SALT EFFECT IN HYDROLYSIS OF 3-ACYL-1,3-DIPHENYLTRIAZENES

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Rate constants of non-catalyzed hydrolysis of 3-acetyl-1,3-diphenyltriazene (*I*) and 3-(N-methylcarbamoyl)-1,3-diphenyltriazene (*II*) have been measured in the presence of salts (ammonium chloride, potassium chloride, lithium chloride, sodium chloride and bromide, ammonium sulphate, potassium sulphate, lithium sulphate, sodium sulphate, and zinc sulphate) within broad concentration ranges. Temperature dependence of the hydrolysis of the substrates studied has been measured in the presence of lithium sulphate within temperature range 20° to 55°C. The results obtained have been interpreted by mechanisms of hydrolysis of the studied substances.

Generally salts influence course of chemical reactions due to changes in free enthalpies of reactants and the activated complex. The most significant influence of salts in reactions between ions is the primary salt effect, which can be described by the Brönsted–Bjerrum equation[1,2]

$$k = k^0 \gamma_A \gamma_B / \gamma^{\neq} \qquad (1)$$

which can be combined with the Debye–Hückel limit law (for low salt concentrations) to give the relation

$$\log k = \log k^0 + 2ab\, I^{1/2}\,, \qquad (2)$$

where a, b are charges of the reactants, and I means ionic strength. According to this equation salt effect should not operate in reactions of uncharged compounds, which, however, disagrees with experiments[3-12]. Reactions of non-electrolytes are influenced by salts in another way. First of all salts induce changed effects of medium (changes in solvation and, hence, in activity coefficients of reactants and the activated complex, changes in structure of solvent, in relative permittivity, salting-out, *etc.*), other effects being association of ions, catalysis etc. In aqueous solutions it is presumed that the salt-induced effects of medium make themselves felt in the same way with respect to both the starting species and the activated complex, *i.e.* they are mutually compensated to some extent[4,8,9]. Salt effects on non-electrolytes in aqueous media are usually described by the relation[10,13,14]

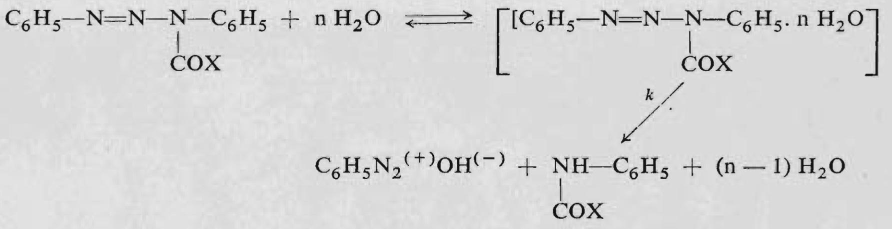
$$k = k_0(1 + bc_S) \qquad (3)$$

or[5,9]

$$\log k = \log k_0 + bc_S\,, \tag{4}$$

where b characterizes the extent of salt effect, and c_S means the salt concentration. Salt effect can make itself felt in various ways even within one mechanism. *E.g.* reactions of S_N2 type exhibit both positive ($b < 0$, ref.[4]) and negative ($b > 0$, refs[4,6]) salt effects. Reactions of S_N1 type exhibit usually positive salt effects[5-7,9,10] due to ionic character of the intermediates being recombined.

The aim of this work was to obtain (using kinetic measurements) more detailed information about mechanism of non-catalyzed hydrolysis of 3-acetyl-1,3-diphenyltriazene (*I*) and 3-(N-methylcarbamoyl)-1,3-diphenyltriazene (*II*), especially so with respect to the transition state of the step in which the bond splitting according to Scheme 1 takes place[15].



$$C_6H_5{-}N{=}N{-}\underset{\displaystyle COX}{N}{-}C_6H_5 + n\,H_2O \rightleftharpoons \left[C_6H_5{-}N{=}N{-}\underset{\displaystyle COX}{N}{-}C_6H_5\,.\,n\,H_2O\right] \xrightarrow{k} C_6H_5N_2^{(+)}OH^{(-)} + \underset{\displaystyle COX}{NH}{-}C_6H_5 + (n-1)\,H_2O$$

SCHEME 1

EXPERIMENTAL

Synthesis of the model compounds and methods of kinetic measurements are described elsewhere[15]. The kinetic measurements in solutions with concentrations above 1 mol l^{-1} were carried out in 5 cm cells within the transparence region $T = 80$—100% using a Specord UV VIS (Zeiss, Jena), so that salting-out of the substrate and consequent irreproducibility of results might be prevented. pH was measured in the most concentrated solutions of the salts used, and its value did not exceed 3—9 (non-catalyzed hydrolysis[15]).

