SOLVENT EFFECT AS A CRITERION OF SOLVOLYSIS MECHANISM. SOLVOLYSIS OF 3-ACYL-1,3-DIPHENYLTRIAZENES

Olřich PYTELA, Petr SVOBODA and Miroslav VEČEŘA

Department of Organic Chemistry,
Institute of Chemical Technology, 53210 Pardubice

Received October 28th, 1980

Solvent dependence of hydrolysis rate constants of 3-acetyl-1,3-diphenyltriazene (*I*) and 3-(N-methylcarbamoyl)-1,3-diphenyltriazene (*II*) has been followed in the solvent mixtures ethanol–water, methanol–water, dioxane–water, and formamide–water within the mole fraction $x = 0{\cdot}0$ to $0{\cdot}5$ at 25, 35 and 45°C. A criterion has been suggested, based on sign of change of logarithm of the observed rate constant in dependence on change of the solvent composition, for evaluation of the reaction molecularity and, hence, participation of water in the hydrolysis mechanism. It has been found that water takes part as a proton donor in the transition state of hydrolysis of the substrates studied.

Change of solvent represents an important way to change of rates and yields of many reactions. Solvent–solute interactions can be divided into two groups. The first one involves the interactions in which specific properties of solvents do not make themselves felt (non-specific solvation). The solvent is taken a homogeneous isotropic medium and is characterized by a macroscopic property *e.g.* relative permittivity ε or refractive index n_D. The second group of interactions (specific solvation) involves those interactions in which solvent and solute molecules form complexes due to their donor–acceptor properties or hydrogen bonds. On the basis of this division and closer specification of the solvent–substrate interaction it is possible to derive the corresponding physical models. In the case of hydrolytic reactions water molecules act simultaneously as both the reactant and solvation medium[1-7]. A number of empirical relations were suggested for interpretation of mechanisms in such systems[8]. At present the equation by Grunwald and Winstein[9] is used most frequently in the form

$$\log(k/k_0) = m \,.\, Y, \qquad (1)$$

where k and k_0 mean the solvolysis rate constants of the given substrate in a solvent characterized by the parameter Y and in 80% v/v ethanol, respectively, and m characterizes sensitivity of the substrate to solvent change. The parameter m has a value about unity for reactions of S_N1 type, and it varies within 0·3 to 0·4 for the reactions of S_N2 type, representing thus a certain measure of polarity of the transition state.

Efforts are made to improve the formerly defined empirical relations[10] or to describe the solvent effects by another way[11]. A universal equation was suggested by Palm and Koppel[12] (5 parameters) who obtained very good correlations. Correlation of logarithm of rate constants with logarithm of water concentration in the form of Eq. (*2*) has greatest importance for hydrolytic reactions[13,14]:

$$\log k_{\mathrm{obs}} = \log k + n \log [\mathrm{H_2O}] \,. \qquad (2)$$

The dependence (*2*) is linear either in the whole range or in separate regions[13-20], and slopes of these dependences are interpreted as number of water molecules participating in the transition state[13]. The slopes given in literature cover a broad range from $n = 0{\cdot}8$ (hydrolysis of ethyl acetate in mixture of dimethyl sulphoxide and water[17]) up to $n = 7$ (hydrolysis of tert-butyl chloride in acetone–water mixture[14]). In all the cases it is presumed that concentration of free water molecules $[\mathrm{H_2O}]$ is the same as or proportional to analytical concentration of water in the mixture ($c_{\mathrm{H_2O}}$).

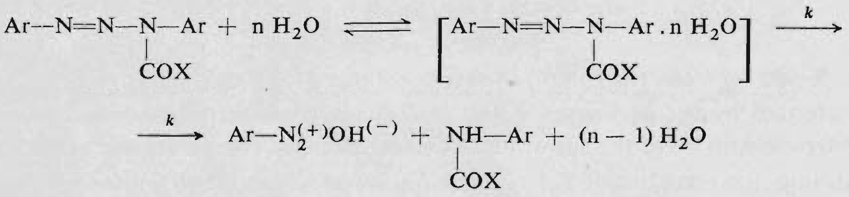
The aim of this work was to suggest a criterion for clasification of the reaction molecularity on the basis of changes of the observed rate constant accompanying changes in solvent composition and, in this way, to decide about participation of water in hydrolysis mechanism of 3-acetyl-1,3-diphenyltriazene (*I*) and 3-(N-methylcarbamoyl)-1,3-diphenyltriazene (*II*).

