experimental results, we concluded that the observed rate constants of Isoprocarb hydrolysis in function of bicarbonate buffer concentration remain constant. So there is no general base catalysis and it doesn't seem that E2 mechanism can be retained. These results are consistent with those obtained for methiocarb, Bendiocarb, Zectran, Ethiofencarb and landrin **[18-22]**.

Determination of the activation entropy $\Delta S^{\neq}$ of Isoprocarb hydrolysis reaction

According to the data in the literature, the activation entropy can be an argument in favor of one or the other E1cB and $B_{AC}2$ mechanisms **[23-25]**.

We therefore proposed to study the influence of temperature on the rate constants k_{obs} of Isoprocarb hydrolysis reaction to determining the activation entropy $\Delta S^{\neq}$.

The observed rate constants were measured at different temperatures (from 25°C to 45°C) in bicarbonate buffer solution at pH = 10.94 and at ionic strength μ = 1.00 (Table-4) (Figure-11).

Table-4: Rate constants of Isoprocarb hydrolysis reaction versus the temperature in bicarbonate buffer solution at pH = 10.94 and at ionic strength μ = 1.00.

Température (°C)	25	30	35	40	45
$\mathbf{k_{obs}\ 10^2\ min^{-1}}$	2.69	4.40	9.79	15.99	26.06

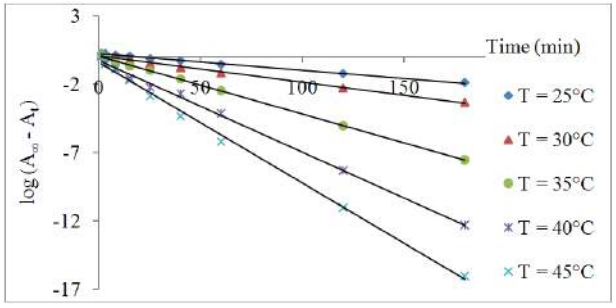

Figure-11: Influence of temperature on the rate constants k_{obs} of Isoprocarb hydrolysis reaction.

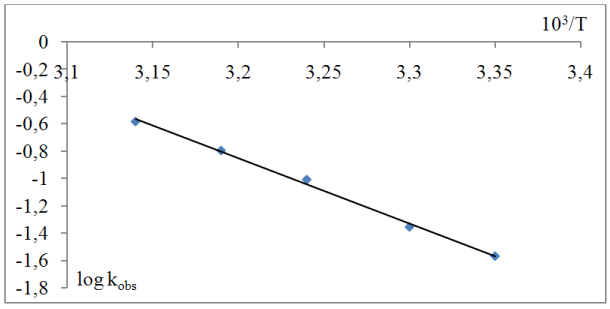

Figure-12: logarithmic variations of the observed rate constants k_{obs} of Isoprocarb hydrolysis reaction versus the temperature at pH = 10.94 and at μ = 1.00.

The value of the activation entropy $\Delta S^{\neq}$ = +21.78 J mol^{-1} K^{-1} is derived from that of the activation energy Ea = 90.73 kJ mol^{-1}, calculated from the slope of the linear equation $\log k_{obs} = -4.786\ 10^3 / T + 14.46$ ($R^2 = 0.996$) (Figure-12).

The obtained positive activation entropy $\Delta S^{\neq}$ indicate an E1cB mechanism for Isoprocarb hydrolysis reaction. For a process in which $k_{OH} = (k_1 K_a) / (Ke/\gamma)$, the ionization entropies relative to K_a and Ke are negative while the value of $\Delta S^{\neq}$ is positive. Anyway, the positive entropy can not be related to $B_{AC}2$ mechanism.

Identification of Isoprocarb hydrolysis mechanism in aqueous medium: Hammett and Bronsted plots

-Spectrophotometric determination of pKa of leaving group corresponding to Isoprocarb: 2-isopropylphenol

The basic principle of this method is to determine the ratio of neutral species and ionized species of 2-isopropylphenol in a variety of buffer solutions of known pH **[26]**. UV spectra A = f (λ) are shown in Figure-13.

The absorbance values of 2-isopropylphenol, measured at several wavelengths between 210 and 235 nm in function of pH at 25 °C, were collected in table-5.

From the graphical representation log u_m = f (0.255 + pH), we determined directly at intersection point with axis of abscissas, pka = 10.89 corresponding to 2-isopropylphenol.

