Solvent Effects on the Kinetics and Mechanism of the Acid-Catalysed Hydrolysis of Di*tert.*-butylsuccinate in Dioxane-Water Mixtures

Adel N. Asaad and Fayez Y. Khalil

Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt

Z. Naturforsch. **40 a**, 84–91 (1985); received October 5, 1984

The acid-catalysed hydrolysis of *ditert.*-butylsuccinate in dioxane-water mixtures proceeds via consecutive first-order reactions. The rate constants k_I and k_{II} corresponding to the two steps decrease with increasing dioxane content of the medium. After reaching a minimum at 90% (w/w) dioxane, both rate constants increase again with further addition of dioxane. The kinetic ratio k_I/k_{II} is smaller than the statistical value 2.0, and is markedly affected both by solvent composition and temperature. The maximum concentration of the intermediate half ester decreases with increasing dioxane content. The observed activation energies E_I and E_{II} of the two steps of the reaction are largely dependent on temperature as well as solvent composition indicating a mixed type of bond fission represented by the $A_{Al}1$ and $A_{Ac}2$ mechanisms, whose relative contributions in the overall rate constants k_I and k_{II} could be calculated on the basis of the number of water molecules incorporated in the corresponding transition states. The effect of bulk dielectric constant on the reaction rate was investigated in the light of the available electrostatic theories and showed the reaction to be an ion-molecular dipole type of interaction. The activation thermodynamic parameters were computed and discussed as criteria of solvent effect and mechanism.

Introduction

The problem of solvent effects on the hydrolysis of dicarboxylic esters involving a consecutive reaction has not yet been clarified completely [1–5]. The study is even more complicated by the presence of tertiary groups in the ester molecule as they lead to the involvement of two concurrent mechanisms. The extent of work published on this problem is small compared to the extensive study done on simple monocarboxylic ester hydrolysis [6]. In order to gain more information concerning the role of solvent in this type of hydrolysis, the system di*tert.*-butylsuccinate in acidified dioxane-water mixtures was chosen for study. From O^{18} isotopic tracer studies it is well known, in general, that acid hydrolysis of esters takes place via alkyl-oxygen bond fission $A_{Al}1$ when the alkyl radicals have relevant carbonium ion stabilities [7–10]. However, the solvent plays an important role in the actual mechanism followed in these cases [11–13]. Thus, although *tert.*-butyl esters are almost completely hydrolysed via $A_{Al}1$ mechanism in pure water, the acyl-oxygen bond fission, $A_{Ac}2$, predominates in slightly aqueous media [12–14]. Since, under all conditions, the observed overall rate constant of the reaction results from two components representing the two mechanistic routes, and this applies to the two tertiary groups of the ester under investigation, one will have four rate constants involved in the reaction. It is of interest, therefore, to analyse the data obtained experimentally into four individual rate constants and to investigate the effects of solvent and temperature on them as well as on the type of bond fission, and to present a thermodynamic approach to the reaction under different conditions.

Reprint requests to Dr. A. N. Asaad, Department of Chemistry, Faculty of Science, Alexandria University, Alexandria/Egypt.

Experimental

Di*tert.*-butylsuccinate was prepared by reacting succinyl chloride and *tert.*-butyl alcohol in presence of diethylaniline [15]. m.p. 31.5 °C, b.p. 107 at 7 mm pressure. IR (film): 300, 1750 (C=O), 1380 and 1160 cm^{-1}; ^{1}H-NMR ($CDCl_3$): $\delta = 1.3$ (s, 18 H, CH_3), 2.3 (s, 4 H, CH_2).

Symmetrical 1,4 dioxane was purified as described before [16]. Dioxane-water mixtures were prepared on a weight basis and consisted of 30.39, 40.16, 50.37, 69.46, 79.12, 89.56 and 94.45% (w/w) dioxane. The kinetic procedure followed involved a

0340-4811 / 85 / 0100-0084 $ 01.30/0. – Please order a reprint rather than making your own copy.

volumetric analysis of samples for the acid produced during the course of the reaction using a screened indicator [17].

Results and Calculation

The specific first-order rate constants k_I and k_{II} of the two consecutive steps of the reaction were calculated using the time ratio method adopted by Swain [18, 19]. These values, together with the kinetic ratio, k_I/k_{II}, in the temperature range between 20 and 90 °C and in all solvent compositions, are compiled in Table 1.

The calculated thermodynamic parameters of activation [20], $\Delta H^{\neq}$, $\Delta G^{\neq}$ and $\Delta S^{\neq}$ are collected in Table 4.