EXPERIMENTAL

Synthesis of the model compounds and methods of the kinetic measurements were described elsewhere[21]. Ethanol, methanol, dioxane and formamide were purified and absolutized according to ref.[22]. The parameters *Y* were taken from ref.[23]. The isokinetic temperatures and statistical criteria were calculated by our own program[24].

RESULTS AND DISCUSSION

Table I gives results of the measurements of hydrolysis rate constants of the compounds *I* and *II* in mixtures ethanol–water and methanol–water at 25, 35 and 45°C,



$$\mathrm{Ar{-}N{=}N{-}\underset{\underset{COX}{|}}{N}{-}Ar} + n\,\mathrm{H_2O} \rightleftharpoons \left[\mathrm{Ar{-}N{=}N{-}\underset{\underset{COX}{|}}{N}{-}Ar}\,.\,n\,\mathrm{H_2O}\right] \xrightarrow{k}$$

$$\xrightarrow{k} \mathrm{Ar{-}N_2^{(+)}OH^{(-)}} + \mathrm{\underset{\underset{COX}{|}}{NH}{-}Ar} + (n-1)\,\mathrm{H_2O}$$

SCHEME 1

in dioxane–water at 35 and 45°C, and those of *I* in mixture formamide–water at 35 and 45°C.

Solvent effect. Scheme 1 represents the mechanism suggested[21,25] for the non-catalyzed hydrolysis of acyltriazenes.

Kinetically the given mechanism can be described as a reaction between the substrate and water molecules

$$\mathrm{S} + \mathrm{n}\,\mathrm{H_2O} \xrightarrow{k_{\mathrm{obs}}} \text{products}\,,$$

the observed rate constant being composed of two terms corresponding to two roles of water in the reaction. First of all, water or its admixtures to other solvents acts as solvating medium (the character of solvent). This effect is complex and depends on composition of solvent, temperature, substrate, and on the presence of other compounds. The second term expresses the participation of water as the reactant (if the mechanism necessitates that) in the rate-limiting step or in a rapid preceding step. This term is an explicit function of water concentration. If this dependence can be found and correctly interpreted, it represents an important support of the hydrolysis mechanism. Hence, for the observed rate constant it can be written

$$k_{\mathrm{obs}} = k(c_{\mathrm{H_2O}}, \text{solvent, substrate, temperature} \ldots) \,.\, f(c_{\mathrm{H_2O}})\,, \tag{3}$$

where k means the complex rate constant, and $f(c_{\mathrm{H_2O}})$ is the explicit function of water concentration depending on the hydrolysis mechanism (most frequently it is $f(c_{\mathrm{H_2O}}) = c^{\mathrm{n}}_{\mathrm{H_2O}}$). Many published studies take into account only one of the two roles of water, which can lead to incorrect conclusions. Such an approach is *e.g.* connected with application of Eq. (*2*) (refs[13,14]) which neglects the changes of log k due to changes of solvent composition. Out of the used correlations of the type Eq. (*3*) the most important is the Grunwald–Winstein[9] equation (*1*) which involves the complex solvent effect in a certain way. Table II gives the results of the Eq. (*1*) applied to the substrates studied by us. The dependences are linear within the whole range of the used concentrations except for the urea *II* in methanol–water mixture in the region $Y = 3{\cdot}0 - 3{\cdot}49$ (Fig. 1). Values of the slope n vary within the limits $0{\cdot}3 - 0{\cdot}6$, which indicates a bimolecular reaction mechanism.

Effect of temperature and solvent. Activation entropy is frequently used as a criterion of reaction molecularity[26]. This approach suffers from inaccuracy of determination of the activation entropy, because this value also involves the action of solvent as the the reactant (according to Eq. (*3*)). A more suitable criterion appears to be the sign of change of logarithm of the rate constant accompanying the changes of composition or quality of solvent. If we start from the expression of dependence

