KINETICS AND MECHANISM OF HYDROLYSIS OF SUBSTITUTED PHENYL N-(4-METHYLPHENYL)SULPHONYLCARBAMATES. SOLVOLYSIS OF 3-NITROPHENYL N-(4-METHYLPHENYL)-SULPHONYLCARBAMATE IN MIXTURES WATER–1,4-DIOXANE AND WATER–TERT-BUTYL ALCOHOL AND ITS DECOMPOSITION TO NEUTRAL MOLECULES IN NON-AQUEOUS MEDIA*

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pH Dependence of hydrolysis rate of the substituted phenyl N-(4-methylphenyl)sulphonylcarbamates has been followed in aqueous medium. The activation parameters and the Hammett reaction constant ($\varrho = 2{\cdot}4$) have been determined at pH 11·3. For hydrolysis of 3-nitrophenyl N-(4-methylphenyl)sulphonylcarbamate (pK about 3·5) no general base catalysis has been found. The hydrolysis mechanism is discussed. Perturbation of the water structure by organic solvents (1,4-dioxane and tert-butyl alcohol) has been used for differentiation of ElcB and BAc2 mechanisms, 2,4-dinitrophenyl acetate being used for comparison. The decomposition rates of 3-nitrophenyl N(4-methylphenyl)sulphonylcarbamate have been determined in six organic solvents. Mechanism of spontaneous splitting of the carbamate molecule in non-aqueous media is discussed.

In alkaline medium most esters are hydrolyzed by two-step mechanism BAc2 (ref.[1]). Hydroxyl ion is added to the carbonyl group in the rate-limiting step, and the formed tetrahedral intermediate is split into products in the subsequent step. The same mechanism applies to alkaline hydrolysis of N,N-dialkylcarbamates, too[2]. On the contrary, *e.g.* malonates[3] and phenyl N-alkylcarbamates[4] with good leaving groups (phenoxide ions) are hydrolyzed in alkaline region by monomolecular ElcB mechanism involving spontaneous decomposition of the conjugated base in the rate-limiting step to give unsaturated intermediate (ketene or isocyanate). The both mechanisms are kinetically indistguishable. The basic criteria used for differentiation of the two altenative mechanisms are *a*) decrease of the alkaline hydrolysis rate by substitution of the acid hydrogen by alkyl group (ElcB is prevented)[2], *b*) much greater Hammett reaction constant for the substrates hydrolyzed by ElcB mechanism as compared with BAc2, *c*) solvation isotopic effect[5] (the esters hydrolyzed by BAc2 mechanism are hydrolyzed at lower rate in D_2O than in H_2O), *d*) sign and magnitude

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of the ΔS^{+} value (for the monomolecular ElcB reaction it should be small and positive, whereas for the bimolecular BAc2 reaction it should be negative).

The aim of this work is to contribute to differentiation of the two mechanisms with the use of perturbation of water structure by organic solvents (tert-butyl alcohol, 1,4-dioxane) which are known to affect strongly the association of water[6]. Substituted phenyl N-(4-methylphenyl)sulphonylcarbamates were chosen as model substances, their low p*K* value enabling to work in neutral or slightly alkaline pH region where the substrate is completely dissociated, and the hydrolysis reaction is not complicated by pre-equilibrium. For comparison we also studied behaviour of 2,4-dinitrophenyl acetate as a representative compound hydrolyzed by the BAc2 mechanism.

EXPERIMENTAL

Model Substances

The phenyl N-(4-methylphenyl)sulphonylcarbamates were prepared by mixing solution of 0·05 mol respective phenol in minimum amount of hot benzene with 0·06 mol 4-methylphenylsulphonyl isocyanate[7]. The reaction was catalyzed by 2 drops of dibutyltin dilaurate. The crystals separated after one hour standing at room temperature were collected by suction, and the product was crystallized from benzene (Table I). The yields were within 80 to 90%. 2,4-Dinitrophenyl acetate