Discussion

An increase of the dioxane content of the medium was found to decrease the specific rate constants k_I and k_{II} of the individual consecutive steps of the reaction to a minimum (Fig. 1) at about 90% dioxane (w/w), reminiscent of the maximum in acidity function of the mixed solvent in this range [21, 22]. The values of the respective rate constants are smaller than those for diethylsuccinate [23], under the same conditions, which can be attributed to the electron repelling and/or steric effects, produced by *tert.*-butyl groups, mainly responsible for the hindrance of the nucleophilic attack of water molecules, since tertiary esters exist only in a cisoid conformation rather than a transoid one [24]. The kinetic ratio of the observed rate constants (k_I/k_{II}) is markedly smaller than 2.0, which is the value expected statistically for symmetric dicarboxylic esters [17, 23, 25] and decreases regularly with increasing dioxane content. It also suffers a slight increase with temperature (cf. Table 1). The decrease of the kinetic ratio below 2.0 can be rationalised as due to the relatively large steric effect of the bulky *tert.*-butyl groups, in the first and second

Table 1. Rate constants k_I, k_{II} and the kinetic factors k_I/k_{II} for the consecutive acid-catalysed hydrolysis of di*tert.*-butylsuccinate in dioxane-water mixtures.

t, °C	$k \cdot 10^6$ min^{-1}	Dioxane, wt% 30.390	40.163	50.373	59.788	69.457	79.119	89.557	94.451
		$[H_2O]$, mol/l 38.573	33.144	27.659	22.242	16.870	11.503	5.704	2.985
20	k_I	35.81	23.92	15.57	10.22	6.47	5.74	5.16	7.70
	k_{II}	20.70	14.28	9.61	6.53	4.28	3.94	3.63	5.30
	k_I/k_{II}	1.730	1.675	1.620	1.565	1.510	1.455	1.420	1.452
30	k_I	87.10	54.44	38.14	26.10	15.45	13.28	11.99	17.42
	k_{II}	50.20	32.39	23.44	16.59	10.18	9.09	8.35	11.82
	k_I/k_{II}	1.735	1.681	1.627	1.573	1.518	1.462	1.436	1.468
40	k_I	254.0	160.0	134.0	87.50	57.54	32.36	31.99	58.21
	k_{II}	146.1	94.65	81.99	55.34	37.68	22.06	22.09	39.46
	k_I/k_{II}	1.742	1.691	1.634	1.581	1.527	1.467	1.448	1.475
50	k_I	1166	631.0	383.6	228.6	151.3	112.2	116.2	138.1
	k_{II}	669.1	373.4	234.2	114.2	98.76	76.12	79.78	93.06
	k_I/k_{II}	1.743	1.692	1.638	1.585	1.532	1.474	1.457	1.484
60	k_I	4276	1987	1416	897.4	619.7	415.4	478.6	602.6
	k_{II}	2450	1172	862.0	564.1	402.9	279.7	326.9	404.4
	k_I/k_{II}	1.745	1.695	1.643	1.591	1.538	1.485	1.464	1.490
70	k_I	14876	6596	4256	3088	1706	1136	1122	1445
	k_{II}	8513	3887	2584	1935	1104	760.5	762.8	966.2
	k_I/k_{II}	1.747	1.697	1.647	1.596	1.545	1.493	1.471	1.496
80	k_I	40000	16859	10641	6185	4641	2541	3107	3647
	k_{II}	22857	9917	6445	3866	2996	1694	2104	2430
	k_I/k_{II}	1.750	1.700	1.651	1.600	1.549	1.500	1.477	1.501
90	k_I	161538	52188	34604	20122	15769	6761	9547	12338
	k_{II}	92202	30644	20909	12529	10128	4486	6442	8192
	k_I/k_{II}	1.752	1.703	1.655	1.606	1.557	1.507	1.482	1.506

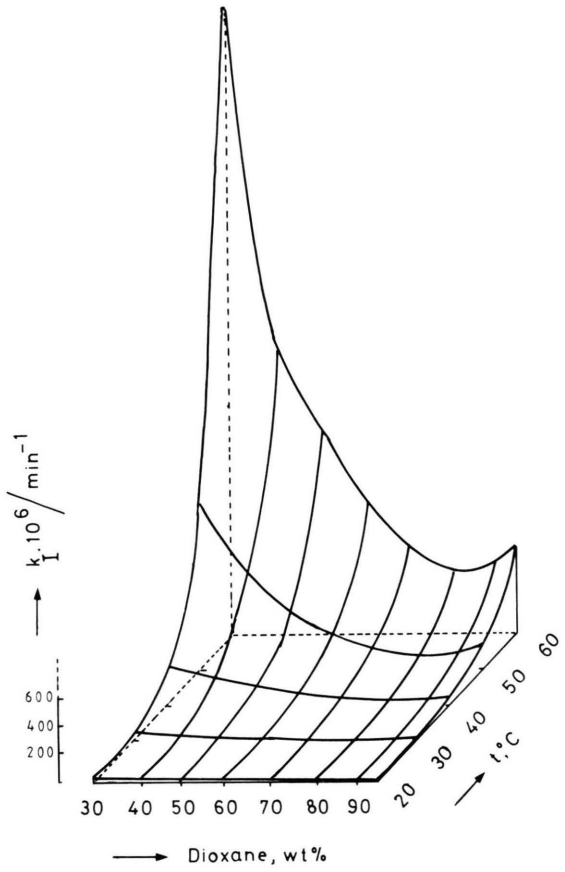

Fig. 1. Variation of the overall rate constant k_I of the first step with dioxane content and temperature.

