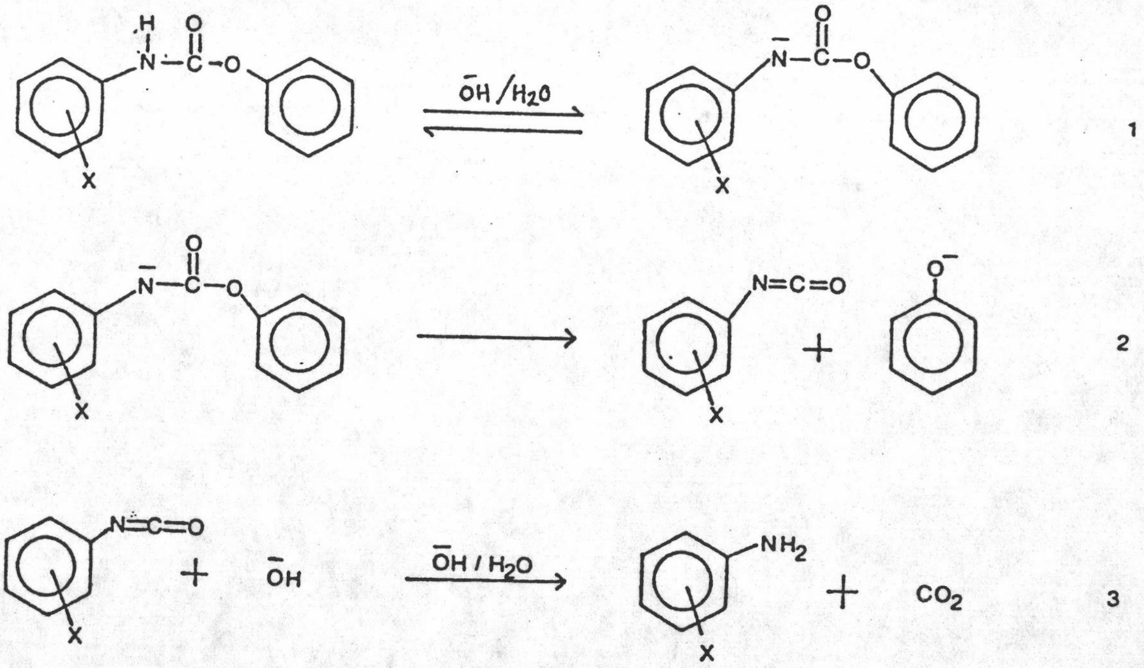
Chapter III

Results and Discussion

The appropriate condition was chosen at pH 11.2 and temperature at 10.C. This condition was used throughout this research. From the results shown in Table 6 and Figure 18, it can be seen that the surfactant has a significant effect upon the hydrolysis rate above the cmc. It clearly shows that micelles indeed catalyse the reaction by approximately 6-570 times as revealed in Table 8 .

Hegaty,et.al.(8-10), reported that the hydrolysis of carbamates in basic solution occurred by competition between elimination-addition(E1cB) mechanism (Scheme3) and intramolecular nucleophilic attack mechanism (Scheme2).

Considering the structures of the carbamate No. I, II, III, IV, V, and VI, the reactions of these carbamates can be taken place under either of both mechanisms only when they are able to undergo to cyclic or isocayanate intermediate. Therefore the carbamates No.II and VI were hydrolyzed very slowly which is consistent with Hegaty's conclusion(9) .



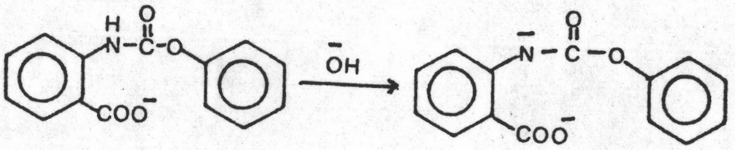
Scheme 3

Using the micelle, which is cationic type, it is found that the micelle can catalyse the reaction . Catalytic effect of micelle to these carbamates is probably due to the electrostatic stabilization of the developing negative charge on the transition state and the local concentration of the substrate in micellar system(5,6) .