TABLE I

The observed rate constants of solvolysis ($10^4 k_T$, s^{-1}) of the studied substrates and their standard deviations (10^5 s, s^{-1}) at various temperatures (T, °C), mole fractions x, water concentrations (c_{H_2O}, mol l^{-1}), and parameters Y

x	c_{H_2O}	Y	k_{25}	s	k_{35}	s	k_{45}	s
Amide *I*, ethanol–water								
0·0	55·56	3·49	17·1	1·1	43·3	3·7	95·1	12
0·05	47·50	3·22	12·4	2·1	38·1	5·4	131	55
0·10	40·89	2·86	10·6	2·7	27·4	6·2	87·1	20
0·15	35·39	2·42	6·81	0·44	24·7	4·0	60.9	12
0·20	30·72	1·95	3·33	0·24	15·0	0·81	44·6	7·9
0·25	26·72	1·58	3·83	0·46	9·51	0·91	29·0	6·2
0·30	23·28	1·24	2·82	0·44	5·69	0·55	22·1	4·6
0·35	20·28	0·97	1·50	0·08	4·99	0·89	20·0	3·4
0·40	17·61	0·70	1·28	0·05	4·39	0·61	16·5	2·8
0·45	15·22	0·45	1·04	0·13	3·48	0·32	15·4	2·6
0·50	13·11	0·22	—	—	2·86	0·43	13·0	2·0
Urea *II*, ethanol–water								
0·00	55·56	3·49	5·46	0·20	16·6	0·88	37·3	4·6
0·05	47·50	3·22	3·88	0·54	12·2	1·2	33·7	5·6
0·10	40·89	2·86	2·91	0·25	8·51	0·50	26·3	2·3
0·15	35·39	2·42	1·74	0·19	5·64	0·61	17·6	1·8
0·20	30·72	1·96	1·28	0·06	4·27	0·36	12·7	0·94
0·25	26·72	1·58	0·962	0·03	3·31	0·26	9·23	2·3
0·30	23·28	1·24	0·781	0·17	2·11	0·16	6·99	0·59
0·35	20·28	0·97	0·584	0·04	2·12	0·20	6·02	0·66
0·40	17·61	0·70	0·494	0·03	1·83	0·58	5·11	0·28
0·45	15·22	0·45	0·442	0·06	1·51	0·09	4·09	0·25
0·50	13·11	0·22	—	—	1·23	0·22	3·37	0·17
Amide *I*, methanol–water								
0·000	55·56	3·49	17·1	1·1	43·3	3·7	95·1	12
0·025	54·08	3·44	—	—	44·8	2·2	87·4	4·5
0·050	52·61	3·39	11·9	0·99	45·4	7·4	100	12
0·075	48·56	3·21	—	—	35·4	2·9	81·2	6·4
0·100	44·50	3·03	8·53	0·50	—	—	67·4	7·7
0·125	42·31	1·89	—	—	30·0	3·7	62·5	7·6
0·150	40·11	2·75	8·48	1·8	25·2	1·7	60·3	5·6
0·175	37·86	2·58	—	—	23·6	3·2	54·3	8·2

TABLE I
(Continued)

x	c_{H_2O}	Y	k_{25}	s	k_{35}	s	k_{45}	s
0·200	35·61	2·42	7·57	1·5	23·5	3·2	51·5	16
0·225	33·69	2·24	—	—	18·9	2·7	41·5	6·5
0·250	31·78	2·04	5·23	0·55	15·2	2·0	41·7	11
0·275	29·49	1·98	—	—	14·5	2·3	35·9	5·1
0·300	27·22	1·92	4·09	0·47	14·6	2·0	38·0	7·8
0·325	26·19	1·83	—	—	12·2	1·4	30·5	2·9
0·350	25·17	1·74	3·76	0·58	12·6	1·3	30·5	6·1
0·375	23·72	1·61	—	—	10·8	0·92	26·8	2·8
0·400	22·28	1·48	2·66	0·26	—	—	29·3	2·8
0·425	20·94	1·36	—	—	8·57	0·75	22·3	2·3
0·450	19·61	1·23	2·54	0·34	7·79	1·0	23·1	3·8
0·475	18·36	1·09	—	—	6·56	1·2	18·6	1·8
0·500	17·11	0·96	—	—	6·39	0·69	19·9	4·0
Urea *II*, methanol–water								
0·00	55·56	3·49	5·46	0·20	16·6	0·88	37·3	4·6
0·05	52·61	3·39	5·06	0·13	14·0	1·3	40·7	4·4
0·10	44·50	3·03	4·71	0·46	13·4	1·8	36·0	6·7
0·15	40·11	2·75	3·92	0·38	11·7	1·0	30·4	3·9
0·20	35·61	2·42	3·47	0·52	9·65	0·72	27·3	3·5
0·25	31·78	2·04	2·24	0·11	8·05	0·85	21·9	2·3
0·30	27·22	1·92	1·59	0·12	6·13	0·26	14·2	1·3
0·35	25·17	1·74	1·63	0·18	5·55	0·19	14·7	0·91
0·40	22·28	1·48	1·27	0·07	3·81	0·23	11·7	0·59
0·45	19·61	1·23	0·953	0·22	3·17	0·30	10·6	0·21
0·50	17·11	0·96	0·802	0·21	2·82	0·29	8·99	0·57
Amide *I*, dioxane–water								
0·00	55·56	3·49	—	—	43·3	3·7	95·1	12
0·05	44·50	2·88	—	—	20·6	1·5	46·3	4·0
0·10	36·44	2·35	—	—	7·35	0·48	25·0	2·0
0·15	30·28	1·62	—	—	3·52	0·34	12·9	1·8
0·20	25·50	1·10	—	—	1·80	0·16	5·98	6·4
0·25	21·56	0·64	—	—	0·985	0·07	3·53	1·5
0·30	18·39	0·22	—	—	0·551	0·12	2·19	1·5
0·35	15·67	−0·14	—	—	0·357	0·06	2·02	5·5
0·40	13·39	−0·48	—	—	0·225	0·15	0·888	0·53
0·45	11·44	−0·78	—	—	—	—	0·680	0·51
0·50	9·72	−1·13	—	—	—	—	0·466	0·79