hydrolysis steps, whereas the dependence on dioxane content is mainly attributed to the different contributions of the acyl oxygen bond fission, $A_{Ac}2$, relative to that of the alkyl-oxygen $A_{Al}1$, at different solvent compositions. The logarithm of the kinetic ratio can be taken as indication of the selectivity between the first and second steps of the reaction. A plot of these selectivity values against the reactivity, represented by log k_{II}, at different dielectric constants gave straight lines with positive slopes, known as anti-reactivity selectivity principle [26, 27] ranging from 0.105 at 20 °C to 0.058 at 90 °C. The correlation coefficients of these linear relationships are almost unity, at all temperatures, indicating uniformity of mechanism followed by the two steps of the reaction in the whole range of solvent composition.

The changes in concentration of the reactant di*tert.*-butylsuccinate, the intermediate *tert.*-butylhydrogensuccinate and the product succinic acid with time were calculated during the course of the reaction in 30.39% (w/w) dioxane-water mixture at 20 °C, and the result represented graphically in Figure 2. It is seen that the maximum concentration of the halfester was reached at $t_{max} = 36.27 \times 10^3$ min, while for diethylsuccinate this parameter is 5.88 $\times 10^3$ min under the same conditions [23]. Figure 2 also shows the variation of maximum halfester concentration as well as the t_{max} values at different solvent compositions. The curve for t_{max} in dioxane-water mixtures has the same features as the variation of k_I and k_{II} with solvent composition and shows the same minimum at almost 90% (w/w) dioxane. On the other hand, the maximum concentration of the halfester shows an interesting trend in which it decreases with increasing dioxane content of the medium and reaches a minimum also at 90% (w/w) dioxane. This behaviour is referred mainly to the variation of the k_I/k_{II} ratio values with solvent composition [22], which cannot exist unless there is an additional factor affecting the rate of the second step as compared to the first one, causing the rate of consumption of the halfester to be larger than its rate of accumulation and that the rate of the second step becomes easier with increase in dioxane content. This argument is evidenced by the fact that for primary dicarboxylic esters like diethylsuccinate [23] and malonate [17] the maximum concentration of the halfester is completely independent of solvent composition.

The Arrhenius plots show a slight deviation near 50 °C, which cannot be attributed solely to solvent effects or other external factors [19] but must mainly be due to the mixed $A_{Al}1$ and $A_{Ac}2$ mechanisms. Statistical treatment, by the least-squares method [19, 28], of the Arrhenius equation in the two temperatures ranges on both sides of 50 °C, namely, 20–50 and 60–90 °C, at different solvent compositions, gave better correlation coefficient values than when these temperatures were examined as one range (Table 3). The resulting E_I and E_{II} values of the two overall steps of the reaction varied from 88.5 to 77.6 kJ mol^{-1} as the dioxane content of the solvent increases from 30 to 95% (w/w) in the lower temperature range and from 110.4 to 99.9 kJ mol^{-1} in the higher one, for the same solvent compositions.

For esters generally hydrolysed by pure $A_{Al}1$ mechanism, the activation energy equals 100–140 kJ mol^{-1}, while for those hydrolysing by pure $A_{Ac}2$