RESULTS AND DISCUSSION

Figs 1 to 4 present results of the measurements of rate constants: dependence of $\log k_{obs}$ of hydrolysis of amide *I* and urea *II* on square root of ionic strength of the added inorganic salt are given in Figs 1 and 2 for uni-univalent electrolytes and in Figs 3 and 4 for uni-bivalent electrolytes and zinc sulphate. As the rate constant changes are small, the F-test was used for hypothesis of equality of the rate constants at various concentrations of the added salt. Table I shows that changes of the rate constants due to changes in concentration of salts are statistically significant as compared with accuracy of the measurements. All the dependences in Figs 1–4 have similar character. Except for the compound *I* in the presence of ammonium

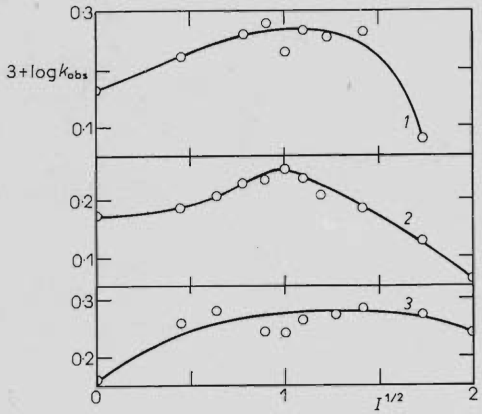


FIG. 1

Salt effect in hydrolysis of the amide *I* at 25°C. *1* KCl, *2* NaCl, *3* NaBr

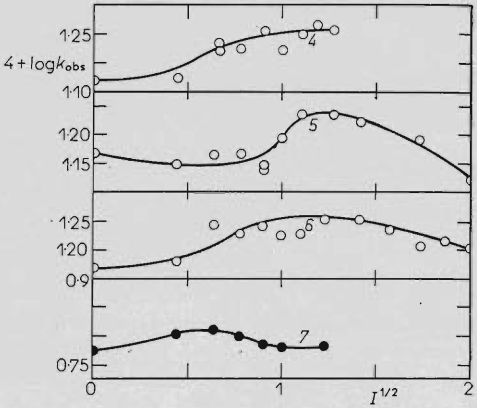


FIG. 2

Salt effect in hydrolysis of the amide *I* ○ and urea *II* ● at 25°C. *4* LiCl, *5* NH_4Cl, *6* $NaClO_4$, *7* $NaClO_4$

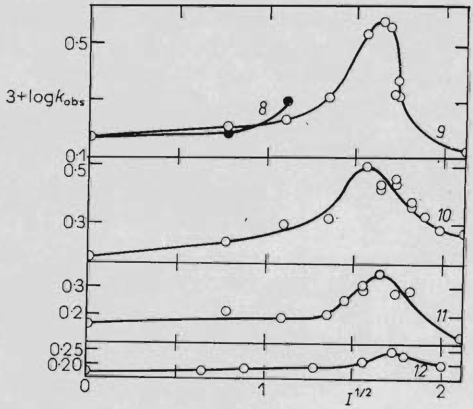


FIG. 3

Effect of sulphates on hydrolysis of the amide *I* at 25°C. *8* K_2SO_4, *9* Na_2SO_4, *10* Li_2SO_4, *11* $(NH_4)_2SO_4$, *12* $ZnSO_4$

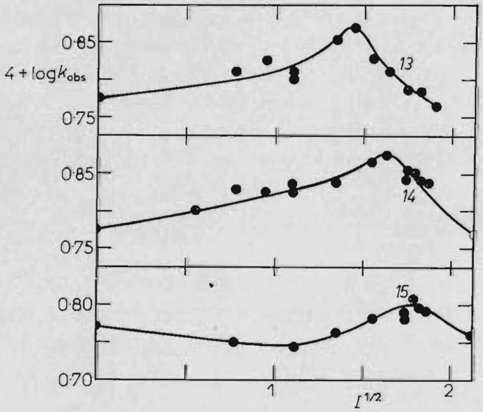
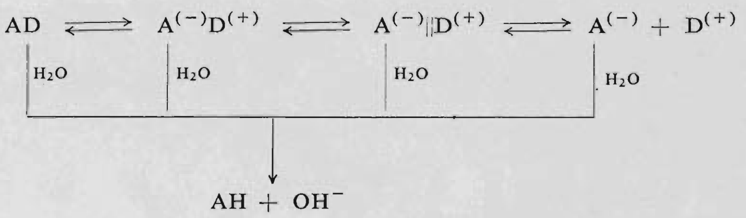


FIG. 4

Effect of sulphates on hydrolysis of the urea *II* at 25°C. *13* Na_2SO_4, *14* Li_2SO_4, *15* $(NH_4)_2SO_4$

chloride (Fig. 2, curve *5*) and compound *II* in the presence of ammonium sulphate (Fig. 4, curve *15*), increasing ionic strength first of all speeds up the reaction and then (at higher ionic strengths) slows it down.

