

# KINETICS AND MECHANISM OF HYDROLYSIS OF 1-NAPHTHYL N-METHYL- AND N,N-DIMETHYLCARBAMATES

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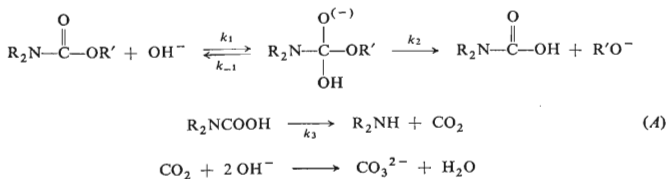
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Hydrolysis rate constants of 1-naphthyl N-methylcarbamate (*I*) and 1-naphthyl N,N-dimethylcarbamate (*II*) have been determined in the pH range 0 to 13 and in  $H_0$  range 0 to  $-8$ . In the alkaline region the carbamate *I* hydrolyzes more rapidly than the carbamate *II* by six orders of magnitude. The solvolysis is slowest and independent of  $OH^-$  ( $H^+$ ) concentration in the pH regions 0–7 and 2–9 for the carbamates *I* and *II* respectively. In the acid medium the hydrolysis rate increases again, and, in the case of the carbamate *I*, it reaches a maximum at 50% sulphuric acid concentration, whereafter it decreases abruptly; in the case of the acid hydrolysis of the carbamate *II*, on the contrary, the maximum has been attained at 70% sulphuric acid concentration, and further increase of the acid concentration has not affected the hydrolysis rate. The mechanism of the hydrolysis of the both carbamates in the medium investigated is discussed.

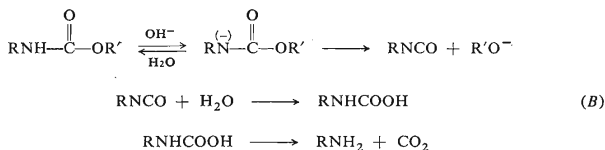
Reactions of carbonic acid derivatives have been the object of intensive studies for a long time. A special attention has been given to the catalytic action of acids and bases during their esterification and hydrolysis. A lot of data have been gathered concerning especially the influence of structure on the reactivity of these systems. Most of the works deal, however, with the reactions of esters, whereas amide hydrolysis has been less studied. The reactions of carbamic acid and its derivatives have been given little attention.

Bender<sup>1</sup> published a survey of works concerning the mechanisms of reactions of carbonic acid derivatives (except for carbamic acid derivatives). Alkaline hydrolysis of some esters of carbamic acid was studied by Christensen<sup>2</sup> who found that the N-substituted carbamates are less resistant to alkaline hydrolysis than the N,N-disubstituted ones. This difference is greater than 6 orders of magnitude in several cases. Therefrom it obviously follows a duality of hydrolysis

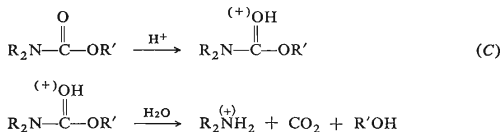


mechanisms of those carbamates caused by the presence of hydrogen at nitrogen. For the alkaline hydrolysis of *N,N*-dialkylcarbamates the mechanism (A) can be accepted in general which is analogous to the hydrolysis mechanism of esters and consists in an acyl-oxygen bond splitting ( $A_{Ac} 2$ ) proceeding in two steps. The addition of  $\text{OH}^-$  ion to the carboxyl group results in a formation of a tetrahedral intermediate which is split into dialkylcarbamic acid and alcoholate. Further reactions of dialkylcarbamic acid leading to final products proceed quickly and do not make themselves felt kinetically.

The rate increase of hydrolysis of *N*-substituted carbamates as compared to *N,N*-dialkylcarbamates was explained<sup>2</sup> by that the acid-base equilibrium was established rapidly in alkaline medium, the conjugate base of *N*-alkylcarbamate being split to give isocyanate in the rate-determining step. Further reaction of isocyanate with water is not significant kinetically. Bender<sup>3</sup> confirmed this mechanism on the basis of studies of alkaline hydrolysis of *p*-nitrophenyl *N*-methylcarbamate. He proved that the hydrolysis rate did not practically depend on buffer concentration, that the NH hydrogen exchanged in neutral deuterium oxide with a half-life smaller than 20 seconds, and that the hydrolysis rate was greater in deuterium oxide than in water. All these findings support the mechanism given (B).



