Kinetics of the Alkaline Hydrolysis of Fenuron in Aqueous and Micellar Media

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ABSTRACT: The kinetics of the hydrolysis of fenuron in sodium hydroxide has been investigated spectrometrically in an aqueous medium and in cationic micelles of cetyltrimethylammonium bromide (CTAB) medium. The reaction follows first-order kinetics with respect to [fenuron] in both the aqueous and micellar media. The rate of hydrolysis increases with the increase in [NaOH] in the lower concentration range but shows a leveling behavior at higher concentrations. The reaction followed the rate equation, $1/k_{obs} = 1/k + 1/(k K [OH^-])$, where k_{obs} is the observed rate constant, k is rate constant in aqueous medium, and K is the equilibrium constant for the formation of hydroxide addition product. The cationic CTAB micelles enhanced the rate of hydrolytic reaction. In both aqueous and micellar pseudophases, the hydrolysis of fenuron presumably occurs via an addition–elimination mechanism in which an intermediate hydroxide addition complex is formed. The added salts decrease the rate of reaction. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 638–644, 2007

INTRODUCTION

Phenylureas are widely used in agriculture as active principles of efficient herbicides. They are absorbed by roots and leaves with translocation and act as photosynthetic electron transport inhibitors upon the photosystem II [1]. Fenuron is widely used for the control of woody plants and perennials plants [2]. It can be used either pre- or post-emergent and is systemic.

The mechanisms of hydrolysis of phenylureas, carboxylic acid, esters, and amide have been subject of investigation by many workers [3-12]. The

hydrolysis of phenylureas pesticides proceeds through an addition–elimination mechanism in both acidic and basic media.

Surfactants are one of the important additives used in formulations of pesticides and herbicides [13,14] to (i) increase the solubility of the pesticide in aqueous medium, (ii) stabilize the pesticide by controlling evaporation or decomposition (above critical micelle concentration (cmc)), (iii) enhance the effectiveness of the pesticide by providing the fine spray, and (iv) explore the mode of action of pesticide (hydrolysis behavior) in biomacromolecular ensembles (e.g., enzymes). The surfactant also acts as a wetting, dispersing, and emulsifying agent. Surfactants at air–water interfaces and in water, or similarly strongly hydrogenbonded solvents, self-associate at concentrations above



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the cmc to form association colloids known as micelles [15]. Aggregate effects of micelles on chemical reactivity are generally interpreted by using the pseudophase model [16,17], which treats micelles and water as separate reaction media, that is, as separate phase or pseudophases. This approach has been successfully applied to a wide range of chemical reactions in micellar solution [18–20]. Surfactant aggregates affect chemical reactivity primarily by binding or excluding reactants and secondarily by changing the free energy of activation.

The micellar pseudophase has been regarded as a microenvironment having varying degrees of polarity, water activity, and hydrophobicity with increasing distance from the interfacial region to its core. Micellecatalyzed reactions are considered as a model for electrostatic and hydrophobic reactions in biological systems [21] and provide information regarding the mechanism of reaction occurring on biological surfaces because the micelle resembles enzymes structurally and functionally. The study in CTAB micelles will be helpful in understanding the mechanism of action of herbicides in the biological process. The influence of temperature and concentrations of OH⁻, CTAB, and fenuron on the rate of hydrolysis of fenuron may be utilized in the determination of the fate of herbicides after its dispersal in the environment.

Keeping in view these reasons, the kinetic investigation on the rate of hydrolysis of fenuron was carried out under varying conditions of temperature and concentration of salts, sodium hydroxide, and cationic micelles. The possible mechanism and the corresponding rate equation are reported in this paper.