TABLE I

Characteristics of the Prepared Phenyl N-(4-Methylphenyl)sulphonylcarbamates

Compound	Formula (mol.wt.)	M.p., °C	Calculated/Found % C	% H	% N
I	$C_{14}H_{12}N_2O_6S$	95	50·44	2·72	8·41
	(336·3)		50·54	2·86	8·53
II	$C_{15}H_{12}N_2O_4S$	114—115	56·96	3·80	8·86
	(316·3)		56·72	3·65	8·98
III	$C_{15}H_{12}N_2O_4S$	100—101	56·96	3·80	8·86
	(316·3)		56·82	3·70	8·75
IV	$C_{14}H_{12}N_2O_6S$	76—77	50·44	2·72	8·41
	(336·3)		50·50	2·65	8·50
V	$C_{14}H_{12}FNO_4S$	106—108	60·63	4·37	5·05
	(309·3)		60·78	4·48	5·26
VI	$C_{14}H_{12}BrNO_4S$	93—94	49·70	3·58	4·14
	(370·2)		49·63	3·67	4·01
VII	$C_{15}H_{15}NO_4S$	107—108	58·98	4·95	4·59
	(305·3)		59·15	5·09	4·68

was prepared by reaction of 2,4-dinitrophenol with acetanhydride with catalysis by one drop of sulphuric acid. M.p. 70—71°C (ref.[8] m.p. 72°C). The N-deuterated carbamate *IV* was prepared from 4-methylphenylsulphonyl isocyanate and deuterated 3-nitrophenol[9].

Kinetic Measurements

The buffer solution (2·9 ml) was placed in the thermostatted cell compartment of Unicam SP 800 or Specord UV VIS spectrophotometer, and 0·1 ml carbamate solution (about 10^{-3}M) in dioxane was added thereto. The latter solution was prepared fresh before each measurement, because the studied carbamates are decomposed even in non-aqueous media (the carbamate *IV* with the half-life of 1 800 s). The reaction was arranged as pseudomonomolecular, so that precise concentration of the carbamate did not need to be known. In the cases where effect of concentration of the carbamate was studied the initial carbamate concentration was estimated from the absorbance difference at λ_{max} of the formed phenol between the time $t = \infty$ and $t = 0$. The kinetic dependence in the whole pH range was followed by the absorbance increase of the formed phenol or phenoxide ion, the borax and phosphate buffers being used[10]. The precise pH values were determined with a PHM 4 pH-meter (Radiometer, Copenhagen). The rate constants were calculated according to the optimization program[11]. Error in the observed rate constant did not exceed ±5%.

Determination of p*K*

The p*K* of the carbamates *VI* and *VII* was determined in water by potentiometric titration 0·1M sodium hydroxide (pH of the half equivalence point). In the same way the dependence of p*K* of the carbamates *VI* and *VII* on composition of the mixed solvent water–dioxane was determined within the mole fractions of dioxane 0 to 0·4691 *i.e.* 0 to 80% by vol. In this media solution 0·1M tetramethylamonium hydroxide in dioxane[12] was used for the titrations.

TABLE II

Hydrolysis Rate Constants of Carbamates *I* and *IV*, 25°C, $J = 0·1$

Carbamate *I*		Carbamate *IV*	
pH	$10^3 k_{obs}$ s^{-1}	pH	$10^4 k_{obs}$ s^{-1}
5·25	8·758	6·78	2·440
6·19	8·448	7·20	2·615
8·41	8·751	7·84	2·352
8·57	8·130	8·41	2·495
10·45	8·956	10·45	2·605
11·63	7·956	11·63	2·343
12·00	8·063	12·99	2·769
12·99	8·485	14·02	2·679

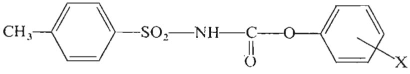
RESULTS AND DISCUSSION

Mechanism of Hydrolysis of Carbamates I *to* V *in Neutral and Alkaline* pH *Regions*

For the carbamate *I* the dependence of the hydrolysis rate on concentration of hydroxyl ion was followed within pH 5 to 13, and it was found that the hydrolysis rate is constant. An analogous plateau was found for the hydrolysis of the carbamate *IV*, too (Table II). The p*K* of the carbamates *VI* and *VII* in water are 4·15 and 4·83, respectively. On the basis of p*K* of the conjugated acid of the leaving group the p*K* of the carbamate *IV* can be expected about the value 3·1. Thus the carbamate *IV* is present in its dissociated form in the region of the plateau. No general base catalysis was found for hydrolysis of the carbamate *IV* at pH 10·5:

$M_{\text{borax buffer}}$	0·0739	0·1477	0·3693	0·5170	0·7385
$10^4 k_{obs}$, s^{-1}	2·386	2·606	2·375	2·325	2·451