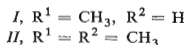
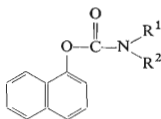
Mechanism of carbamate hydrolysis in acid medium was studied in the case of urethan and its *N*-alkyl derivatives substituted differently at oxygen<sup>4-6</sup>. It is presumed that, in acid medium, the reaction rate is determined by nucleophilic attack of water at the carbonyl carbon atom of the molecule protonated in a foregoing equilibrium step:



Studying the influence of substituents, Armstrong<sup>6</sup> arrived at the conclusion that the carbamate protonated at ether oxygen is the most probable tautomer undergoing the splitting by the attack of a water molecule. A change in mechanism can take place in strongly acid medium, the decomposition of the protonated carbamate being not assisted by solvent (A1 mechanism). Kinetics and mechanism of carbamate hydrolysis in regions near to neutral have not yet been carried out.

The aim of this work was a study of hydrolysis of suitably chosen derivatives of carbamic acid in media of very different acidities which would make it possible to estimate the behaviour of a given compound from a strongly alkaline to strongly acid region. 1-Naphthyl *N*-methylcarbamate (I) and 1-naphthyl *N,N*-dimethylcarbamate (II) were chosen as models because of their suitable properties for kinetic

studies. These compounds are readily available in sufficient purity, they are enough soluble in water, and the course of their hydrolysis can be followed by analytical methods of sufficient accuracy.



## EXPERIMENTAL

### Reagents

*1-Naphthyl N-methylcarbamate (I)*. 20.6 g (0.1 mol) 1-naphthyl chloroformate<sup>7</sup> was dissolved in 100 ml toluene and mixed with a solution of 6.8 g (0.22 mol) methylamine in 70 ml toluene. After 1.5 hours standing the precipitated methylamine hydrochloride was filtered off. The filtrate was evaporated *in vacuo* to about 20 ml and cooled. The raw product precipitated was recrystallized from ethyl acetate. Yield 11.05 g (55%), m.p. 143–144°C in accord with ref.<sup>8</sup>.

*1-Naphthyl N,N-dimethylcarbamate (II)*. The raw product was obtained by the above-mentioned procedure from the solutions of 20.6 g (0.1 mol) 1-naphthyl chloroformate in 100 ml toluene and 9.9 g (0.22 mol) dimethylamine in 70 ml toluene. It was recrystallized from *n*-hexane to give 11.0 g (51.1%) product melting<sup>8</sup> at 55–56°C.

### Kinetic Measurements

*Spectral method*. The buffer solution (3 ml) was placed into a cell located in the thermostated cell-holder ( $25 \pm 0.1^\circ\text{C}$ ) of a spectrophotometer Unicam SP 800. After 5 minutes,  $0.16 \text{ ml } 4 \cdot 10^{-2} \text{ M}$  carbamate *I* or *II* was injected from a syringe. The time dependence of extinction was followed at the wavelength of the maximum absorption of 1-naphthol ( $\lambda_{\text{max}}$  325 nm). A discontinuous method was chosen for those pH ( $H_0$ ) ranges where the reaction was slow. The reaction was carried out in sealed glass tubes at 100°C, or 120°C. At definite time intervals samples were withdrawn and the extinction of 1-naphthol measured by means of a VSU 2P spectrophotometer (Zeiss, Jena). Buffer solutions<sup>9</sup> and aqueous sulphuric acid<sup>10</sup> were used for the proper measurements. The buffers were prepared from p.a. chemicals, deionized redistilled water, and 98% deuterium oxide. The pH values were determined by means of a PHM 4c apparatus (Radiometer, Copenhagen) using a G 200 b glass and a saturated calomel electrodes separated by agar bridge. The sulphuric acid concentration was determined by potentiometric titration<sup>11</sup>. Each sample was titrated three times and the corresponding  $H_0$  value was read from graphs.

*Kinetic measurements in strongly acid medium*. In this region the rate constant was determined on the basis of determination of the carbon dioxide formed<sup>12</sup>. About 0.1 g of the substance was placed in a 250 ml flask located in a thermostat and equipped with a nitrogen inlet tube (carrier-gas), separating funnel and an outlet tube. After adjusting the required temperature, the solution of sulphuric acid of known concentration was added. The gas leaving the reaction flask passed through a safety bottle with glass wool and through a three-way tap into an absorption bottle containing 0.1M-Ba(OH)<sub>2</sub>. The free barium hydroxide was determined beside barium carbonate