EXPERIMENTAL

Materials

Fenuron, 1,1-dimethyl-3-Phenylurea (Bharat Pesticides Ltd., Mumbai, India), sodium hydroxide (97%; Merck, Mumbai, India), sulfuric acid (99%; Merck, Mumbai, India), methanol (99%; Merck, Mumbai, India), cetyltrimethylammonium bromide (99.9%; CDH, Mumbai, India), sodium chloride (99%; Qualigens, Mumbai, India) potassium nitrate (99%; CDH, Mumbai, India) were used as received. All the other chemicals used were of analytical reagent grade. Doubly distilled and deionized water was used throughout the experimental work.

Stock solutions of sodium hydroxide (1.0 mol dm⁻³), cetyltrimethylammonium bromide (0.1 mol dm⁻³), and sulfuric acid (2.0 mol dm⁻³) were prepared in distilled water. The stock solution of fenuron $(1.0 \times 10^{-2} \text{ mol dm}^{-3})$ was prepared in methanol.

Kinetic Measurement

The requisite amounts of surfactants, sodium hydroxide, and methanolic solution of fenuron were taken in a three-necked reaction vessel. The reaction vessel was fitted with a double surface condenser to prevent any evaporation. The reaction vessel was kept in a thermostated water bath at the desired temperature ($\pm 0.1^{\circ}$ C). The rate of reaction was monitored by measuring absorbance in a water-methanol mixture (9:1) and surfactants on an Elico SL-164 UV-vis spectrophotometer using 1-cm-pathlength quartz cuvettes. All the kinetic experiments were run under the first-order reaction condition in which the concentration of OH⁻ and surfactant was kept in large excess over the fenuron concentration. During basic hydrolysis of fenuron, the corresponding carbamate formed has a slightly different value of λ_{max} (248 nm). On addition of few drops of acid, carbamate decomposes immediately to give the spectrum of aniline. The absorbance was measured by taking 3-mL aliquots in 1 mL of 2 M sulfuric acid. The pseudo-first-order rate constant was determined from the slope of in $(A - A_{\alpha})$ versus time, where A is the absorbance of fenuron at λ_{max} (239 nm). The reaction was followed up to 70% of its completion (2 half-life periods). A nonlinear leastsquare technique was used for the treatment of data to obtain the value of $K_{\rm S}$ and $k_{\rm m}$. The best values, which fit the curves, were obtained from the computer program. The cmc of CTAB containing fenuron and sodium hydroxide was determined conductometrically at 80°C and its value was 8.2×10^{-4} mol dm⁻³.

RESULTS AND DISCUSSION

Reaction in the Aqueous Medium

The alkaline hydrolysis of fenuron was studied kinetically in water-methanol solutions (9:1) under varying conditions of temperature and concentrations of fenuron, surfactant, sodium hydroxide, and salts.

The order of the hydrolytic reaction with respect to fenuron was investigated at different initial concentrations of fenuron in the range of 4.0×10^{-5} to 1.0×10^{-4} mol dm⁻³ in 0.1 mol dm⁻³ NaOH at 80°C. The calculated values of pseudo-first-order rate constants were found to be independent of the initial concentrations of fenuron, thus confirming that the reaction follows first-order kinetics in [fenuron]. A number of kinetic experiments were carried out at fixed [fenuron] $(5.0 \times 10^{-5} \text{ mol dm}^{-3})$ at 80°C in different concentrations of NaOH $(1.0 \times 10^{-2} \text{ to } 1.0 \text{ mol dm}^{-3})$. The obtained values of pseudo-first-order rate constants were found to increase with the increase in [NaOH] linearly



Figure 1 Effect of variation of k on [NaOH] in (O) [aqueous] and (\bullet) [CTAB] media. Reaction conditions: [fenuron] ($5.0 \times 10^{-5} \text{ mol dm}^{-3}$) and [CTAB] ($1.0 \times 10^{-2} \text{ mol dm}^{-3}$) at 80°C.

at low basicity. At higher [NaOH], the values of the rate constant remained almost constant (Fig. 1).