We also determined effect of ionic strength on the hydrolysis rate of the carbamate *IV* at pH 10·5. The found value of slope of the dependence log k_{obs} − log k_0 *vs* $(J)^{1/2}$ was $A = 0·163$ which is close to zero and can be assigned to a reaction characterized by charge dispersion in the activated complex[13]. The found value of the Hammett constant (Fig. 1) $\varrho = 2·4$. The alkaline hydrolysis of phenyl N-methylcarbamates[4] (going *via* the ElcB mechanism) has the value $\varrho = 2·5$. From the measured results and the discussion the hydrolysis of the substituted phenyl N-(4-methylphenyl)-sulphonylcarbamates can be suggested to go *via* the ElcB mechanism in neutral and alkaline pH regions.



I, X = 4-NO_2
II, X = 3-CN
III, X = 4-CN
IV, X = 3-NO_2
V, X = 3-F
VI, X = 4-Br
VII, X = 4-CH_3

Validity of the Hammett correlation was checked by plotting the log k_{obs} values against σ or σ^- for three various temperatures (Fig. 1). Value of the reaction constant remains practically unchanged at various temperatures (ϱ/°C: 2·4/25; 2·48/35; 2·30/50). The dependence $\Delta H^{\neq}$ *vs* $\Delta S^{\neq}$ is linear for the carbamates *I*, *III*, *IV* and *V* (Table III). In the series of the measured substances which are hydrolyzed by the same mechanism (the Hammett correlation shows no break) a great $\Delta S^{\neq}$ is observed with the change of substituent. In this context it is noteworthy that $\Delta S^{\neq}$ value is often used as a criterion differentiating between mono- and bimolecular mechanisms[14]. In the system there exists a general trend of mutual compensation of enthalpy and entropy[15], which makes the $\Delta G^{\neq}$ values small (Table III).

Hydrolysis of Carbamates I, II, IV *and 2,4-Dinitrophenyl Acetate in Mixture Water–Dioxane*

Dependence of log k_{obs} on mole fraction of dioxane (Fig. 2) for the carbamates *I*, *II* and *IV* shows a maximum at $n_{water} = 0{\cdot}7$ to $0{\cdot}8$. A similar dependence was found for neutral hydrolysis of arylsulphonylmethyl perchlorates[16] with kinetic maximum

TABLE III

Activation Parameters of Hydrolysis of Carbamates *I*, *III*, *IV* and *V*, pH 11·3, $J = 0{\cdot}1$

Carbamate	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, JK^{-1} mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}
IV	103·1	31·8	93·7
III	97·8	21·0	9·15
I	80·6	—46·0	94·3
V	70·8	—90·0	97·9

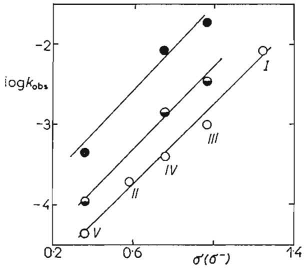


FIG. 1

The Hammett Correlation of Hydrolysis of Carbamates *I* to *V* at pH 11·3 (25°C — ○, 35°C — ◒, 50°C — ●)

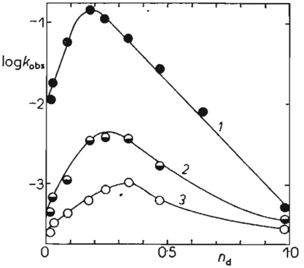
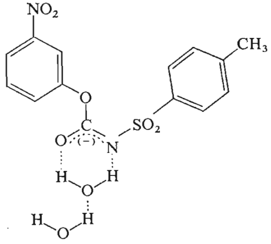


FIG. 2

Dependence of Logarithm of the Hydrolysis Rate Constant on Mole Fraction of Dioxane in Mixture Water–Dioxane at 25°C

The hydrolyzed carbamate *I* 1, *II* 3, *IV* 2.