TABLE I
(*Continued*)

x	c_{H_2O}	Y	k_{25}	s	k_{35}	s	k_{45}	s
				Urea *II*, dioxane–water				
0·00	55·56	3·49	—	—	16·6	0·88	37·3	4·5
0·05	44·50	2·88	—	—	6·79	0·24	16·4	1·7
0·10	36·44	2·35	—	—	3·23	0·15	6·69	0·80
0·15	30·28	1·62	—	—	1·35	0·06	3·31	0·91
0·20	25·50	1·10	—	—	0·713	0·09	1·74	0·75
0·25	21·56	0·64	—	—	0·424	0·09	1·52	0·15
0·30	18·39	0·22	—	—	0·235	0·02	0·95	0·15
0·35	15·67	−0·14	—	—	0·142	0·03	—	—
				Amide *I*, formamide–water				
0·00	55·56	—	—	—	43·3	3·7	95·1	1·2
0·05	49·78	—	—	—	35·3	4·3	101	1·0
0·10	44·67	—	—	—	29·8	2·1	78·5	1·1
0·15	40·00	—	—	—	24·4	2·4	59·7	1·2
0·20	35·83	—	—	—	20·0	1·5	60·3	1·4
0·25	32·06	—	—	—	17·4	0·69	49·7	0·74
0·30	28·61	—	—	—	15·2	0·84	40·4	0·57
0·35	25·44	—	—	—	12·6	0·98	37·5	0·80
0·40	22·50	—	—	—	11·1	0·54	35·1	0·42
0·45	19·83	—	—	—	9·34	2·5	30·9	0·83
0·50	17·33	—	—	—	7·82	0·27	25·5	0·53

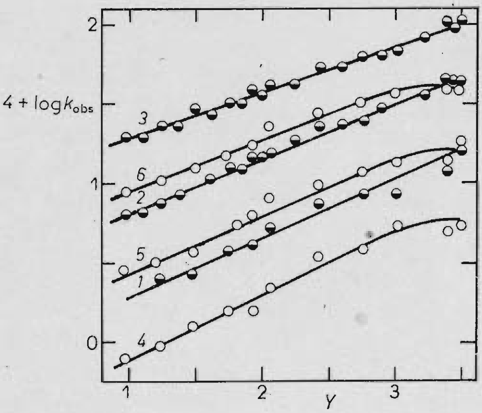


FIG. 1

Dependence of log k_{obs} on parameter Y for hydrolysis of amide *I* in mixture methanol–water at 25°C *1*, 35°C *2*, 45°C *3* and for urea *II* in mixture methanol–water at 25°C *4*, 35°C *5* and 45°C *6* reaction rate *vs* temperature

$$k = (kT/h)\exp(-\Delta G^{\ddagger}/RT) \tag{4}$$

and if the solvent composition change is expressed generally as a perturbance described by a parameter P, then the LFER type equation reads as follows

$$\partial \ln k/\partial P = -(RT)^{-1}\,\partial \Delta G^{\ddagger}/\partial P\,, \tag{5}$$

wherefrom Eq. (*6*) follows on proper substitution for the activation free enthalpy $\Delta G^{\ddagger}$.