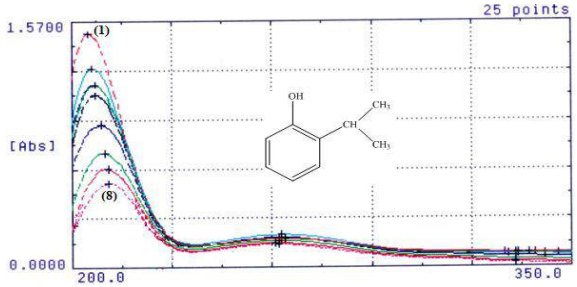

Figure-13: UV absorption spectra A = f (λ) of 2-isopropylphenol. Spectrum N°1: pH = 9.11; Spectrum N°8: $[OH^-]$ = 1M (T = 25 °C, μ = 1.00).

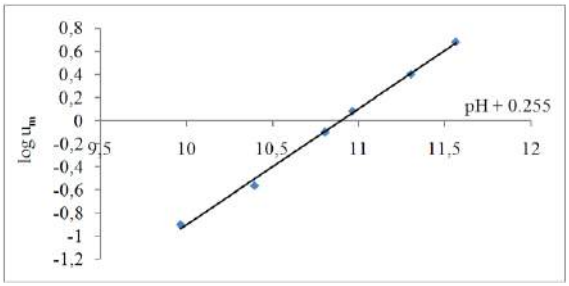

Figure-14: Spectrophotometric Determination of pKa of 2-isopropylphenol at 25°C and μ = 1.00.

Table- 5: UV spectra absorbance variation of 2-isopropylphenol 510^{-5} M versus pH at T = 25°C and μ = 1.00.

pH + 0.255	**Absorbance à λ (en nm)**		
	211	221	231
9.36	1.50404	0.91706	0.21345
9.96	1.43228	0.85012	0.19145
10.39	1.29479	0.80568	0.17816
10.80	0.98942	0.72123	0.15172
10.96	0.93438	0.68467	0.12130
11.30	0.75104	0.61909	0.10267
11.56	0.71688	0.50012	0.07583
NaOH 1M	0.57023	0.34295	1.05406

The obtained straight line is represented by the following equation: $\log u_m = 1.005\ pH - 10.95$ (Figure-14). The value of the slope of this line is almost equal to unity; this is considered as an excellent control of behaviour of studied compound, also its purity and accuracy of measurements.

-Influence of pKa of leaving group on bimolecular rate constant K_{OH} of Isoprocarb hydrolysis: *Bronsted plot*

The linear relationship of Bronsted between logarithm of bimolecular rate constant of Isoprocarb hydrolysis reaction and pKa of the leaving group of equation $\log k_{OH} = -1.15\ pKa + constant$, is a good argument to differentiate E1cB and $B_{AC}2$ mechanisms. Thus, the slope β of this line is characterized by either E1cB mechanism **[27]** (when $\beta < -0.1$) or $B_{AC}2$ mechanism (when $\beta > -0.5$).

This line was determined by Williams for the hydrolysis reaction of esters series derived from N-methylcarbamic acid, who's the elimination process is E1cB **[28]**.

The point corresponding to Isoprocarb coordinates (pKa = 10.89; $\log k_{OH} = 1.27$) is well on Bronsted line, implying that insecticide hydrolyse according to E1cB mechanism (Figure-15). The logarithmic value of bimolecular hydrolysis rate constant $\log k_{OH} = 1.27$ relative to Isoprocarb was determined from the y-intercept of the straight line of equation $\log k_{obs} = 0.999 \log pH - 12.48$ ($R^2 = 0.999$).

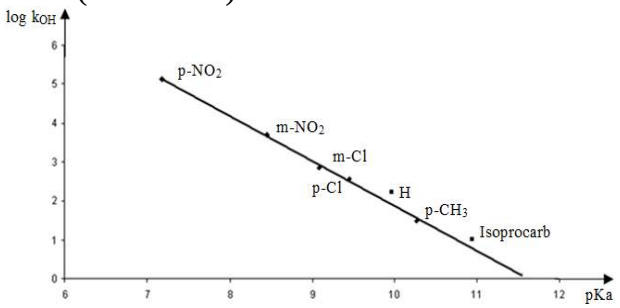

Figure-15: Bronsted relationship between logarithm of hydrolysis bimolecular rate constants at 25°C of a series of aryl-N-methylcarbamates and pKa of leaving groups.

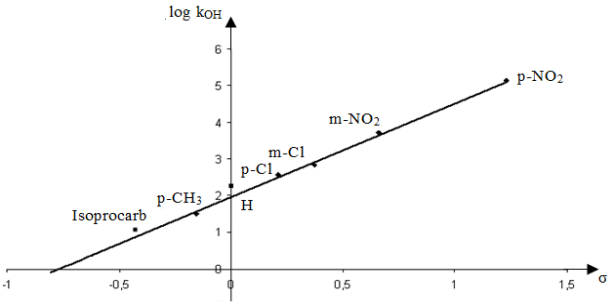

Figure-16: Hammett relationship between logarithm of hydrolysis bimolecular rate constants at 25°C of a series of aryl-N-methylcarbamates and σ parameters.