The activation energy and other thermodynamic parameters were calculated from the kinetic runs carried out at fixed concentrations of NaOH (0.1 mol dm⁻³) and fenuron (5.0×10^{-5} mol dm⁻³) within the temperature range of 40–90°C. A straight line (with $r^2 = 0.996$) was obtained for the plot of log k_{obs} versus 1/T. Arrhenius and Eyring equations were used to obtain the values of activation energy, ΔH^{\neq} , ΔS^{\neq} , and ΔG^{\neq} , and these values are given in Table I.

Fenuron is an active phenylurea herbicide consisting of an aromatic ring and a ureic or diamide group in which two methyl groups are attached to the N-atom.



Table IValues of Activation Parameters for theHydrolysis of Fenuron by Sodium Hydroxide in theAbsence and in the Presence of CTAB

Activation Parameters	In the Absence of CTAB	In the Presence of CTAB
$\overline{E_{\rm a}({\rm kJmol^{-1}})}$	51.8	48.3
$\Delta H^{\#} (\mathrm{kJ}\mathrm{mol}^{-1})$	49.3	45.8
$-\Delta S^{\#} (\text{J K}^{-1} \text{ mol}^{-1})$	223.5	235.2

$$\label{eq:constraint} \begin{split} & [Fenuron] = 5.0 \times 10^{-5} \text{ mol } dm^{-3}, \\ & [NaOH] = 1 \times 10^{-1} \text{ mol } dm^{-3}, \\ & [CTAB] = 1.0 \times 10^{-2} \text{ mol } dm^{-3}. \end{split}$$



The reactivity of such a diamide group depends upon the electron-donating or electron-withdrawing nature of the groups attached to N-atoms. The presence of the electron-donating methyl groups in fenuron allows the hydroxyl ion (nucleophile) to attack different basicity sites of the molecule [22].

At lower basicity, OH^- attacks the carbonyl carbon to form intermediate hydroxide ion addition complex. Water acts as a general acid and protonates the intermediate to facilitate the elimination of dimethyl amine along with the formation of carbamate. Therefore, the reaction proceeds through an addition–elimination mechanism as presented in Scheme 1.

The attack by a water molecule on the tetrahedral intermediate followed by the elimination of dimethyl amine is the rate-determining step [7,8]. This results in the formation of phenyl carbamate. The carbamate ion is stable in basic medium [23,24].

Corresponding to Scheme 1, the rate equation is give by

$$Rate = k_{obs} [fenuron]_{T}$$
(1)

$$Rate = \frac{dp}{dt} = k[B]$$
(2)

$$= kK[OH^{-}][A]$$
(3)

where k is the rate constant and K is the equilibrium constant for the formation of hydroxyl addition product B. A is the initial concentration of fenuron.

The total fenuron concentration is given by

$$[A]_{T} = [A] + [B]$$

= [A] + K[OH⁻] [A]
= [A] (1 + K[OH⁻])
$$[A] = \frac{[A]_{T}}{1 + K[OH-]}$$

or



Figure 2 Plot of 1/rate constant (k_{obs} and k_{ψ}) versus 1/[NaOH] for (\bigcirc) [aqueous] and (\bullet) [CTAB] media. Reaction conditions: [Fenuron] (5.0×10^{-5} mol dm⁻³) and [CTAB] (1.0×10^{-2} mol dm⁻³) at 80°C.

On putting the value of [A] in terms of total fenuron concentration, Eq. (3) becomes

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \frac{kK[\mathrm{OH}^-][\mathrm{A}]_{\mathrm{T}}}{1+K[\mathrm{OH}^-]} \tag{4}$$

(5)

or

by inverting Eq. (5), we get

$$\frac{1}{k_{\rm obs}} = \frac{1}{k} + \frac{1}{kK[\rm OH^-]}$$

 $k_{\rm obs} = \frac{kK[\rm OH^-]}{1 + K[\rm OH^-]}$

Thus, a plot of $1/k_{obs}$ versus 1/[NaOH] should give a straight line. The observed results are plotted in Fig. 2, which supports the mechanism presented in Scheme 1, and the intercept and slope of the plot gave the values of *k* and *K*. The values are given in Table II.