at $n_{\text{water}} = 0{\cdot}79$ and for water-catalyzed detritiation of tert-butylmalonnitrile[17], in the latter case, however, the rate-limiting step consists in formation of the conjugated base by splitting off of the proton. Increase in the hydrolysis rate of the carbamates *I*, *II* and *IV* agrees with the Ingold's rule[18], because decomposition of the conjugated base of carbamate (ElcB mechanism) is accompanied by charge dispersion in the activated complex, and addition of dioxane to water (decrease in the solvent polarity) accelerates the hydrolysis. We presume that the acceleration of hydrolysis of the carbamates *I*, *II* and *IV* is also due to changes in solvation of initial species and the activated complex. Addition of both polar and non-polar solvent to water supports formation of three-dimensional associates of water molecules[19]. The ground state of the reaction can be solvated in various ways, out of them the cyclic complex *VIII* with one or more water molecules will obviously be probable. In the activated complex charge is dispersed to another centre (phenolic oxygen), the C—O bond is substantially split, because in the Hammett correlation the exalted values of substituent constants had to be used. The activated complex will be solvated (*i.e.* stabilized) less than the ground state. Addition of solvent lowers solvation of the ground state whereby the reaction is accelerated. This presumption is also supported by the magnitude of the kinetic maximum of the carbamate *IV* (Fig. 3) being decreased with increasing temperature, as the influence of the solvent supporting formation of hydrogen bonds between water molecules stands in contrast to the increase of energy of water molecules.



VIII

Dependence of the hydrolysis rate of 2,4-dinitrophenyl acetate (a typical representative of the compounds hydrolyzed by the bimolecular BAc2 mechanism[14]) on composition of the mixture water–dioxane was measured at three temperatures and extrapolated to 25°C (Fig. 4). Increasing dioxane content lowers the hydrolysis rate in similar way as the hydrolysis rate of 4-nitrophenyl dichloroacetate in mixture water–tert-butyl alcohol[20] (Fig. 4). With respect to that neutral hydrolysis of ethyl dichloroacetate is subject to general base catalysis, the Brönsted relation being also fulfilled by water[21], it must be considered that in the ester hydrolysis with water the carbonyl group is attacked by at least two water molecules. One of them acts as a nucleophile, the other acts as a medium transferring the proton, participation of another molecules being not excluded. Similarly addition of acetone or alcohol retards strongly hydrolysis of ethyl trifluoroacetate by water[22]. The dependence $\log k_{obs}$ *vs* $\log [H_2O]$ for the hydrolysis of 2,4-dinitrophenyl acetate is linear with the slope 3·2 wherefrom it can be concluded (on the basis of presumptions given by Tommila[23]) that three water molecules participate in the activated complex of the rate-limiting reaction step. Probably the cyclic activated complex *IX* will be the most favourable energetically, being decomposed into the tetrahedral intermediate by splitting off of two water molecules.

The hydrolysis rates of the carbamate *I* in water and in deuterium oxide were compared to support the elimination mechanism of hydrolysis of the studied carbamates. This criterion was suggested by Tobias and Kezdy[5] for differentiation between the reactive (ElcB) and unreactive (BAc2) anion in ester hydrolysis. For the carbamate *I* the ratio found was $k_{H_2O}/k_{D_2O} = 1{\cdot}04$ which agrees with the value found for hydro-

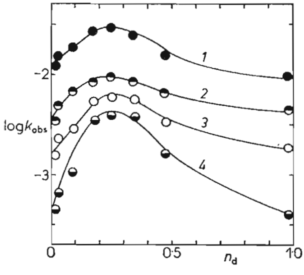


FIG. 3

Dependence of Logarithm of Hydrolysis Rate Constant of Carbamate *IV* on Mole Fraction of Dioxane

25°C *4*, 35·7°C *3*, 47·5°C *2*, 51·5°C *1*.

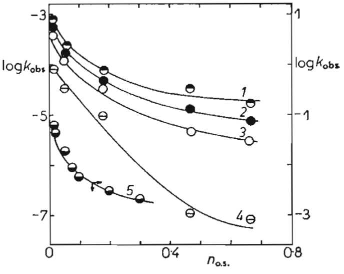


FIG. 4

Dependence of Logarithm of Hydrolysis Rate Constant of 2,4-Dinitrophenyl Acetate on Composition of Mixture Water–Dioxane at Various Temperatures 25°C *4*, 59·5°C *3*, 70·3°C *2*, 79·5°C *1* and that of 4-Nitrophenyl Dichloroacetate in Mixture Water–-tert-Butyl Alcohol[20] at 25°C *5* lysis of phenyl malonates going *via* the ElcB mechanism[3]. On the contrary, for 2,4-dinitrophenyl acetate the ratio found was $k_{H_2O}/k_{D_2O} = 2{\cdot}06$ which corresponds to the BAc2 mechanism as it is the case for the value 3 found in hydrolysis of 4-nitrophenyl dichloroacetate[20].