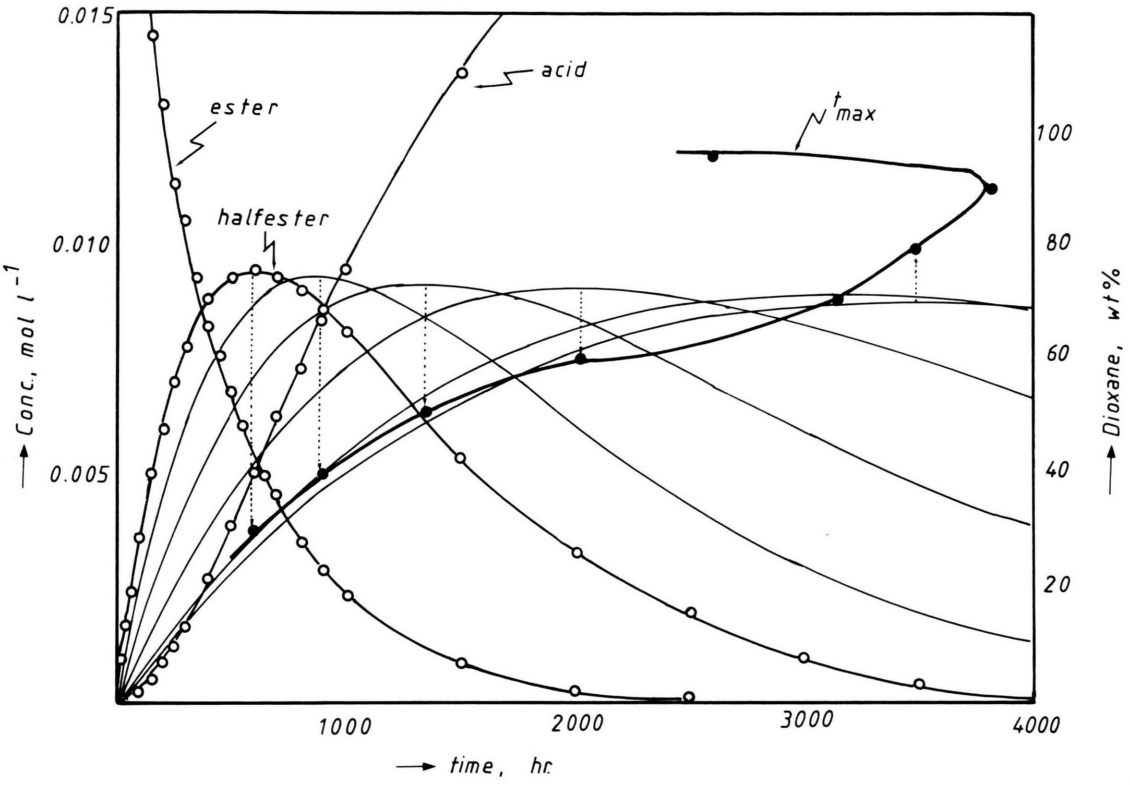

Fig. 2. Variation of concentration of reactant ester, half ester and product acid with time during the course of the reaction, and of t_{max} with dioxane content of the medium.

mechanism the values are 50–80 kJ mol^{-1} [8, 12] and are independent of temperature and solvent composition [23]. In the light of these data one can conclude that the contribution of $A_{Ac}2$ mechanism increases with dioxane content and decreases with temperature. The reverse is, of course, true for the $A_{Al}1$ mechanism.

Now, it is instructive at this stage to analyse the observed kinetic data in order to calculate the contribution of these two mechanisms. The method adopted depends on the number of water molecules incorporated in the transition states of the two steps. Generally, the observed overall specific rate constant is a linear combination of the specific rate constants characteristic for different components of the reaction

$$k_{(obs)} = \sum_i k_i \qquad (1)$$

or in our case, where only uni- and bimolecular reactions are present,

$$k_{I(obs)} = k_{I1} + k_{I2}, \qquad (2)$$

where k_{I1} and k_{I2} are the rate constants corresponding to the unimolecular and bimolecular mechanisms of the first step, respectively. Assuming that the rate of the $A_{Al}1$ and $A_{Ac}2$ mechanisms are proportional to the nth and mth power of water concentration, respectively, ($n > m$) one has

$$k_{I(obs)} = k'_{I1}[H_2O]^n + k'_{I2}[H_2O]^m, \qquad (3)$$

where k'_{I1} and k'_{I2} are the specific reaction rate constants for the unimolecular and bimolecular mechanisms, respectively, hence

$$k_{I(obs)}/[H_2O]^m = k'_{I1}[H_2O]^{n-m} + k'_{I2}. \qquad (4)$$

The plot of the left hand side of this equation against $[H_2O]^{n-m}$ should yield a straight line of slope k'_{I1} and intercept k'_{I2}. A number of trial plots of $k_{I(obs)}/[H_2O]^m$ ($m = 1 - 4$) against $[H_2O]$ raised to varied powers ranging also from 1 to 4, have been statistically treated using the least squares method. Best correlation coefficients were obtained with $m = 1$ and $n = 4$, and k_{I1} and k_{I2} could accordingly be calculated at all temperatures and solvent compositions. Following the same procedure with k_{II} it