In stronger basic media, the hydrolytic reaction is initiated by the formation of conjugate base of phenyl-

Table IIValues of k and K in the Aqueous andPresence of Micelles at 80° C

Reaction Medium	$10^5 k \ (s^{-1})$	$K(\mathrm{mol}^{-1} \mathrm{dm}^3)$
Aqueous	5.87	79.56
CTAB	8.59	72.17

 $[Fenuron] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}, [CTAB] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}.$



Scheme 2

ureas caused by deprotonation of the aryl-NH group as presented in Scheme 2.

In this mechanism (Scheme 2) too, the ratedetermining step is elimination of dimethyl amine from the anion of phenylurea to give phenyl isocyanate. The phenyl isocyanate then reacts rapidly either with water or at pH >8 with hydroxides ion to yield carbamate. Thus, under various concentration ranges of NaOH, the reaction proceeds through the formation of phenyl carbamate (Schemes 1 and 2). In the alkaline medium (at pH >10), the carbamate is relatively long lived. In the acidic and neutral media, the carbamate decarboxylates rapidly to yield aniline [25]. With the increase in basicity, the activity of water (which acts as a general acid) decreases and, therefore, the rate of hydrolysis becomes constant.

Reaction in the Presence of Cationic (CTAB) Micelles

The influence of cationic micelles on the rate of hydrolysis of fenuron was studied under various concentrations of CTAB in the range from 5.0×10^{-4} mol dm⁻³ to 6.0×10^{-2} mol dm⁻³ at a fixed NaOH concentration (0.1 mol dm⁻³) at 80°C. The obtained values of the pseudo-first-order rate constant, k_{ψ} , at different surfactant concentrations are plotted in Fig. 3. The plot shows a peaked behavior in CTAB micelles, in which the maximum rate of hydrolysis is obtained at [CTAB] $(1.0 \times 10^{-2} \text{ mol dm}^{-3})$, and then the rate of hydrolysis decreases on further increase in [CTAB].

The values of the pseudo-first-order rate constant obtained in the presence of cationic ([CTAB] = 1.0×10^{-2} mol dm⁻³) micelles were found to be independent of the initial concentrations of fenuron. The rate of reaction was linearly dependent on [NaOH] initially, but at higher [NaOH] the rate became independent of [NaOH] (Fig. 1). Thus, a similar behavior of variation



Figure 3 Effect of variation of k_{ψ} on [CTAB]. Reaction conditions: [fenuron] (5.0 × 10⁻⁵ mol dm⁻³) and [NaOH] (0.1 mol dm⁻³) at 80°C.

of rate constants on [fenuron] and [NaOH] was observed in the absence and presence of surfactants. A straight-line plot (Fig. 2) for $1/k_{\psi}$ versus 1/[NaOH]too suggests that the reaction followed the same mechanism in both the aqueous and micellar media. The activation parameters were determined from the values of k_{ψ} obtained at different temperatures in the range 40–80°C. The concentrations of fenuron, NaOH, and CTAB were kept constant at 5.0×10^{-5} mol dm⁻³, 0.1 mol dm⁻³, and 1.0×10^{-2} mol dm⁻³, respectively. The values of activation parameters are given in Table I.

The observed variation on the rate of hydrolysis of fenuron in the micellar medium can be explained by means of the pseudophase kinetic model proposed by Menger and Portnoy [26] and later developed by Bunton [16], Romsted [27,28], and Vera and Rodenas [29]. According to the pseudophase kinetic model, the total volume of micelle is considered as a separate phase uniformly distributed in the aqueous phase and the reaction occurs in both the aqueous and micellar phases.