-Influence of substituents electronic effect on bimolecular rate constant K_{OH} of Isoprocarb hydrolysis: *Hammett plot*

Williams **[29]** studied the effect of substituents on hydrolysis rate constants, on a variety of carbamates. Hammett relationship $\log k_{OH} = f(\sigma)$ of hydrolysis reaction of alkyl and aryl

N-monosubstituted carbamates of the formula CH_3-NH-COO-C_6H_4X **[30]** according to E1cB mechanism established by Williams, is a straight line of equation log k_{OH} = 2.56 σ + 2.09. The experimental point corresponding to Isoprocarb coordinate (σ = -0.43 ; log k_{OH} = 1.27) is perfectly positioned on Hammett line. Thus, the slope of this line is in favor of E1cB elimination (Figure-16). The electronic parameter σ = -0.43 relating to 2-isopropylphenol was calculated from the relationship; pKa = 9.92 - 2.23 Σσ **[31]**.

CONCLUSION

We discussed in this work the kinetic study and the degradation mechanism in aqueous medium of Isoprocarb by UV spectrophotometry.

Based on literature data and obtained kinetic results on other N-methyl carbamates **[32]**, E1cB hydrolytic degradation has been attributed to Isoprocarb.

Thus, the obtained positive activation entropy ($\Delta S^{\neq}$ = +21.78 J mol^{-1} K^{-1}) and the absence of basic general catalysis indicate an E1cB mechanism involving unimolecular collapse of the Isoprocarb via a methylisocyanate intermediate which is converted to 2-isopropylphenol and methylamine.

This elimination process is confirmed by the position of the point corresponding to the Isoprocarb on the Brönsted and Hammett plots, determined for a serie of substituted N-methylcarbamate which the decomposition mechanism in aqueous media procede via E1cB.

EXPERIMENTAL PROCEDURES

Reagents and Solvents

- Ultrapure water
- Isoprocarb (Sigma Aldrich) of 99 % purity
- Buffer solutions prepared in the laboratory
- Carbonate $NaHCO_3$ (POCH)
- Phosphate Na_2HPO_4 (LAB-SCAN)
- Borax $Na_2B_4O_7$, 10 H_2O (Merck)
- NaOH (SHAM LAB)
- KCl (LAB-SCAN)
- HCl (Across)
- Spectroscopic grade methanol (LAB-SCAN, analytical sciences)

Instrumentation

- PH-meter: Digital pH meter Ph 744
- UV double beam spectrophotometer: Beckman DU 640B

Preparation of solutions

The stock standard solution of Isoprocarb of 10^{-2} M was prepared by dissolving 0.04831 g in 25 mL of spectroscopic grade methanol solution. The different aqueous solutions were prepared at different pH by the dilution of stock standard solution at a concentration of 510^{-5} M in the appropriate buffer. The ionic strength μ of these solutions was kept constant by addition of KCl. The various buffers used were obtained from the following mixtures:

- $NaHCO_3$ (0.05 M) + NaOH (0.1 M)
- Na_2HPO_4 (0.05 M) + NaOH (0.1 M)
- $Na_2B_4O_7$, 10 H_2O (0.025 M) + NaOH (0.1 M)
- $Na_2B_4O_7$, 10 H_2O (0.025 M) + HCl (0.1 M)
- KCl (0.2 M) + NaOH (0.2 M)

Calculation of activation entropy $\Delta S^{\neq}$

The activation free enthalpy has the following equation $\Delta G^{\neq}$ = -RT ln h k_{obs}/TK_B where h and K_B represent respectively the Planck and Boltzmann constants (h = 6.63 10^{-34} Js, K_B = 1.38 10^{-23} JK^{-1}). Such as ΔG

= ΔH – TΔS and ΔH = Ea – RT (for a reaction in homogeneous liquid medium): we can relate the rate constant k_{obs} to the activation entropy: $\Delta S^{\neq} = 2.3\ R \left(\log k_{obs} - \log \frac{e K_B}{h} - \log T\right) + \frac{Ea}{T}$ with log (eK_B/h) = 10.755 and $\Delta S^{\neq}$ for each temperature. The activation energy Ea can be determined from the slope Ea / 2.3 R of the line log k_{obs} = f (1/T) where T and R represent respectively the absolute temperature and the perfect gas.

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