$$\partial \ln k/\partial P = -(RT)^{-1}\,\partial \Delta H^{\ddagger}/\partial P + R^{-1}\,\partial \Delta S^{\ddagger}/\partial P\,. \tag{6}$$

TABLE II

Regression coefficients of Eq. (*1*) for non-catalyzed solvolysis of the compounds *I* and *II*

Compound Medium	T, °C	$\log k_0$	$s_{\log k_0}$	m	s_m	n	r
I	25·0	−4·14	0·05	0·396	0·022	10	0·998
Ethanol–water	35·0	−3·64	0·03	0·379	0·015	11	0·992
	45·0	−2·98	0·04	0·309	0·017	11	0·986
II	25·0	−4·55	0·02	0·344	0·011	10	0·996
Ethanol–water	35·0	−4·00	0·03	0·333	0·012	11	0·994
	45·0	−3·54	0·01	0·331	0·005	11	0·999
I	25·0	−4·03	0·06	0·342	0·024	10	0·981
Methanol–water	35·0	−3·51	0·02	0·337	0·008	19	0·995
	45·0	−2·99	0·02	0·281	0·008	21	0·992
II	25·0	−4·51	0·04	0·410	0·020	11	0·992
Methanol–water	35·0	−3·89	0·05	0·351	0·023	11	0·986
	45·0	−3·35	0·04	0·309	0·017	11	0·989
I	35·0	−4·38	0·02	0·571	0·011	9	0·999
Dioxane–water	45·0	−3·75	0·02	0·498	0·011	11	0·999
II	35·0	−4·76	0·02	0·557	0·008	8	0·999
Dioxane–water	45·0	−4·20	0·07	0·481	0·031	7	0·989

TABLE III

Isokinetic temperatures and statistical criteria of model reaction in mixed solvents

No	Compound, solvent	Reaction type	β^e, K	s_β, K	F_1	F_2	F_3	$F_{0.95}$	$10^2 s_0$	$10^2 s_{00}$	$10^2 \psi$
1	t-butyl chloride[23], C_2H_5OH–H_2O	S_N1	—	—	—	33·74	13·83	2·25	—	0·76	—
2	t-butyl chloride[23], CH_3OH–H_2O	S_N1	—	—	—	36·24	11·26	3·35	—	0·61	—
3	t-butyl chloride[23], CH_3COOH–$HCOOH$	S_N1	−228·9	110·3	4·10	8·66	8·26	19·30	5·07	0·88	3·31
4	t-butyl chloride[23], $HCOOH$–H_2O	S_N1	150·0	18·4	0·77	5·26	1·89	234·0	2·94	0·63	3·22
5	t-butyl chloride[23], CH_3COOH–H_2O	S_N1	−169·4	39·9	2·29	5·90	4·54	240·5	44·8	0·46	3·47
6	t-butyl chloride[23], dioxane–H_2O	S_N1	—	—	—	81·06	7·82	4·95	—	0·75	—
7	t-butyl chloride[23], acetone–H_2O	S_N1	—	—	—	29·57	1·63	19·39	—	0·50	—
8	t-butyl chloride[23], dioxane–HCOOH	S_N1	—	—	—	14·42	2·18	224·6	—	0·82	—
9	t-butyl chloride[23], FA[b]–H_2O	S_N1	—	—	—	13·25	0·63	199·5	—	1·17	—
10	benzyl chloride[31], C_2H_5OH–H_2O	S_N1	—	—	—	36·32	15·23	3·48	—	1·13	—
11	benzyl chloride[32], acetone–H_2O, OH^-	S_N1	184·9	16·6	3·93	22·98	10·42	5·14	0·67	0·42	1·22

TABLE III
(*Continued*)