Scheme 3 is, therefore, proposed for the micellarcatalyzed reaction, where S denotes fenuron, D_n the micellized surfactant ($D_n = [\text{total surfactant}] - \text{cmc}]$), and K_s the binding constant ($K_s = [S_m]/[S_w][D_n]$) of fenuron with micelles. Subscripts "w" and "m" denote aqueous and micellar pseudophases, respectively.





Overall, the rate is expressed as

$$V = k_{\psi}[\mathbf{S}_{\mathrm{T}}] = k[\mathrm{OH}_{\mathrm{T}}^{-}][\mathbf{S}_{\mathrm{T}}] = k_{\mathrm{w}}[\mathbf{S}_{\mathrm{w}}] + k_{\mathrm{m}}[\mathbf{S}_{\mathrm{m}}]$$

where

$$[S_T] = [S_w] + [S_m]$$
$$[OH_T^-] = [OH_w^-] + [OH_m^-]$$

and

$$k_{\psi} = \frac{k'_{\rm w} + k'_{\rm m} K_{\rm s}[{\rm D}_{\rm n}]}{1 + K_{\rm s}[{\rm D}_{\rm n}]} \tag{6}$$

The pseudo-first-order rate constants in aqueous (k'_w) and micellar (k'_m) pseudophase are given by

$$k'_{\rm w} = k_{\rm w}[\rm OH_{\rm w}^-] \tag{7}$$

$$k'_{\rm m} = \frac{k_{\rm m}[{\rm OH}_{\rm m}^-]}{D_{\rm n}} = k_{\rm m} m_{\rm OH}$$
 (8)

where m_{OH} is the mole ratio of micellar bound $[OH_m^-]$ to micellar head group. k_m and k_w are second-order rate constants for reactions occurring in micellar and aqueous pseudophases, respectively.

Equation (6) can now be expressed in terms of second-order rate constants as

$$k_{\Psi} = \frac{k_{\rm w}[{\rm OH}_{\rm T}^-] + (k_{\rm m}K_{\rm s} - k_{\rm w})m_{\rm OH}^-[{\rm D}_{\rm n}]}{1 + K_{\rm s}[{\rm D}_{\rm n}]} \quad (9)$$

For a reaction involving ions, Romsted [27] proposed a theoretical method assuming that ions bind to micelles, according to the ion exchange model developed for an ion exchange resin. For the reactive OH^- ion and Br^- as the micelles counterion, the ion exchange equilibrium can be expressed as [29]

$$OH_{w}^{-} + Br_{m}^{-} \rightleftharpoons^{K_{OH/BR^{-}}^{-}} OH_{m}^{-} + Br_{w}^{-}$$
(10)

with an equilibrium constant

$$K_{\rm OH^-/Br^-}^- = \frac{[\rm OH_m^-][\rm Br_w^-]}{[\rm OH_w^-][\rm Br_m^-]}$$
(11)

 m_{OH} in terms of $K_{\text{OH}}^{-}/\text{Br}^{-}$ is given by the following quadratic equation:

$$m_{\rm OH}^{2} + m_{\rm OH} \left[\frac{[\rm OH_{T}^{-}] + K_{\rm OH^{-}/\rm Br^{-}}[\rm Br_{T}^{-}]}{(K_{\rm OH^{-}/\rm Br^{-}} - 1)[\rm D_{n}]} - \beta \right] - \frac{\beta[\rm OH_{T}^{-}]}{(K_{\rm OH^{-}/\rm Br^{-}} - 1)[\rm D_{n}]} = 0$$
(12)

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Table IIIParameter Used to Simulate k_{ψ} – [CTAB]Profile

Parameters	Values	
$\overline{K_{\rm s}~({\rm mol}^{-1}{\rm dm}^3)}$	220.00	
$k_{\rm m} ({\rm mol}^{-1} {\rm dm}^3 {\rm s}^{-1})$	$(1.52 \pm 0.24) \times 10^{-2}$	
β	0.80	
$K_{OH^-/Br}^-$	6.00	
$\operatorname{cmc} (\operatorname{mol} \operatorname{dm}^{-3})$	8.20×10^{-4}	

 $[Fenuron] = 5.0 \times 10^{-5}$ mol dm $^{-3}$, [NaOH] = 0.1 mol dm $^{-3}$, and temperature = $80^\circ C.$

where β is the fraction of neutralized micellar surface and its value for CTAB is 0.80 [11,29].