If dioxane mole fraction exceeds 0·3, then the hydrolysis rate decreases (Fig. 2), which is obviously due to concentration decrease of the carbamate conjugated base. Addition of solvent to water affects strongly the p*K* value of carbamates (Table IV). Changing water content in the mixture water–dioxane results in changing value of the Hammett ϱ constant from the value 2·53 (water) through 3·06 ($n_{\text{dioxane}} = 0{\cdot}17$) to 0·21 (dioxane). Such a big decrease of the reaction constant indicates a change in the reaction mechanism from splitting of the conjugated base of the carbamates *I*, *II* and *IV* by the mechanism ElcB to decomposition of the neutral molecule. Difference between the reactivities of the anion and the neutral molecule will be greatest with the carbamate *I* which exhibits the highest kinetic maximum (Fig 2). With decreasing acidity of the carbamates the differences in reactivities of the anion and the non-ionized substrate is decreased, too, so that, in the case of the carbamate *II*, decomposition of the neutral molecule is also significant in the region of the reaction rate decrease due to concentration decrease of the conjugated base.

The hydrolysis rate of the carbamate *IV* shows similar course in both water–dioxane and water–tert-butyl alcohol mixtures (Table V).

Transition from pure water to mixture water–dioxane or water–tert-butyl alcohol results in decrease of $\Delta S^{\neq}$ value of the hydrolysis of the carbamate *IV* (Table VI). The same finding applies for neutral hydrolysis of ethyl trifluoroacetate[22] and arylsulphonylmethyl perchlorates[16], too. In the whole concentration range of tert-butyl

TABLE IV

Dependence of p*K* of Carbamates *IV*, *VI* and *VII* on Composition of Mixture Water–Dioxane

n_{dioxane}	p*K*		
	VI	*VII*	*IV*[a]
0	4·15	4·83	3·50
0·0523	5·73	6·71	4·55
0·0865	6·13	7·05	5·20
0·1809	6·99	7·44	6·60
0·4691	7·86	8·61	7·10
0·6653	8·28	9·03	7·52

[a] The values extrapolated according to p*K* value of the leaving group.

alcohol the enthalpy factor is dominant (Fig. 5) with a shallow maximum at mole fraction 0·5. Course of the activation parameters of the carbamate *IV* hydrolysis in mixture water–dioxane shows a sharp maximum and minimum at $n_{\text{dioxane}} = 0{\cdot}3$ (Fig. 6), and the hydrolysis is enthalpy-controlled ($n_{\text{dioxane}} = 0$ to $0{\cdot}17$), entropy-controlled ($n_{\text{dioxane}} = 0{\cdot}17$ to $0{\cdot}4$) and again enthalpy-controlled. In the both cases the $\Delta G^{\neq}$ value goes through a shallow maximum. Whereas the character of changes of the parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ of the carbamate *IV* hydrolysis is similar in mixtures water–dioxane and water–tert-butyl alcohol, behaviour of 2,4-dinitrophenyl acetate is quite different (Fig. 7). Up to the mole fraction 0·25 of dioxane the entropy factor is more significant. In highly aqueous medium the arrangement of water associates in the activated complex *IX* of the rate-limiting reaction step is obviously decisive. With increasing concentration of organic solvent the enthalpy factor becomes more important. The water structure is broken, and the

TABLE V

Rate Constants of Hydrolysis of Carbamate *IV* in Mixture Water–tert-Butyl Alcohol, 25°C

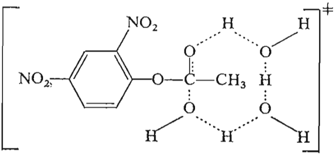
$n_{t-\text{BuOH}}$	$10^3 k_{\text{obs}}$ s^{-1}	$n_{t-\text{BuOH}}$	$10^3 k_{\text{obs}}$ s^{-1}
0	0·440	0·2204	5·222
0·0205	0·831	0·3054	5·208
0·0450	1·700	0·3616	3·611
0·0747	2·805	0·4298	2·255
0·1116	3·797	0·6291	2·125
0·1586	4·373	1·0	1·840