No	Compound, solvent	Reaction type	β[e], K	s_β, K	F_1	F_2	F_3	F_0l_{95}	$10^2 s_0$	$10^2 s_{00}$	$10^2\psi$
12	t-butyl acetate[19], dioxane–H_2O, H^+	$A_{Al}1$	186·4	38·6	0·40	1·46	0·77	3·87	5·22	2·92	7·53
13	benzyl chloride[33], DMSO[c]–H_2O	S_N1–S_N2	—	—	—	74·53	6·20	2·39	—	0·47	—
14	BCTAH[d], ref[34], DMF[e]–H_2O	—	131·6	31·0	6·90	13·06	8·20	3·84	1·91	0·79	3·62
15	BCTAH[d], ref.[34], acetone–H_2O	—	216·3	13·1	9·36	60·86	35·17	4·07	2·67	1·16	3·49
16	methyl benzenesulphonate[35], CH_3OH–H_2O, OH^-	S_N1–S_N2	218·4	15·9	—[f]	[f]	—[f]	—[f]	2·03	0·005	3·25
17	methyl benzenesulphonate[35], C_2H_5OH–H_2O, OH^-	S_N1–S_N2	—	—	—[f]	—[f]	—[f]	—[f]	—	0·005	—
18	methyl benzenesulphonate[35], i-C_3H_7OH–H_2O, OH^-	S_N1–S_N2	114·0	14·1	—[f]	—[f]	—[f]	—[f]	0·99	0·004	1·52
19	methyl benzenesulphonate[35], t-C_4H_9OH–H_2O, OH^-	S_N1–S_N2	—	—	—[f]	—[f]	—[f]	[f]—	—	0·005	—
20	ethyl benzenesulphonate[13], acetone–H_2O	S_N1–S_N2	—	—	—	52·87	7·19	2·64	—	0·49	—
21	n-propyl benzenesulphonate[13], acetone–H_2O	S_N1–S_N2	−142·9	22·95	8·36	32·20	7·14	3·87	1·73	0·38	2·17
22	isopropyl benzenesulphonate[13] acetone–H_2O	S_N1–S_N2	—	—	—	48·25	12·22	2·02	—	0·46	—
23	benzyl chloride[32], DMSO[c]–H_2O, OH^-	S_N2	617·6	27·7	0·39	16·90	66·18	2·85	1·21	0·89	1·71

TABLE III
(*Continued*)

No	Compound, solvent	Reaction type	β^e, K	s_β, K	F_1	F_2	F_3	$F_0 l_{95}$	$10^2 s_{00}$	$10^2 s_{00}$	$10^2 \psi$
24	benzyl chloride[36], DMSO[c]–CH_3OH, CH_3O^-	S_N2	1 844·3	550·1	5·04	4·61	47·56	2·15	2·08	0·79	1·79
25	2,4-dinitrophenyl alkyl ether[16], CH_3OH–H_2O, OH^-	S_N2	565·7	28·1	1·87	18·15	56·13	3·29	0·84	0·34	1·32
26	2,4-dinitrophenyl alkyl ether[16], C_2H_5OH–H_2O, OH^-	S_N2	567·9	535·5	69·08	70·07	72·20	2·95	3·05	0·27	6·50
27	phenyl acetate[15], dioxane–H_2O, H^+	$A_{Ac}2$	414·9	19·5	2·57	10·34	16·18	3·87	1·23	0·44	3·53
28	ethyl acetate[17], DMSO[c]–H_2O, H^+	$A_{Ac}2$	155·7	10·3	16·58	152·12	51·95	2·51	1·93	0·49	2·80
29	ethyl acetate[37], DMSO[c]–H_2O, OH^-	$B_{Ac}2$	169·0	7·7	2·11	56·58	20·35	2·85	1·10	0·64	2·13
30	ethyl benzoate[38], DMSO[c]–H_2O, OH^-	$B_{Ac}2$	—	—	—	25·91	17·74	3·36	—	0·44	—
31	*I*, C_2H_5OH–H_2O	—	541·5	3 855·4	0·13	0·15	0·17	2·98	3·82	4·23	11·9
32	*II*, C_2H_5OH–H_2O	—	−1 255·6	573·4	0·09	0·10	0·11	2·98	1·57	1·68	4·43
33	*I*, CH_3OH–H_2O	—	395·3	26·7	0·28	0·44	0·54	3·15	2·88	1·10	7·15
34	*II*, CH_3OH–H_2O	—	493·0	171·1	0·22	0·37	0·53	2·85	2·12	1·66	6·54
35	*I*, dioxane–H_2O	—	455·2	78·8	—[f]	—[f]	—[f]	—[f]	1·42	15·86	3·01
36	*II*, dioxane–H_2O	—	367·0	11·6	—[f]	—[f]	—[f]	—[f]	1·49	0·23	2·87
37	*I*, FA[b]–H_2O	—	375·3	16·2	—[f]	—[f]	—[f]	—[f]	1·26	0·08	4·01

[a] Only the isokinetic temperatures within the interval $\beta^{-1} \in \langle -7{\cdot}0; 10{\cdot}5 \rangle$ are given; [b] FA formamide: [c] DMSO dimethyl sulphoxide; [d] BCTAH 1,7-dichloro-2,4,6-trinitro-2,4,6-triazaheptane; [e] DMF dimethylformamide; [f] the criterion cannot be calculated due to insufficient number of degrees of freedom.