TABLE I  
Hydrolysis Rate Constants of Carbamate I for Various pH Values, Temperatures and Buffer Concentrations

pH	°C	$k', s^{-1}$	$k, l mol^{-1} s^{-1}$
11.87	25	$3.74 \cdot 10^{-1}$	$5.03 \cdot 10^1$
11.39	25	$1.23 \cdot 10^{-1}$	$5.01 \cdot 10^1$
11.20	25	$7.21 \cdot 10^{-2}$	$4.99 \cdot 10^1$
10.70	25	$2.47 \cdot 10^{-2}$	$5.00 \cdot 10^1$
10.56	25	$7.67 \cdot 10^{-3,a}$	—
		$7.67 \cdot 10^{-3,b}$	—
		$7.66 \cdot 10^{-3,c}$	—
		$7.67 \cdot 10^{-3,d}$	—
10.42	25	$1.20 \cdot 10^{-2}$	$5.01 \cdot 10^1$
10.00	25	$4.61 \cdot 10^{-3}$	$5.01 \cdot 10^1$
9.54	25	$1.73 \cdot 10^{-3}$	$5.01 \cdot 10^1$
9.48	40	$5.50 \cdot 10^{-3}$	$1.81 \cdot 10^3$
	50	$1.44 \cdot 10^{-2}$	$4.91 \cdot 10^3$
	60	$3.37 \cdot 10^{-2}$	$1.11 \cdot 10^4$
	70	$7.55 \cdot 10^{-2}$	$2.48 \cdot 10^4$
9.08	25	$5.73 \cdot 10^{-4}$	$5.00 \cdot 10^1$
8.20	25	$8.06 \cdot 10^{-5}$	$5.02 \cdot 10^1$
7.01	25	$4.99 \cdot 10^{-6}$	$4.99 \cdot 10^1$
6.77	100	$1.13 \cdot 10^{-4,e}$	—
		$1.17 \cdot 10^{-4,f}$	—
		$1.13 \cdot 10^{-4,g}$	—
		$1.13 \cdot 10^{-4,h}$	—
6.23	80	$3.69 \cdot 10^{-5}$	—
	90	$6.61 \cdot 10^{-5}$	—
	100	$1.15 \cdot 10^{-4}$	—
	25	$8.85 \cdot 10^{-7,i}$	—
5.09	100	$1.24 \cdot 10^{-4}$	—
	25	$9.03 \cdot 10^{-7,i}$	—
4.48	100	$1.19 \cdot 10^{-4}$	—
	25	$8.89 \cdot 10^{-7,i}$	—
2.87	100	$1.19 \cdot 10^{-4}$	—
	25	$8.97 \cdot 10^{-7,i}$	—
0.83	100	$1.16 \cdot 10^{-4}$	—
	25	$8.98 \cdot 10^{-7,i}$	—
-0.28	25	$8.52 \cdot 10^{-7}$	—
-0.67	25	$8.52 \cdot 10^{-7}$	—
-1.06	25	$1.61 \cdot 10^{-6}$	$1.41 \cdot 10^{-7}$
-2.01	25	$1.38 \cdot 10^{-5}$	$1.39 \cdot 10^{-7}$
-2.80	25	$9.12 \cdot 10^{-5}$	$1.43 \cdot 10^{-7}$
	50	$6.54 \cdot 10^{-4}$	$1.04 \cdot 10^{-6}$
	70	$1.42 \cdot 10^{-3}$	$2.25 \cdot 10^{-6}$

TABLE I  
(Continued)

pH	°C	$k'$ , s <sup>-1</sup>	$k$ , l mol <sup>-1</sup> s <sup>-1</sup>
-3.95	25	$1.35 \cdot 10^{-3}$	$1.39 \cdot 10^{-7}$
-3.97	25	$9.44 \cdot 10^{-4}$	—
-4.27	25	$1.02 \cdot 10^{-4}$	—
-4.51	25	$2.07 \cdot 10^{-5}$	—
-5.82	25	$6.14 \cdot 10^{-6}$	—
7.36	25	$2.75 \cdot 10^{-6}$	—

<sup>a</sup>Buffer concentration  $2.91 \cdot 10^{-3}$  mol l<sup>-1</sup>; <sup>b</sup> $3.84 \cdot 10^{-3}$  mol l<sup>-1</sup>; <sup>c</sup> $5.74 \cdot 10^{-3}$  mol l<sup>-1</sup>; <sup>d</sup> $7.87 \cdot 10^{-3}$  mol l<sup>-1</sup>; <sup>e</sup> $1.0 \cdot 10^{-4}$  mol l<sup>-1</sup>; <sup>f</sup> $1.5 \cdot 10^{-4}$  mol l<sup>-1</sup>; <sup>g</sup> $2.0 \cdot 10^{-4}$  mol l<sup>-1</sup>; <sup>h</sup> $2.5 \cdot 10^{-4}$  mol l<sup>-1</sup>; <sup>i</sup> extrapolated value of rate constant.

by titration with 0.1M oxalic acid using phenolphthalein as indicator. The absorption bottles were closed by means of tubes packed with soda lime and connected with the three-way tap, so that the exchange of the absorber could be done without interruption of the absorption.