TABLE VI

Dependence of $\Delta S^{\neq}$ of Hydrolysis of Carbamate *IV* on Composition of Solvent Water–Organic Solvent

n_{dioxane}	$\Delta S^{\neq}$, JK^{-1} mol^{-1}	$n_{t-\text{BuOH}}$	$\Delta S^{\neq}$, JK^{-1} mol^{-1}
0·0240	— 82·5	0·0205	— 59·8
0·0865	— 83·3	0·0747	— 77·7
0·1809	—167·9	0·1586	— 82·1
0·3401	—181·1	0·3054	—116·2
0·4691	—137·4	0·6291	—133·8
1·0	— 51·9	1·0	— 75·3

reaction rate only depends on energy of the involved bonds. $\Delta G^{\neq}$ value of the reaction increases with increasing dioxane content. The same course of the activation parameters was found for the BAc2 mechanism of hydrolysis of 4-nitrophenyl dichloroacetate in mixture water–tert-butyl alcohol.



IX

It is supposed that the obtained data and above discussion allow certain conclusions concerning differentiation between the ElcB and BAc2 mechanisms: *a*) The bimolecular mechanism is characterized by monotonous decrease of the hydrolysis rate with addition of organic solvent, as water is present in the activated complex of the rate-limiting step. The $\Delta G^{\neq}$ of the reaction steadily increases. *b*) In the elimination mechanism water only acts as a solvation agent, and its effect on the hydrolysis rate is manifested through different solvation of the ground and the transition

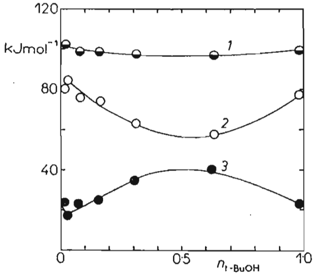


FIG. 5

Dependence of Activation Parameters of Hydrolysis of Carbamate *IV* on Composition of Mixture Water–tert-Butyl Alcohol
—$T\Delta S^{\neq}$ *3*, $\Delta H^{\neq}$ *2*, $\Delta G^{\neq}$ *1*.

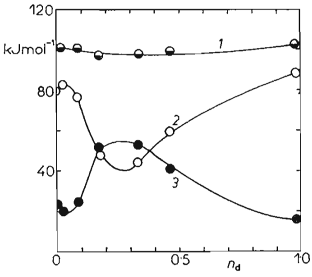


FIG. 6

Dependence of Activation Parameters of Hydrolysis of Carbamate *IV* on Composition of Mixture Water–Dioxane
—$T\Delta S^{\neq}$ *3*, $\Delta H^{\neq}$ *2*, $\Delta G^{\neq}$ *1*.

states. The $\Delta G^{\ddagger}$ shows a shallow minimum. At the same time it is obvious that the $\Delta S^{\ddagger}$ value must be carefully used for differentiation between the mono- and bimolecular mechanisms (and preferably always combined with other suitable criteria), as its sign and magnitude strongly depend on the solvation degree.

Decomposition of the Carbamate IV *in Non-Aqueous Medium*

The carbamate *IV* is decomposed even in non-aqueous media at a rate comparable with that in water (Table VII), so that it is obvious that spontaneous decomposition of the carbamate molecule takes place without assistance of water. The found rate constants did not correlate with any of usual characteristics of solvents (dielectric constant, Y values[24,25], E_T constants[26], Z values[27]). As there is no dependence between the decomposition rate of the carbamate *IV* and basicity of solvent, it can be suggested that the solvent molecule does not act as a proton-transfer agent in the process. Decomposition of the neutral carbamate molecule into the starting components

TABLE VII

Decomposition Rate Constant of Carbamate *IV* in Solvents, 25°C

Solvent	$10^3 k_{obs}$, s^{-1}	Solvent	$10^3 k_{obs}$, s^{-1}
Dioxane	0·3925	n-Heptane	0·9147
Tetrahydrofurane	0·4040	Cyclohexane	1·3970
Water	0·4400	t-Butyl alcohol	1·8400
Ethyl alcohol 0·7798	0·7798		