Interpretation of Eq. (*6*) can differentiate three cases. If the activation enthalpy $\Delta H^{\ddagger}$ does not change with the solvent composition (isoenthalpic reaction), then Eq. (*6*) changes to Eq. (*7*). If the activation entropy $\Delta S^{\ddagger}$ does not change with the solvent composition (isoentropic reaction), then Eq. (*6*) changes to Eq. (*8*). If there is linear relation between the activation enthalpy and activation entropy with changing solvent composition. *i.e.* isokinetic relation is valid, then Eq. (*6*) changes to Eq. (*9*), in which β means the isokinetic temperature.

$$\partial \ln k/\partial P = R^{-1}\, \partial \Delta S^{\ddagger}/\partial P \tag{7}$$

$$\partial \ln k/\partial P = -(RT)^{-1}\, \partial \Delta H^{\ddagger}/P \tag{8}$$

$$\begin{aligned}\partial \ln k/\partial P &= (T - \beta)\,(RT)^{-1}\, \partial \Delta S^{\ddagger}/\partial P = \\ &= (T/\beta - 1)\,(RT)^{-1}\, \partial \Delta H^{\ddagger}/\partial P\,.\end{aligned} \tag{9}$$

If choice of the parameter P allows to use differences instead of derivatives in Eqs (*7*)–(*9*), then it is possible to determine the sign of the slope of the simple linear dependence (the right-hand sides of Eqs (*7*)–(*9*)) and to use it as a criterion of mechanism (sign of the reaction constant ϱ in the Hammett equation). So far for solvolytic reactions such a scale of parameters valid for all or at least for most solvents (which would enable to use linear dependences) is not available. However, the sign criterion can be used even without detailed knowledge of dependence $\ln k$ *vs* P, if at least one of Eqs (*7*)–(*9*) is fulfilled. Table III summarizes results of calculations of the isokinetic temperature[24] with the corresponding statistical criteria for various mixed solvents and various types of reactions. For evaluation of validity of the isokinetic relation we give the criteria F_1 (refs[27,28]) and ψ (ref.[29]) along with the standard deviations s_0 and s_{00} (ref.[30]). The criteria F_3 and F_2 indicate whether the reaction is isoenthalpic (Eq. (*7*)) or isoentropic[27,28] (Eq. (*8*)). The given results show that monomolecular reactions exhibit positive sign of the slope (Eqs (*7*) and (*9*) for $\beta < T_{\text{exp}}$). It is possible to include in the same category also the reactions for which the isokinetic temperature lies outside the interval (used for technical reasons) $\beta^{-1} \in \langle -7; 10{\cdot}5 \rangle$, because these reactions can be classed among isoenthalpic reactions (within experimental error). On the contrary, bimolecular reactions exhibit negative slopes (Eqs (*8*) and (*9*) for $\beta > T_{\text{exp}}$). An exception to this rule are specifically catalyzed hydrolyses of esters in mixtures dimethyl sulphoxide–water (Table III, Nos 28–30), although the isokinetic relation is well fulfilled in the case of ethyl acetate (No 29). Application of the given criterion to the substrates studied by us is more complex. The criterion F_3 (which cannot be calculated in all cases) indicates an isoenthalpic reaction (within experimental error) and, hence, monomolecular mechanism. From this point of view the found isokinetic temperatures have no statistical significance. On the contrary, it can be expected that increasing number of experimental temperatures (and, hence, increasing accuracy) will lead to confirmation of the isokinetic temperature higher than the experimental temperature range (even in the case of the compound *II* in ethanol–water mixture). This conclusion indicates bimolecular character of the reaction studied. If also the results obtained by the Grunwald–Winstein equation (Eq. (*1*), Table II) are taken into account, it can be stated that water participates in the transition state of hydrolysis of the substrates studied by us.