The rate constants  $k'$  were computed from the time dependence of the concentration increase of the 1-naphthol (CO<sub>2</sub>) formed according to the relations (1) and (2)

$$k't = 2.303 \log (E_{\infty}/(E_{\infty} - E_t)), \quad (1)$$

$$k't = 2.303 \log (100/(100 - A)), \quad (2)$$

where  $E_t$  and  $E_{\infty}$  stand for the extinction of 1-naphthol at a time  $t$  and  $t = \infty$  respectively, and  $A$  for the percentage of the carbon dioxide formed. The  $k'$  constant was obtained from the plots of  $\log (E_{\infty}/(E_{\infty} - E_t))$  resp.  $\log (100/(100 - A))$  vs time, or otherwise the values  $t$  were plotted against  $\log (E_{\infty} - E_t)$  and the reaction half-life obtained therefrom ( $t_{1/2}$ ). The  $k'$  constant was then computed according to Eq. (3).

$$k' = 2.303 \log 2/t_{1/2}. \quad (3)$$

## RESULTS AND DISCUSSION

### Hydrolysis in Alkaline Medium

From the results of the measurements of the carbamate I hydrolysis (Table I, Fig. 1) it follows that the reaction rate obeys the relation (4) in the pH range 7.0–11.8.

$$k' = k[\text{OH}^-]. \quad (4)$$

TABLE II

Hydrolysis Rate Constants of Carbamate II for Various pH Values, Temperatures and Buffer Concentrations

pH	°C	$k', s^{-1}$	$k, l mol^{-1} s^{-1}$
0.06 <sup>a</sup>	25	$1.73 \cdot 10^{-5}$	$2.87 \cdot 10^{-4}$
0.10 <sup>a</sup>	25	$2.53 \cdot 10^{-5}$	$2.53 \cdot 10^{-4}$
0.20 <sup>a</sup>	25	$5.00 \cdot 10^{-5}$	$2.50 \cdot 10^{-4}$
0.40 <sup>a</sup>	25	$1.15 \cdot 10^{-4}$	$2.77 \cdot 10^{-4}$
0.60 <sup>a</sup>	25	$1.50 \cdot 10^{-4}$	$2.89 \cdot 10^{-4}$
13.44	120	$3.08 \cdot 10^{-4}$	$1.12 \cdot 10^{-3}$
	100	$8.64 \cdot 10^{-5}$	$3.13 \cdot 10^{-4}$
	90	$3.30 \cdot 10^{-5}$	$1.20 \cdot 10^{-4}$
	80	$3.08 \cdot 10^{-4}$	$4.55 \cdot 10^{-5}$
	25 <sup>b</sup>	$5.61 \cdot 10^{-8,b}$	$2.04 \cdot 10^{-7}$
12.56	100	$1.15 \cdot 10^{-5}$	—
	25	$7.48 \cdot 10^{-9,b}$	$2.05 \cdot 10^{-7}$
12.26	100	$5.99 \cdot 10^{-6}$	
	25	$3.89 \cdot 10^{-9,b}$	$2.06 \cdot 10^{-7}$
11.26	100	$5.53 \cdot 10^{-7}$	
	25	$3.89 \cdot 10^{-10,b}$	$2.03 \cdot 10^{-7}$
10.11	100	$3.46 \cdot 10^{-8,c}$	
		$3.45 \cdot 10^{-8,d}$	
		$3.46 \cdot 10^{-8,e}$	
		$3.46 \cdot 10^{-8,f}$	
10.01	120	$8.08 \cdot 10^{-7}$	
	25	$1.76 \cdot 10^{-11,b}$	
8.95	120	$8.06 \cdot 10^{-7}$	
	25	$1.75 \cdot 10^{-11,b}$	
7.03	120	$8.06 \cdot 10^{-7}$	
	25	$1.75 \cdot 10^{-11,b}$	
4.98	120	$8.08 \cdot 10^{-7}$	
	100	$1.45 \cdot 10^{-7}$	
	90	$6.24 \cdot 10^{-8}$	
	80	$2.30 \cdot 10^{-8}$	
	25	$1.76 \cdot 10^{-11,b}$	
3.01	120	$8.06 \cdot 10^{-7}$	
	25	$1.75 \cdot 10^{-11,b}$	
2.99	120	$8.05 \cdot 10^{-7,g}$	
		$8.04 \cdot 10^{-7,h}$	
2.99	120	$8.04 \cdot 10^{-7,i}$	
		$8.05 \cdot 10^{-7,j}$	
2.29	120	$8.08 \cdot 10^{-7}$	
	25	$1.76 \cdot 10^{-11,b}$	
0.88	90	$1.97 \cdot 10^{-7}$	
	25	$1.72 \cdot 10^{-10,b}$	$1.26 \cdot 10^{-9}$