became possible to calculate k_{II1} and k_{II2} corresponding to the second step of the reaction, and hence to calculate the percentage contributions of each bond fission in each step (Table 2). The values $m = 1$ and $n = 4$ imply the incorporation of one and four water molecules in the transition states of bimolecular $A_{Ac}2$ and unimolecular $A_{Al}1$ mechanisms, respectively. The former is in accordance with that normally reported for mono- and dicarboxylic esters hydrolysing via $A_{Ac}2$ mechanism [17, 23, 29], whereas the incorporation of four water molecules in the unimolecular reaction, $A_{Al}1$, is greater than that reported earlier for monocarboxylic esters by one water molecule [9]. This may be due to the expansion of the cyclic transition state [30, 31] by an extra water molecule due to the presence of the two carbonyl groups of the diester. This view is supported by calculation of the radius of the activated complex [31] which was found to be 4.9 and 4.8 Å for the first and second steps, respectively, compared to 4.5 and 4.4 Å for diethylsuccinate [23] and 4.0 Å for *tert.*-butylacetate [9] in which only 3 water molecules are involved in the solvation sheath of the transition complex.

Examination of the data in Table 2 shows that the sum of the individual rate constants ($k_{I1} + k_{I2}$) and

Table 2. Kinetic and mechanistic data for the overall, unimolecular and bimolecular reactions.

t, °C	$k \cdot 10^6$ min^{-1}	Dioxane, wt%							
		30.390	40.163	50.373	59.788	69.457	79.119	89.557	94.451
20	k_{I1}	22.80	12.43	6.03	2.52	0.83	0.18	(0.01)	(0.02)
	k_{I2}	13.18	11.32	9.45	7.60	5.76	3.93	(1.95)	(1.02)
	$(k_{I1} + k_{I2})_{calc}$	35.98	23.75	15.48	10.12	6.59	4.11	(1.96)	(10.4)
	$k_{I(obs)}$	35.81	23.92	15.57	10.22	6.47	5.74	5.16	7.70
	$\%(A_{Al}1)_I$	63.37	52.33	38.95	24.91	12.64	4.38	(1.31)	(0.08)
	k_{II1}	12.42	6.77	3.28	1.37	0.45	0.10	(0.01)	(0.01)
	k_{II2}	8.22	7.06	5.89	4.74	3.59	2.45	(1.26)	(0.64)
	$(k_{II1} + k_{II2})_{calc.}$	20.64	13.83	9.17	6.11	4.04	2.45	(1.27)	(0.65)
	$k_{II(obs)}$	20.70	14.28	9.61	6.53	4.28	3.94	3.63	5.30
	$\%(A_{Al}1)_{II}$	60.18	48.93	35.89	22.46	11.21	3.84	(0.04)	(0.01)
40	k_{I1}	172.33	104.53	66.09	27.47	10.44	1.46	(0.16)	(0.01)
	k_{I2}	72.91	63.83	62.55	58.34	45.67	32.36	15.07	7.83
	$(k_{I1} + k_{I2})_{calc.}$	245.24	168.36	128.64	85.81	56.11	33.82	(15.23)	(7.84)
	$k_{I(obs)}$	254.0	160.0	134.0	87.50	57.54	32.36	31.91	58.21
	$\%(A_{Al}1)_I$	70.27	62.09	51.38	32.01	18.61	4.32	(1.05)	(0.11)
	k_{II1}	95.44	43.90	30.19	13.46	4.73	0.67	(0.02)	(0.01)
	k_{II2}	46.57	59.76	48.36	37.61	31.05	21.45	(11.35)	(5.96)
	$(k_{II1} + k_{II2})_{calc.}$	142.01	103.66	78.55	51.07	35.78	22.12	(11.37)	(5.97)
	$k_{II(obs)}$	146.1	94.65	81.99	55.34	37.68	22.06	22.09	39.46
	$\%(A_{Al}1)_{II}$	67.21	42.35	38.43	26.35	13.21	3.01	(0.21)	(0.01)
60	K_{I1}	2998.07	1634.29	792.61	331.43	109.68	23.71	(1.43)	(0.11)
	k_{I2}	940.77	808.36	974.58	542.47	411.45	280.55	(139.12)	(72.80)
	$(k_{I1} + k_{I2})_{calc.}$	3938.84	2442.65	1767.19	873.90	521.13	304.26	(140.55)	(72.91)
	$k_{I(obs)}$	4276	1987	1416	897.4	619.7	415.4	478.6	602.6
	$\%(A_{Al}1)_I$	76.16	66.91	54.02	37.92	21.05	7.75	(1.02)	(0.15)
	k_{II1}	1602.97	873.80	423.78	177.21	158.64	12.68	(0.77)	(0.06)
	k_{II2}	652.65	560.79	467.98	376.33	285.44	194.63	(96.61)	(50.51)
	$(k_{II1} + k_{II2})_{calc.}$	2255.62	1434.59	891.76	553.54	344.08	207.31	(97.38)	(50.57)
	$k_{II(obs)}$	2450	1172	862	564.1	402.9	279.7	326.9	404.4
	$\%(A_{Al}1)_{II}$	71.06	60.91	47.52	32.01	17.04	6.1	(0.78)	(0.12)
80	k_{I1}	31639.13	17246.97	8364.52	3497.67	1157.50	250.25	(15.15)	(1.13)
	k_{I2}	4742.06	4074.64	3400.32	2734.37	2073.95	1414.15	(701.23)	(366.97)
	$(k_{I1} + k_{I2})_{calc.}$	36381.19	21321.61	11764.84	6232.04	3231.45	1664.40	(716.38)	(368.10)
	$k_{I(obs)}$	40000	16859	10641	6185	4641	2541	3107	3647
	$\%(A_{Al}1)_I$	86.96	80.89	71.10	56.12	35.82	15.03	(2.11)	(0.31)
	k_{II1}	17289.43	9224.73	4570.85	1911.33	632.52	136.75	(8.28)	(0.62)
	k_{II2}	3509.76	3015.77	2516.69	2023.80	1535.00	1046.66	(519.01)	(217.60)
	$(k_{II1} + k_{II2})_{calc.}$	20799.19	12240.50	7087.54	3935.13	2167.52	1183.41	(527.29)	(218.22)
	$k_{II(obs)}$	22857	9917	6445	3866	2996	1694	2104	2430
	$\%(A_{Al}1)_{II}$	8312	75.36	64.49	48.57	29.18	11.55	(1.57)	(0.23)