REFERENCES

1. Sendega R. V.: Ukr. Khim. Zh. *44*, 89 (1978).
2. Sendega R. V., Gorbatenko N. G.: Reakts. Sposobnost Org. Soedin. *10*, 689 (1973).
3. Drenth W., Cocivera M.: Can. J. Chem. *54*, 3944 (1976).
4. Pihl A., Talvik A., Rohtla I., Sonn R.: Reakts. Sposobnost Org. Soedin. *8*, 277 (1971).
5. Sendega R. V., Gorbatenko N. G.: Reakts. Sposobnost Org. Soedin. *10*, 673 (1973).
6. Laidler K. J., Landskroener A. P.: Trans. Faraday Soc. *52*, 200 (1956).
7. Engbersen J. F. J., Engberts J. B. F. N.: J. Amer. Chem. Soc. *97*, 1563 (1975).
8. Amis E. S.: *Solvent Effects on Reaction Rates and Mechanisms*, p. 147. Academic Press, New York 1966.
9. Winstein S., Grunwald E.: J. Amer. Chem. Soc. *70*, 846 (1948).
10. Kaspi J., Rappoport Z.: Tetrahedron Lett. *1977*, 2035.
11. Koppel I. A., Körgesaar A. O., Palm V. A.: Reakts. Sposobnost Org. Soedin. *1*, 125 (1964).
12. Koppel I. A., Palm V. A.: Reakts. Sposobnost Org. Soedin. *8*, 291 (1971).
13. Tommila E.: Acta Chem. Scand. *9*, 975 (1955).
14. Tommila E., Tiilikainen M., Voipio A.: Ann. Acad. Sci. Fennicae A II, *65* (1955); Chem. Abstr. *50*, 4601 (1955).
15. Sadek H., Khalil F. Y.: Z. Phys. Chem., Neue Fol. *61*, 63 (1968).
16. Tommila E., Murto J.: Acta Chem. Scand. *16*, 63 (1962).
17. Tommila E., Murto ;. L.: Acta Chem. Scand. *17*, 1957 (1963).
18. Pekkarinen L., Tommila E.: Acta Chem. Scand. *13*, 1019 (1959).
19. Sadek H., Khalil F. Y.: Z. Phys. Chem., Neue Fol. *57*, 306 (1968).
20. Popov A. F., Tokarev V. J., Litvinenko L. M., Torjanik A. I.: Reakts. Sposobnost Org. Soedin. *4*, 658 (1967).
21. Pytela O., Večeřa M., Vetešník P.: This Journal *45*, 1269 (1980).
22. Pitra J., Veselý Z., Kavka F.: *Laboratorní úprava chemikálií a pomocných látek.* Published by SNTL, Prague 1969.
23. Fainberg A. H., Winstein S.: J. Amer. Chem. Soc. *78*, 2770 (1956).
24. Pytela O., Večeřa M., Vetešník P.: This Journal, *46*, 898 (1981).
25. Pytela O., Večeřa M., Vetešník P.: This Journal *45*, 2108 (1980).
26. Schaleger L. L., Long F. A.: Advan. Phys. Org. Chem. *1*, 1 (1963).
27. Šimulis V. I.: Kinet. i Katal. *10*, 1026 (1969).
28. Džuntini B., Šimulis V. I.: Kinet. Katal. *15*, 210 (1974).
29. Exner O.: This Journal *31*, 3222 (1966).
30. Exner O., Beránek V.: This Journal *38*, 781 (1973).
31. Hyne J. B., Wills R., Wonkka R. E.: J. Amer. Chem. Soc. *84*, 2914 (1962).
32. Tommila E., Pitkänen I. P.: Acta Chem. Scand. *20*, 937 (1966).

33. Tommila E.: Acta Chem. Scand. *20*, 923 (1966).
34. Starostin B. S., Krauklish I. V., Sinev V. V.: Org. Reactions *16*, 429 (1979).
35. Hyne J. B., Robertson R. E.: Can. J. Chem. *34*, 863, 931 (1956).
36. Tommila E., Savolainen M.: Acta Chem. Scand. *20*, 946 (1966).
37. Tommila E., Murto M. L.: Acta Chem. Scand. *17*, 1947 (1963).
38. Roberts D. D.: J. Org. Chem. *29*, 2039 (1964).

Translated by J. Panchartek.