TABLE II

(Continued)

pH	°C	$k'$ , s <sup>-1</sup>	$k$ , l mol <sup>-1</sup> s <sup>-1</sup>
-0.20	90	2.28 · 10 <sup>-6</sup>	
	25	1.99 · 10 <sup>-9,b</sup>	1.09 · 10 <sup>-9</sup>
-1.10	90	1.59 · 10 <sup>-5</sup>	
	25	1.38 · 10 <sup>-8,b</sup>	1.11 · 10 <sup>-9</sup>
-1.88	90	9.57 · 10 <sup>-5</sup>	
	25	8.35 · 10 <sup>-8,b</sup>	1.09 · 10 <sup>-9</sup>
-3.01	25	1.09 · 10 <sup>-6</sup>	1.10 · 10 <sup>-9</sup>
-4.08	25	1.34 · 10 <sup>-5</sup>	1.09 · 10 <sup>-9</sup>
-5.28	120	2.75	1.44 · 10 <sup>-5</sup>
	100	5.07 · 10 <sup>-1</sup>	2.66 · 10 <sup>-6</sup>
	90	2.11 · 10 <sup>-1</sup>	1.11 · 10 <sup>-6</sup>
	80	8.64 · 10 <sup>-2</sup>	4.53 · 10 <sup>-7</sup>
	25	2.07 · 10 <sup>-4</sup>	1.09 · 10 <sup>-9</sup>
-5.80	25	5.78 · 10 <sup>-4</sup>	1.10 · 10 <sup>-9</sup>
-6.50	25	4.70 · 10 <sup>-4</sup>	
-7.21	25	3.29 · 10 <sup>-4</sup>	
-8.00	25	3.10 · 10 <sup>-4</sup>	

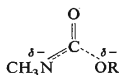
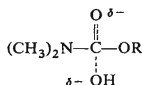
<sup>a</sup>Concentration of hydroxyl ion; <sup>b</sup>extrapolated value of rate constant; <sup>c</sup>buffer concentration 2.0 · 10<sup>-3</sup> mol l<sup>-1</sup>; <sup>d</sup>2.5 · 10<sup>-3</sup> mol l<sup>-1</sup>; <sup>e</sup>3.0 · 10<sup>-3</sup> mol l<sup>-1</sup>; <sup>f</sup>3.5 · 10<sup>-3</sup> mol l<sup>-1</sup>; <sup>g</sup>1.0 · 10<sup>-4</sup> mol l<sup>-1</sup>; <sup>h</sup>1.5 · 10<sup>-4</sup> mol l<sup>-1</sup>; <sup>i</sup>2.0 · 10<sup>-4</sup> mol l<sup>-1</sup>; <sup>j</sup>2.5 · 10<sup>-4</sup>.

At a constant pH value the concentration of the carbamate *I* has no influence on the experimental rate constant. At a pH higher than 11.9 the reaction proceeds so rapidly that it cannot be followed with sufficient accuracy by the method used.

The hydrolysis of the carbamate *I* proceeds about 100× more slowly than that of *p*-nitrophenyl N-methylcarbamate<sup>5</sup> under the same conditions<sup>3</sup> ( $k_i/k_{ph} = 1.27 \cdot 10^{-2}$ ). Using the value  $\rho = 2.5$  for the alkaline hydrolysis of the substituted phenyl esters of N-methylcarbamic acid<sup>3</sup>, we can estimate that the phenyl ester hydrolyzes at about the same velocity as the carbamate *I* measured by us. Thus we can presume that the alkaline hydrolysis of the carbamate *I* proceeds by the same mechanism as that of *p*-nitrophenyl N-methylcarbamate (Scheme (B)). This presumption is also supported by the fact that the respective N,N-dimethyl derivative hydrolyzes more slowly by 6 orders of magnitude at the same pH (Table II). A further support is supplied by the fact that the solvolysis rate is independent of buffer concentration (Table I) (The angular coefficient of the dependence pH vs log  $k'$  equals 1.01 in the pH range 7.0–11.8).

The activation energy of the hydrolysis of the carbamate *I* ( $E_a = 16.5$  kcal/mol), stands in good accord with the values found<sup>2</sup> for hydrolyses of carbamates having similar structures. The activation entropy of its hydrolysis ( $\Delta S = 0.6$  e.u.) is more positive than that of the carbamate *II* by 28 e.u. This finding agrees with the steric arrangement of the activated complex *III* of the splitting of 1-naphthyl N-methylcarbamate anion being more advantageous than the arrangement of the activated complex *IV* of the hydrolysis of 1-naphthyl N,N-dimethylcarbamate anion which needs an oriented collision of two particles.