Table 3. Activation energies of the overall, unimolecular and bimolecular reactions in the two steps.

E, kJ mol^{-1}		Dioxane, wt%							
		30.390	40.163	50.373	59.788	69.457	79.119	89.557	94.451
$E_{I\,obs}$	20–50 °C	88.5 ± 0.04	85.4 ± 0.6	85.4 ± 0.6	82.8 ± 2.1	84.6 ± 1.4	76.9 ± 0.8	80.9 ± 1.3	77.60 ± 1.2
	60–90 °C	110.4 ± 2.1	100.1 ± 1.1	97.7 ± 0.6	100.6 ± 0.4	107.7 ± 0.6	92.0 ± 1.3	95.20 ± 0.9	99.9 ± 1.2
$E_{II\,obs}$	20–50 °C	88.2 ± 0.3	85.1 ± 0.5	85.1 ± 0.6	81.4 ± 1.0	84.3 ± 1.2	76.6 ± 0.9	80.3 ± 0.4	77.0 ± 1.1
	60–90 °C	110.3 ± 1.2	100.0 ± 1.2	97.4 ± 0.7	100.3 ± 0.5	106.8 ± 0.6	91.5 ± 1.1	99.7 ± 1.0	99.5 ± 1.8
E_{I1}	20–50 °C	117.33 ± 0.7	116.95 ± 0.4	115.99 ± 0.2	116.02 ± 0.9	115.60 ± 0.2	117.11 ± 0.6	–	–
E_{I2}		97.39 ± 0.3	97.33 ± 0.5	99.43 ± 1.2	96.21 ± 0.4	96.11 ± 0.9	95.96 ± 0.8		
E_{II1}		117.17 ± 0.6	117.52 ± 1.7	116.55 ± 0.6	116.34 ± 0.5	117.49 ± 1.8	117.32 ± 0.4	–	–
E_{II2}		100.18 ± 2.1	98.75 ± 0.8	98.87 ± 0.6	98.66 ± 1.9	98.69 ± 0.3	98.63 ± 0.5		

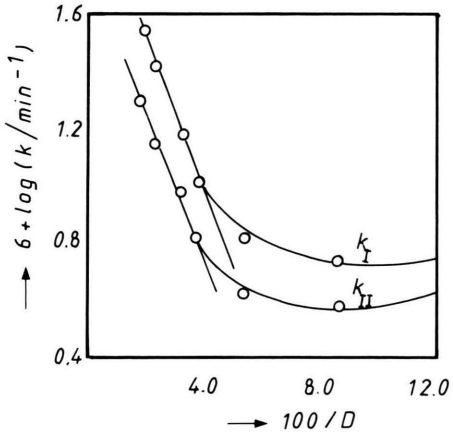

Fig. 3. Dependence of the overall rate constants of the two steps of the reaction on the dielectric constant of the medium.

($k_{II1} + k_{II2}$) calculated from (4) agrees quite satisfactorily with the observed overall specific rate constants k_I and k_{II} only in media containing less than 80% dioxane. The deviation observed at higher dioxane constants is probably due to the maximum in acidity function in this range [21, 22], i.e., a non-kinetic factor. The contribution of the $A_{Al}1$ mechanism is higher for the first step than for the second one, which is quite understandable, as the steric effect in the former case is larger than that in the latter.