The reactants exist in dynamic equilibrium between the aqueous and micellar pseudophases. The fitting values of $k_{\rm m}$, $K_{\rm OH^-/_{Br^-}}$, and $K_{\rm S}$ were obtained from the computer program by minimizing the deviation between the simulation and the observed values for the k_{ψ} – [CTAB] profile. The values of these parameters are given in Table III.

The observed higher rate in CTAB could be attributed to the binding of fenuron onto the positively charged micellar surface. The electron-rich carbonyl part of fenuron is oriented toward the positively charged surface of CTAB micelles. The OH- and reactive part of fenuron lie in close proximity to the micellar Stern layer. The other factors that influence the rate of reaction involve the interaction of the polar transition states with asymmetric charged interfacial region, depletion of water in the interfacial region, and its different characteristics as compared to bulk water (polarity of micelles is lower relative to bulk water), the presence of high-ionic concentration in the Stern layer of cationic micelles, the difference in the stabilization of reactant state, and the transition state by hydrophobic interactions with surfactant. With the increase in [CTAB], the local molarities of fenuron and OH⁻ ions in the micellar pseudophase increase and, therefore, the enhancement in the rate of hydrolysis is observed.

Two distinct effects can be considered for the decrease in the rate of hydrolysis at higher CTAB concentrations. First, as the concentration of CTAB increases, the number of the unreactive Br^- ions also increases and replaces micelles-bound OH^- ions. The displacement of OH^- from the vicinity of the Stern layer causes a decrease in $[OH^-]$ in the micellar pseudophase. Second, the increase in CTAB concentration results in the formation of an increased number of micelles and causes dilution of micellar-bound $[OH^-]$. Thus, in both cases, the OH^- concentration in the micellar pseudophase is decreased. It results in the dilution of OH^- in the micellar pseudophase and, therefore, reduces the rate of reaction.



Figure 4 Effect of variation of k_{ψ} on [NaCl] and [KNO₃]. (\blacktriangle for KNO₃ and \blacklozenge for NaCl). Reaction conditions: [fenuron] (5.0 × 10⁻⁵ mol dm⁻³), [CTAB] (1.0 × 10⁻² mol dm⁻³] and [NaOH] (0.1 mol dm⁻³) at 80°C.

Figure 4 shows the effect of added [NaCl] and [KNO₃] on the rate of hydrolysis of fenuron by NaOH in the presence of CTAB micelles. The decreased rate of reaction in the presence of CTAB by NaCl and KNO₃ is attributed to the competitive binding of counterions present with the micelles; therefore, the addition of salt decreases the concentration of OH⁻ in the Stern layer [30–32]. The inhibition is also due to the presence of salts, which increase the aggregation number and reduce catalytic efficiency of the surfactant.

CONCLUSION

The influence of NaOH, CTAB, and temperature on the hydrolytic reaction of fenuron gave detailed information about the reaction pathway. The rate equation consistent with the mechanism of reaction is deduced. The obtained result supports the proposed mechanism. The cationic CTAB micelles enhanced the rate of reaction, and the pseudophase ion exchange model is successfully applied. The hydrolysis of fenuron proceeds through the formation of isocyanate and dimethylamine. The study will be helpful in understanding the mechanism of action of herbicides in biological processes as the surfactant aggregates mimic the enzymes structurally and functionally. The study will also be helpful in predicting the fate of herbicide after its dispersal in the environment

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