In the aqueous solution alone, the observed rate (k_w) of the reaction increases as the following order.

$$V > I \approx IV > III$$

From the mechanism which was proposed by Hegaty, et.al. (8-10), the stable six-memberred ring intermediate which was stabilized with fused benzene ring and the methyl group, the electron donating group, could be found from the carbamate No.V, hence the k_{obs} of the carbamate No.V was fastest in the series. The carbamate No.III gave the least value of k_w. This is due to the two negative charges (dianion) in equation 6 which are close to each other. Therefore a great influence on the stability of the intermediate is observed.



(6)

At the same time, the reactions of the carbamate No.I and IV can take place by the formation of an isocyanate . Though, there is COO group in the carbamate No.IV, no effect on the reaction is observed . Indeed, the o-value had been reported(14) as zero.

In the micellar system, the electrostatic stabilization and the local concentration of the substrate around a micelles will have a role to the reaction. From k_m and K/N value of different carbamates (Table 8) indicate that the order of k_m parallels to the order of k_m/k_w and inverts to the order of k_w as shown below:

III > IV > I > V

This phenomenon is consistent with the result reported by Berndt,D.C. and Utrapiromsuk,N.(15) . It has been shown that the intramolecular nucleophilic catalysis is enhanced by micelles of CTAB(16,17). The rates of reactions of carbamate No.III and V in CTAB are faster by 570 times and 6 times than in water, respectively.

The inversion of the order of the rate constants in water(k_w) and in micellar environment(k_m) of carbamate No.IV is probably due to the electrostatic stabilization of the cationic stern layer to either the anion or dianion of carbamate No.III. For carbamate No.V, it gave the lowest k_m in the series. This is probably due to the methyl group at the nitrogen atom which makes it more soluble into the core of the micelle. Hence, there was low concentration of either the water molecule or the hydroxyl ions (3,18) in this region. Therefore the k_m is the lowest. The similar reason could be explained for carbamate No.IV and I. Because of the presence of the carboxylate group, carbamate No.IV, is more polar than carbamate No.I . Thus, the k_m value of carbamate No.IV is higher than carbamate No.I .

The location of a substrate in the micelle can roughly be located from the value of both k_m and K(1). The high k_m means the reaction is likely occurred at either outside the micelle but close to the stern layer as shown in Figure 20 (position 1) or inside the micelle but close to the layer (position 2). The low k_m means the reaction is likely occurred at either a far distance from the micelle (position 3) or in the core of the micelle (position 4) and the K values will be in order as following.

$$K_4 > K_2 > K_1 > K_3$$

From the K value, one can predict the more exact location of the reaction which occurs.

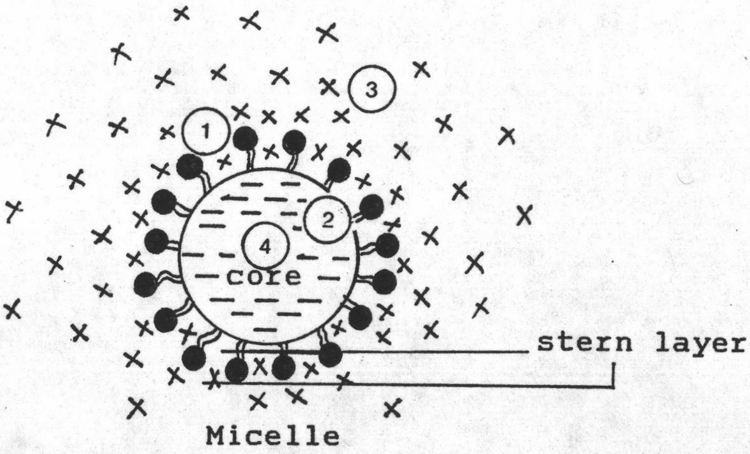


Figure 20. The position of the substrate which affects to the reaction.

In conclusion, the micelles can indeed catalyze the basic hydrolysis of the carbamates provided that the structures these carbamates must be able to transform to the cyclic or isocyanate intermediates. The electrostatic stabilization, the local concentration of the reagents and the location of the substrate play the major effects to the rate of the reaction (k_m).

In order to elucidate substituent effect and to correlate with the reaction rates ,k_m , k_w and K/N , further investigation of more and different substituents such as -OMe, -COOMe, -Br, -Cl at either meta or para position must be studied.