It is noteworthy that the least squares treatment of the linear Arrhenius equation [28] for the four calculated rate constants gave a correlation coefficient equal to unity and the respective values for the activation energies of the two mechanisms for each step of the reaction were found equal to those normally characteristic for them [8] (Table 3).

The dependence of the specific rate constants of both steps on the solvent composition of the reaction mixture can be better visualised by application of the well known electrostatic theories [1, 32, 33] based on the effect of bulk dielectric constant of the medium. The latter values were taken or interpolated from the data available [34] for different dioxane-water mixtures. Figure 3 represents the linear plot of log k_I and log k_{II} against $1/D$, which is indicative of an ion-molecular dipole [31, 35] interaction rather than a molecular dipole-molecular dipole one [36]. However, the deviations of the plots of Fig. 3 from linearity, at low dielectric constants, are to be attributed to preferential solvation effects [37, 38].

Table 4 contains the values of the free energies $\Delta G^{\neq}$, enthalpies $\Delta H^{\neq}$ and entropies $\Delta S^{\neq}$ of activation for the overall, unimolecular and bimolecular reactions at 20 °C. It is noticed that $\Delta G^{\neq}$ increases regularly with increasing dioxane content of the medium for the uni- and bimolecular reactions of both steps. The $\Delta H^{\neq}$ values for the overall reaction

Table 4. Thermodynamic parameters of activation for the reaction at 20 °C.

Parameter		Dioxane, wt%							
		30.390	40.163	50.373	59.788	69.457	79.119	89.557	94.451
					First step (I)				
$\Delta G_I^{\neq}$	$kJ\ mol^{-1}$	106.70	107.68	108.73	109.76	110.87	111.16	111.42	110.45
$\Delta H_I^{\neq}$	$kJ\ mol^{-1}$	104.60	101.48	96.32	95.00	94.23	93.53	94.96	91.72
$\Delta S_I^{\neq}$	$J\ mol^{-1}\ deg^{-1}$	− 7.16	− 21.16	− 42.33	− 50.33	− 56.76	− 60.15	− 56.15	− 63.88
$\Delta G_{I1}^{\neq}$		107.82	109.28	111.04	113.29	115.88	119.60	–	–
$\Delta H_{I1}^{\neq}$		114.89	114.51	113.55	113.58	113.16	114.67	–	–
$\Delta S_{I1}^{\neq}$		24.19	17.85	8.56	1.40	− 9.26	− 16.82	–	–
$\Delta G_{I2}^{\neq}$		109.14	109.51	109.95	110.48	111.16	112.09	–	–
$\Delta H_{I2}^{\neq}$		94.95	94.89	96.99	93.77	93.67	93.52	–	–
$\Delta S_{I2}^{\neq}$		− 48.39	− 49.86	− 52.20	− 56.99	− 59.64	− 63.33	–	–
					Second step (II)				
$\Delta G_{II}^{\neq}$	$kJ\ mol^{-1}$	108.04	108.94	109.91	110.85	111.88	112.08	112.28	111.36
$\Delta H_{II}^{\neq}$	$kJ\ mol^{-1}$	104.46	97.12	96.27	95.03	93.84	92.53	94.36	91.28
$\Delta S_{II}^{\neq}$	$kJ\ mol^{-1}\ deg^{-1}$	− 12.20	− 40.32	− 46.51	− 53.96	− 61.53	− 66.69	− 61.16	− 68.48
$\Delta G_{II1}^{\neq}$		109.28	110.76	112.52	114.66	117.37	121.04	–	–
$\Delta H_{II1}^{\neq}$		114.73	115.08	114.11	113.90	115.05	114.88	–	–
$\Delta S_{II1}^{\neq}$		18.59	14.74	5.40	− 2.57	− 7.91	− 20.99	–	–
$\Delta G_{II2}^{\neq}$		100.29	109.02	110.02	111.02	112.02	113.24	–	–
$\Delta H_{II2}^{\neq}$		97.74	96.31	96.43	96.22	96.25	96.39	–	–
$\Delta S_{II2}^{\neq}$		− 42.80	− 43.35	− 46.36	− 50.45	− 53.79	− 57.47	–	–

decrease with increasing dioxane content due to the change in mechanism. This is evidenced by the fact that the $\Delta H^{\neq}$ for the separated uni- and bimolecular reactions are more or less constant and lie within regions characteristic for these types of mechanism.

The overall entropy of activation decreases regularly from − 7.16 to − 63.38 and from − 12.2 to − 68.48 J $mole^{-1}$ deg^{-1} for the first and second steps, respectively, as the dioxane content increases. This is a direct consequence of the decrease in the contribution of the $A_{Al}1$ mechanism. These conclusions can be clearly noticed from ΔS_{I1} and ΔS_{II1} values, which are more positive in the former than in the latter steps, as the contribution of the $A_{Al}1$ mechanism runs parallel to this change. The values of $\Delta S^{\neq}$ for $A_{Al}1$ mechanism are usually positive or slightly negative compared to those of $A_{Ac}2$ mechanism [8].