Hydrolysis	<i>I</i>		<i>II</i>	
	$E_a$ , kcal mol <sup>-1</sup>	$\Delta S$ , e.u.	$E_a$ , kcal mol <sup>-1</sup>	$\Delta S$ , e.u.
Alkaline	16.5	+0.6	21.9	-28.6
Neutral	20.7	-25.6	26.5	-31.4
Acid	16.5	-23.8	23.5	-25.8

*III**IV*

R = 1-naphthyl

The kinetic measurements of the alkaline solvolysis of the carbamate *II* (Table II, Fig. 1) were carried out in an excess of the substrate under the conditions of pseudo-

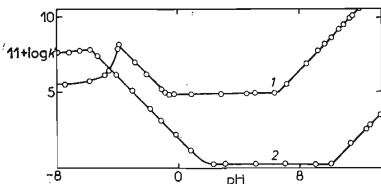


FIG. 1

Dependence of Logarithm of Hydrolysis Rate Constant of Carbamates *I* (1) and *II* (2) on pH

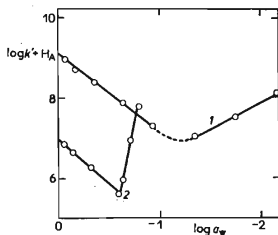


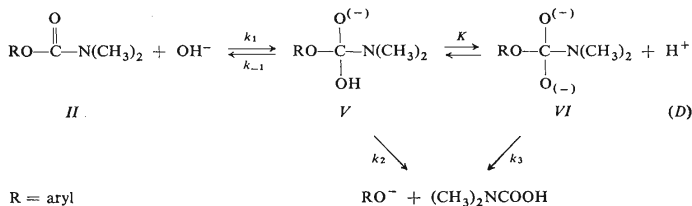
FIG. 2

Dependence of  $(\log k' + H_A)$  on  $\log a_w$  for Carbamates *I* (2) and *II* (1)



monomolecular reaction. In the pH range 10.0–13.5 the reaction rate follows the Eq. (4). It was found that the rate constant observed does not depend on the carbamate II concentration at a constant pH (Table II). The found higher  $E_a = 21.9$  kcal/mol and  $\Delta S = -28.6$  e.u. show that the base catalyzed hydrolysis proceeds by a mechanism different from the previous one. This is also supported by the large difference between the both rate constants.

We measured the alkaline hydrolysis rate of the carbamate II in a strongly basic medium. From Table II it can be seen that the observed rate constant  $k'$  of the pseudo-monomolecular reaction is directly proportional to the  $\text{OH}^-$  concentration.



The relation (5) can be derived for the velocity of the reaction represented by Eq. (D) ( $K$  stands for  $[VI]/[V][\text{OH}^-]$ ).

$$v = k_{\text{exp}}[\text{II}][\text{OH}^-] = \frac{k_1[\text{II}][\text{OH}^-](k_2 + k_3K[\text{OH}^-])}{k_{-1} + (k_2 + k_3K[\text{OH}^-])} \quad (5)$$

Eq. (5) can be simplified to give Eqs (6), (7) or (8), if  $(k_2 + k_3K[\text{OH}^-]) \gg k_{-1}$ ,  $k_{-1} \gg k_2 \gg k_3K[\text{OH}^-]$ , or  $k_2 \ll k_3K[\text{OH}^-] \ll k_{-1}$  respectively.

$$v = k_1[\text{II}][\text{OH}^-], \quad (6)$$

$$v = k_1k_2/k_{-1}[\text{II}][\text{OH}^-] = k'[\text{II}][\text{OH}^-], \quad (7)$$

$$v = k_1k_3K[\text{II}][\text{OH}^-]^2/k_{-1} = k''[\text{II}][\text{OH}^-]^2. \quad (8)$$

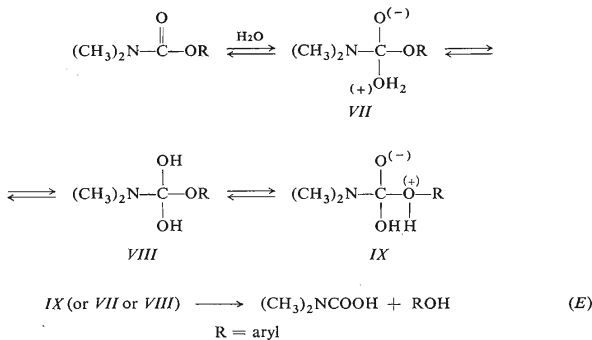
As the reaction was found to be 1. order in  $\text{OH}^-$  ions, the mechanism characterized by the splitting of dianions<sup>13</sup> (Eq. (D)) cannot be considered at least in the hydroxyl ion concentration range studied.

The kinetic experiments cannot differentiate between the following two alternatives of mechanism: a) A slow attack of the substrate by  $\text{OH}^-$  ion in the rate-determining step, the subsequent decomposition of the intermediate into products being rapid and the reverse splitting of the intermediate into the starting species being negligible.