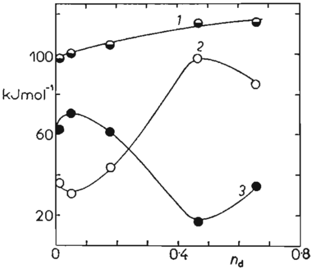
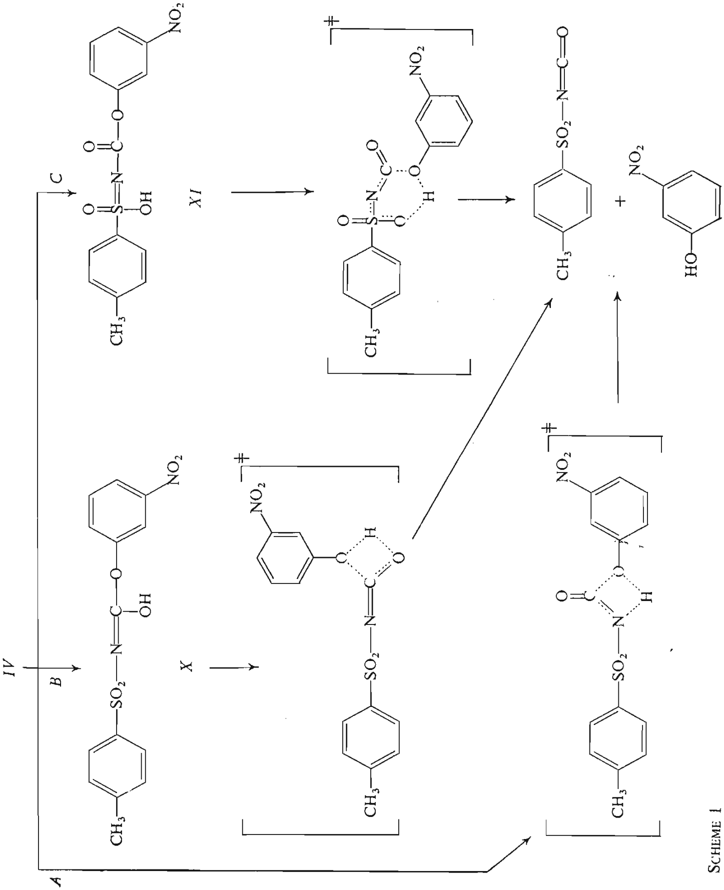


FIG. 7

Dependence of Activation Parameters of Hydrolysis of 2,4-Dinitrophenyl Acetate Composition of Mixture Water–Dioxane

$-T\Delta S^{\ddagger}$ *3*, $\Delta H^{\ddagger}$ *2*, $\Delta G^{\ddagger}$ *1*.



SCHEME 1

(phenol and isocyanate) necessitates a proton transfer which can be either inter- or intramolecular. Therefore, the decomposition rate of the carbamate *IV* of various initial concentrations was studied in cyclohexane at 25°C:

$A_\infty - A_0$	4·503	3·05	2·05	1·17	0·90	0·61	0·15
$10^3 k_{obs}$, s^{-1}	1·44	1·90	1·10	1·36	1·44	1·40	1·15

The reaction was always first order in carbamate, and its rate did not depend on concentration. Therefrom it can be concluded that the proton transfer is intramolecular. The decomposition rate of the carbamate *IV* in cyclohexane was measured and showed $k_H/k_D = 1·97$. The rate-limiting step involves a proton transfer. Therefore, the reaction has only one step (*A*, Scheme 1) or some of the tautomers *X*, *XI* is decomposed (*B* and *C*, Scheme 1). The tautomer *XI* is not so unlikely, as Kice and Legan found[28] (for reaction of nucleophiles with phenyl-α-disulphone) that sulphonyl group resembles carbonyl group in electrophilic properties. The route *C* is not unfavourable energetically, since the rate-limiting step (the proton transfer) takes place in a sterically advantageous six-membered transition state.

The hydrolysis of the carbamates *I*, *II* and *IV* in dioxane exhibits a low value (0·21) of the Hammett reaction constant as compared with that in water (2·53). Electronic effects of substituents in benzene nucleus are important for the hydrolysis by ElcB mechanism, the decisive factor being the p*K* value of the conjugated acid of the leaving group. In non-aqueous medium the rate-limiting step involves the proton transfer to phenolic oxygen. The ring substituent has two opposite effects – if it facilitates the leaving of phenol from the carbamate molecule, then it hinders the proton transfer to oxygen, and *vice versa*.

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