[1] J. D. H. Homan, Rec. Trav. Chem. **63,** 181 (1944); **64,** 189 (1944).
[2] E. S. Amis and J. F. Hinton, Solvent Effects on Chemical Phenomena, Academic Press, New York and London 1973.
[3] E. Tommila and A. Hella, Ann. Acad. Sci. Fennicae AII, **53,** 1 (1954).
[4] M. L. Bender, Chem. Rev. **60,** 53 (1960).
[5] R. K. Wolford, J. Phys. Chem. **67,** 632 (1963).
[6] N. J. Cleve, Suomen Kemistilehti **B 45,** 385 (1972).
[7] C. K. Ingold, Structure and Mechanism in Organic Chemistry, Cornell University Press, New York 1953.
[8] K. R. Adam, I. Lauder, and V. R. Stimson, Austral. J. Chem. **15,** 467 (1962).
[9] H. Sadek and F. Y. Khalil, Z. Physik. Chem. **57,** 306 (1971).
[10] T. Yrjana, Suomen Kemistilehti **B 37,** 108 (1964).
[11] V. R. Stimson and E. A. Watson, J. Chem. Soc. **1954,** 2848.
[12] V. R. Stimson, J. Chem. Soc. **1955,** 2010, 2673, 4020.
[13] G. J. Harvey and V. R. Stimson, J. Chem. Soc. **1956,** 3629.
[14] F. Y. Khalil and M. T. Hanna, Croatica Chem. Acta **52,** 329 (1979) and reference cited therein.
[15] H. J. Backer and J. D. H. Homan, Rec. Trav. Chem. **58,** 1048 (1939).
[16] K. Hess and H. Frahm, Ber. **17,** 2633 (1938)

[17] A. N. Asaad and F. Y. Khalil, Z. Naturforsch. **39 a,** 95 (1984).
[18] C. G. Swain, J. Amer. Chem. Soc. **66,** 1696 (1944).
[19] A. A. Frost and R. G. Pearson, Kinetics and Mechanism, John Wiley, New York 1960; H. Mauser, Formal kinetic, Bertelsmann Universitätsverlag 1974.
[20] S. Glasstone, K. J. Laidler, and H. Eyring, The Theory of Rate Processes, McGraw-Hill, New York 1941.
[21] E. A. Braude and E. S. Stern, J. Chem. Soc. **1948,** 1976.
[22] K. Schwetlick, Kinetische Methoden zur Untersuchung von Reaktionsmechanismen, VEB Deutscher Verlag der Wissenschaften, Berlin 1971.
[23] F. Y. Khalil, F. M. Abdel Halim, and A. N. Asaad, Z. Naturforsch. **37 a,** 390 (1982).
[24] T. B. Grindley, Tetrahedron Lett. **23,** 1757 (1982).
[25] C. K. Ingold, J. Chem. Soc. **1930,** 1375; R. S. Radhakrishnamurti and R. C. Parto, J. Indian Chem. Soc. **46,** 903 (1969); **48,** 811 (1971).
[26] B. Giese, Angew. Chem. **89,** 162 (1977); Angew. Chem. Int. Ed. Engl. **16,** 125 (1977).
[27] C. D. Johnson, Tetrahedron **36,** 3461 (1980).
[28] E. S. Swinbourne, Analysis of Kinetic Data, Thomas Nelson and Sons Ltd., London 1971.
[29] E. Tommila, E. Paakkala, U. K. Virtanen, A. Erva, and S. Varila, Ann. Acad. Sci. Fennicae **AII,** 91 (1959).
[30] G. S. Hammond, J. Amer. Chem. Soc. **77,** 334 (1955).
[31] K. J. Laidler and C. A. Landskroener, Trans. Faraday Soc. **52,** 200 (1956).
[32] A. J. Parker, Chem. Rev. **69,** 1 (1969).
[33] K. K. Kundu and L. Aiyar, J. Chem. Soc. Perkin Trans. II, 715 (1975).
[34] G. Åkerlof, J. Amer. Chem. Soc. **54,** 4125 (1932).
[35] Ref. No. 22 p. 171 and references cited therein.
[36] K. J. Laidler and H. Eyring, Ann. N.Y Acad. Sci. **39,** 303 (1940).
[37] H. Böhme and W. Schürhoff, Ber. **84,** 28 (1951).
[38] A. H. Fainberg and S. Winstein, J. Amer. Chem. Soc. **28,** 2770 (1956).