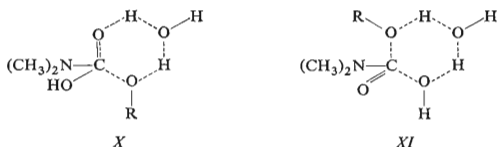
b) The reaction rate is determined by the attack of the substrate by  $\text{OH}^-$  ions, the reverse splitting of the intermediate into starting species being, however, faster than its decomposition into the reaction products. As 1-naphtholate is a far better leaving group than hydroxyl ion, the first possibility of the reaction course seems much more probable.

### Hydrolysis in Neutral Medium

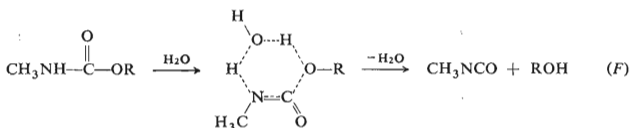
The solvolysis rate in neutral medium at  $25^\circ\text{C}$  is so low that it cannot be determined experimentally. Therefore, we followed the solvolysis at the temperatures  $10$  and  $120^\circ\text{C}$  and converted the results of measurements to the temperature  $25^\circ\text{C}$  (Tables I, II). As it can be seen in Table I, the reaction is not base catalyzed, and the solvolysis rate does not change with buffer concentration at a constant ionic strength. In the pH range  $6.2$  to  $-0.8$  the reaction is independent of hydroxyl ion resp. proton concentration. In this pH range, only a spontaneous hydrolysis by water takes place. The ratio of the reaction rate constant in deuterium oxide to that in water is  $0.33$ . This kinetic isotopic effect suggests<sup>14</sup> a splitting of  $\text{O}-\text{H}$  resp.  $\text{O}-\text{D}$  bond in the activated complex of the rate-determining step. The results of hydrolyses of the carbamate *II* in neutral medium are presented in Table II. In the pH range  $2.3-9.0$ , the reaction is independent of the proton resp. hydroxyl ion concentration. According to the analogy with the spontaneous ester solvolysis, we could consider a mechanism characterized by formation of the tetrahedral intermediate *VII* or its tautomers *VIII* or *IX* for the solvolysis of the carbamates *I* and *II* (Eq. (E)).



From the kinetic isotopic effect it follows that the activated complex of the rate-determining step of the spontaneous solvolysis could be represented as *X* or *XI*.



We found that the spontaneous hydrolysis of the carbamate *I* is faster than that of *II* by  $5.15 \cdot 10^4$ . Therefore it is not quite out of the question that the substantially faster solvolysis of the carbamate *I* is caused by a more advantageous arrangement of the activated complex of the rate-determining step characterized by splitting of N—H bond (Eq. (F)).



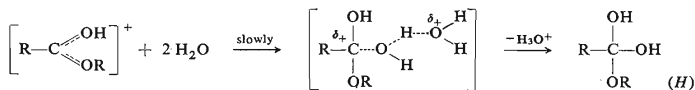
#### Hydrolysis in Acid Medium

The results of kinetic measurements of the hydrolysis of the carbamate *II* in the medium of 10–85% aqueous sulphuric acid are given in Table II. The reaction rate is unmeasurably low in 10–45% sulphuric acid at 25°C, and, therefore, we carried out the kinetic measurements at 90°C. The reaction rate follows the relation (9) in the pH and  $H_0$  ranges 1.0 – 0.0 and –0.2 to –5.8 respectively. Number of the water molecules involved in the activated complex can be estimated from the dependence  $(10)^{15-17}$  (Table III) in the acidity region  $H_0 < K_A$ .

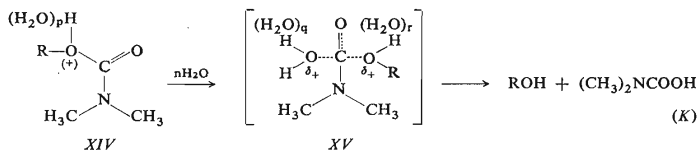
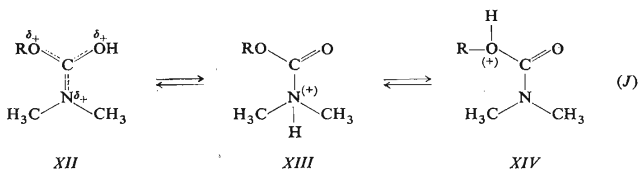
$$\log k' = \log k - H_0, \quad (9)$$

$$\log k' + H_A = r \log a_w + \text{const.} \quad (10)$$

From the angular coefficient  $r = 2.1$  of the dependence it would follow that the attack of the protonated carbamate *II* by two water molecules represented the rate-determining step. With respect to the fact that the dependence on water activity ( $a_w$ ) was ascertained by means of the  $H_A$  scale constructed for the protonation of amides, the value calculated ( $r = 2.1$ ) must be taken as preliminary. A mechanism of  $A_{Ac}^2$  type was suggested<sup>18</sup> for the ester hydrolysis, the respective activated complex of the rate-determining step consisting of the protonated ester molecule attacked by two water molecules and then decomposing to the tetrahedral intermediate (Eq. (H)).