With respect to the reaction mechanism[15] (Scheme 1) the reaction consists in splitting of neutral molecule into a relative stable cation of diazonium salt and non--stable anion of amide or urea. Except for involving opposite charges, this mechanism is formally identical with the S_N1 type. The latter mechanism is presumed to involve several steps in the course of bond splitting between alkyl and leaving groups[16-18], *viz* the intimate and the solvent-separated ion pairs. From the above-mentioned analogy it is possible to suggest Scheme 2 for hydrolysis of the substrates studied by us, where $D^{(+)}$ means diazonium salt, and $A^{(-)}$ stands for amide or urea section. Here it must not be forgotten that the individual phases in Scheme 2 need not be real intermediates and can only represent some important moments during the bond split-



SCHEME 2

TABLE I

Testing of hypothesis of independence between the observed rate constant of hydrolysis of the compounds *I* and *II* at 25°C and salt addition

Curve[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Substrate	*I*	*I*	*I*	*I*	*I*	*I*	*II*	*I*	*I*	*I*	*I*	*I*	*II*	*II*	*II*
Electrolyte	KCl	NaCl	NaBr	LiCl	NH_4Cl	$NaClO_4$	$NaClO_4$	K_2SO_4	Na_2SO_4	Li_2SO_4	$(NH_4)_2SO_4$	$ZnSO_4$	Na_2SO_4	Li_2SO_4	$(NH_4)_2SO_4$
F	264·7	94·4	13·2	183·7	188·4	111·3	4·6	227·1	898·0	558·4	341·5	29·0	99·7	38·0	19·8
$F_{0.05}$	2·0	1·9	2·0	2·0	1·9	1·8	2·3	3·1	1·9	1·7	1·9	2·0	1·8	1·7	1·9

[a] See Figs 1—4.

ting. The observed positive salt effect (Figs 1–4) can be interpreted on the basis of the given Scheme 2 by retardation of back recombination of the transient ions. This conclusion agrees with the results obtained for solvolysis (S_N1) of some alkyl halides[5–7] and esters[9,10,13,14]: *e.g.* tert-butyl chloride hydrolysis exhibits positive salt effect in a broad range of added salts[5] (b = 0·02 to 0·74; 15°C). Existence of partial negative charge at nitrogen atom of amide or urea fragment during the N—N bond splitting is also confirmed by small value of the reaction constant $\varrho = 0{\cdot}62$ found for non-catalyzed hydrolysis of 3-(N-substituted phenylcarbamoyl)-1,3-diphenyltriazenes[15]. The decrease in the curves log k_{obs} *vs* $I^{1/2}$ observed at higher ionic strength is explained by decomposition of the primary hydrated structure of substrate connected with changes in solvent structure. This process leads as far as to salting-out of the substrate.

Dependence of salt effect on temperature. Fig. 5 represents effect of lithium sulphate on hydrolysis of 3-acetyl-1,3-diphenyltriazene (*I*) at various temperatures. The marked maximum observed at 25–35°C in the region $I^{1/2} = 1{\cdot}3–2$ is shifted to lower ionic strengths at 20 °C, whereas at higher temperatures the maximum is shifted in opposite direction and, furthermore, it diminishes or even disappears (45°C and above). Marked changes with temperature were observed in the case of alkaline hydrolysis of benzoates (in the presence of NaCl, KCl) (ref.[19,20]), whereas, on the contrary, other substrates (alkaline hydrolysis of sulphonates[21]) exhibited dependences which the authors denoted as "plateau formation". Hence the results are not quite unambiguous and are obviously connected with specific properties of substrate, added electrolyte, and solvent. In our case the temperature changes probably result in changed structure of hydratation.

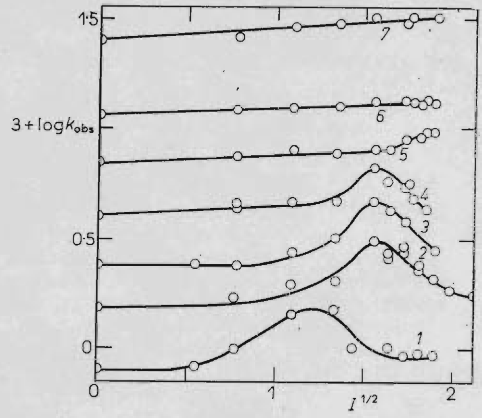


FIG. 5

Effect of lithium sulphate on hydrolysis of the amide *I* at various temperatures. *1* 20°C, *2* 25°C, *3* 30°C, *4* 35°C, *5* 40°C, *6* 45°C, *7* 55°C

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