According to Armstrong<sup>4-6</sup> the carbamate hydrolysis seems to be similar to the  $\text{S}_{\text{N}}2$  mechanism in contrast to the acid hydrolysis of esters and amides going through tetrahedral intermediates. In our case, the tautomer *XIV* could be considered to be the most probable of possible tautomers of the protonated carbamate *II* (Eq. (J)) in this mechanism, and the activated complex of the substitution mechanism could be represented<sup>15,17</sup> as *XV* (Eq. (K)) where  $(p+n) = (q+r)$ , and  $n = 2$ .



The solvolysis rate of the carbamate *I* (Table I) in the  $\text{H}_0$  range  $-1.0$  to  $-4.0$  agrees with the relation (10). It was found  $r = 2.2$  similarly to the previous case. The constant ratio of the rate constants of hydrolyses of the carbamates *I* and *II* ( $k^{\text{I}}/k^{\text{II}} = 1.27 \cdot 10^2$ ) in the region of 15–45% aqueous sulphuric acid suggested that the both reactions followed the same mechanism. It was, however, found that N-methyl substitution increased the reaction rate in the case of carbamate hydrolysis in sulphuric acid. *E.g.* the hydrolysis rate of ethyl N,N-dimethylcarbamate is about 4 times higher than that of ethyl N-methylcarbamate in 39% sulphuric acid<sup>6</sup> at 64°C. In our case, however, the hydrolysis rate of the N-methylcarbamate *I* is higher than that of the N,N-dimethylcarbamate *II* by more than 2 orders of magnitude. Hence the identity of the mechanisms of the hydrolyses of the carbamates *I* and *II* is not very probable. The proton at nitrogen seems to have a specific role in the hydrolysis mechanism even in acid medium.

In the case of the hydrolysis of the carbamate *I* an abrupt break is encountered at 50% concentration of sulphuric acid (Table I, Fig. 1), and in the region of 50–65% sulphuric acid the reaction rate decreases. In 50% sulphuric acid, almost all the carbamate is protonated and the rate decrease is caused by the decreasing water activity with increasing acidity of the medium. As we could not determine the dissociation constant of the conjugate acid of the carbamate *I*, we cannot decide whether the solvolysis proceeds by the same mechanism in the region of 50–65% sulphuric acid. The solvolysis rate of the carbamate *I* in 65% sulphuric acid is practically constant again. Owing to the lack of experimental data, we cannot suggest the reaction mechanism in this strongly acid medium yet. It seems, however, that the assistance of water molecules need not be considered in the rate-determining step.

The carbamate *II* solvolyzes substantially more rapidly than the carbamate *I* in strongly acid medium, and in the range of 70–85% sulphuric acid the solvolysis rate does not practically depend on the water activity (the angular coefficient of the dependence  $k_{\text{obs}}$  on  $H_0$  equals  $-0.16$ ). From this dependence it can be judged that the reaction mechanism differs from that of the solvolysis of the carbamate *I*, the dominant reaction being probably of an  $A_{Ac}1$  type, *i.e.* the carbamate protonated at the ether oxygen is split into 1-naphthol and N,N-dimethylcarbamoyl cation (*XVI*) in the rate-determining step, and the cation *XVI* decomposes quickly to the final products (Eq. (L)).

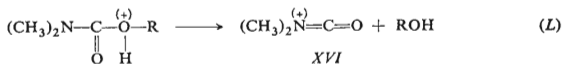


TABLE III

Values of  $(\log k' + H_A)$  and  $\log a_w$  for Carbamates *I* and *II*

<i>I</i>			<i>II</i>		
$\log k' + H_A$	$-\log a_w$	$\text{H}_2\text{SO}_4, \%$	$\log k' + H_A$	$-\log a_w$	$\text{H}_2\text{SO}_4, \%$
-6.789	0.065	21.02	-7.187	0.927	66.50
-6.589	0.170	34.05	-7.775	0.640	56.80
-6.245	0.324	44.95	-8.270	0.361	46.50
-5.614	0.610	55.05	-8.661	0.157	32.80
-5.875	0.630	56.03	-8.908	0.072	22.00
-7.733	0.780	58.07	-7.460	1.740	75.00
-6.938	0.710	60.00	-8.035	2.150	79.00
			-8.660	2.698	84.00
			-6.987	1.352	70.00

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