

CCA-1168

YU ISSN 0011-1643

541.124:547.29

Original Scientific Paper

Kinetics, Activation Parameters, and Mechanism of the Acid Hydrolysis of *tert*-Butyl Acetate in Aqueous DMSO

F. Y. Khalil and M. T. Hanna

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

Received December 12, 1978

The rate of the acid-catalysed hydrolysis of *tert*-butyl acetate was found to decrease pronoucnly in the presence of increasing amounts of DMSO. The observed activation energy decreased progressively with increasing DMSO content of the medium and the change was attributed to a gradual interconversion of the two concurrent and competing reaction mechanisms A_{AL1} and A_{AC2} . The overall reaction rate was analysed theoretically as two individual rate constants corresponding to the respective mechanisms. The percentage contribution of each mechanism was then estimated and found to be concordant with the values determined experimentally by others using ^{18}O tracer technique. The proportion of the A_{AL1} mechanism was found to increase both with increasing temperature and decreasing DMSO content. The relative abundance of the transition state belonging to each of the involved mechanisms was discussed in the light of the solvating power of the binary DMSO- H_2O solvent system. The effect of the molar concentration of water as well as the dielectric constant of the medium on the reaction kinetics was studied. The thermodynamic parameters of activation showed strong dependence on solvent composition and their values were determined by the relative contributions of the two mechanistic routes of the reaction.

INTRODUCTION

Extensive studies of the effect of solvents on the rates of simple hydrolysis reactions in which one mechanism only (A_{AC2} or A_{AL1}) is involved have been increasingly reported in the last decades¹. However, only relatively little informations are available on the solvent effects on hydrolysis reactions proceeding via mixed mechanisms²⁻⁶. Thus, *tert*-butyl acetate is known to hydrolyse in acid solution simultaneously by unimolecular as well as bimolecular mechanisms⁷⁻⁹. The electron release from the *tert*-butyl group allows for the formation of the carbonium ion, $(CH_3)_3C^+$, and hence facilitates the unimolecular alkyl-oxygen bond fission. On the other hand, the decrease in the water concentration of the reaction mixture favours the bimolecular acyl-oxygen fission, in relation to the unimolecular one. Several experimental evidences have been reported for the differentiation between a unimolecular hydrolysis mechanism, whose critical complex contains no covalently bound water molecule, and a bimolecular mechanism with a transition complex containing a water molecule in addition to the proton and the substrate^{2,10}. Among these

evidences are the values of the activation energies⁸, activation entropies¹¹, activation volumes¹² and the use of the Zucker-Hammett hypothesis¹³. The objective of the present work was to calculate the contribution of each mechanism under various conditions of temperature and solvent composition using only purely kinetic data. This was carried out also to investigate the effect of dimethyl sulphoxide (DMSO), a dipolar aprotic solvent with unique properties¹⁴ on the present reaction, particularly because the solvation requirements of the two concurrent mechanisms in this solvent system are expected to be strongly dependent on solvent composition.

EXPERIMENTAL

Materials and Procedure

Tert-butyl acetate was prepared as described before¹⁵. The boiling point of the pure ester was 97–98 °C at normal pressure. Dimethyl sulphoxide (BDH) was purified by distillation twice from calcium hydride under reduced pressure, the first and last portions were rejected and the middle fraction boiling at 70 °C and 8 mmHg* was collected. The purified DMSO had a melting point of 18.5 °C. The water used in the kinetic experiments was freshly distilled from alkaline potassium permanganate.

The kinetic experiments involved a direct analysis of the acid produced during the reaction course¹⁶. In all rate measurements at temperatures higher than 30 °C, allowance was made for the volume change of the solvent with temperature.

Calculations

The first-order rate constants k'_{obs} for the overall reaction in water and in the mixed solvents were calculated from the slopes of the linear plots of $\log [a/(a-x)]$ against time. The observed rate constant k'_{obs} includes two specific rates, one due to the unimolecular mechanism k_1' and the other due to the bimolecular mechanism k_2' , i. e.,

$$k'_{\text{obs}} = k_1' + k_2' \quad (1)$$

At constant acid concentration, the remarkable dependence of the hydrolysis rate of an ester on the water concentration of the solvent can be represented generally by the following expression¹⁷ (k being a proportionality constant):

$$\frac{dx}{dt} = k [\text{H}_2\text{O}]^y (a - x)$$

in which the overall reaction rate is assumed to be proportional to the y^{th} power of the molar water concentration of the solvent mixture and $(a-x)$ being the ester concentration. As the water concentration can be taken as practically constant during the course of the reaction, $k [\text{H}_2\text{O}]^y$ will be equal to the experimental rate constant k'_{obs} . Assuming that the rates of the $A_{AC}2$ and $A_{AL}1$ mechanisms are proportional to the first¹⁰ and n^{th} ¹⁶ power of the water concentration, respectively, then y will be equal to $n + 1$.

The corresponding rate constants will then be given by:

$$k_2' = k_2 [\text{H}_2\text{O}]$$

and

$$k_1' = k_1 [\text{H}_2\text{O}]^n$$

where k_2 and k_1 are two proportionality constants.

Therefore, equation (1) becomes

$$k'_{\text{obs}} = k_1 [\text{H}_2\text{O}]^n + k_2 [\text{H}_2\text{O}] \quad (2)$$

* 1 mmHg = 133.332 Pa

hence

$$\frac{k'_{\text{obs}}}{[\text{H}_2\text{O}]} = k_1 [\text{H}_2\text{O}]^{n-1} + k_2 \quad (3)$$

Accordingly, a plot of $k'_{\text{obs}}/[\text{H}_2\text{O}]$ against $[\text{H}_2\text{O}]^{n-1}$ should yield a straight line with a slope and intercept of k_1 and k_2 , respectively. A number of trial plots of $k'_{\text{obs}}/[\text{H}_2\text{O}]$ against several powers of $[\text{H}_2\text{O}]$ ranging from 1 to 4 have been made, as shown in Figure 1. Best linear plots were obtained with $[\text{H}_2\text{O}]^2$, indicating that n amounts to 3†. From the values of k_1 , k_2 , $[\text{H}_2\text{O}]$ and $[\text{H}_2\text{O}]^3$, it became possible to calculate k_1' and k_2' at all temperatures and solvent compositions. The results are depicted in Table I along with the observed rate constants. The percentage fission by the $A_{\text{AL}}1$ mechanism was calculated using the expression:

$$\% A_{\text{AL}}1 = \frac{k_1'}{k_1' + k_2'} \times 100$$

TABLE I

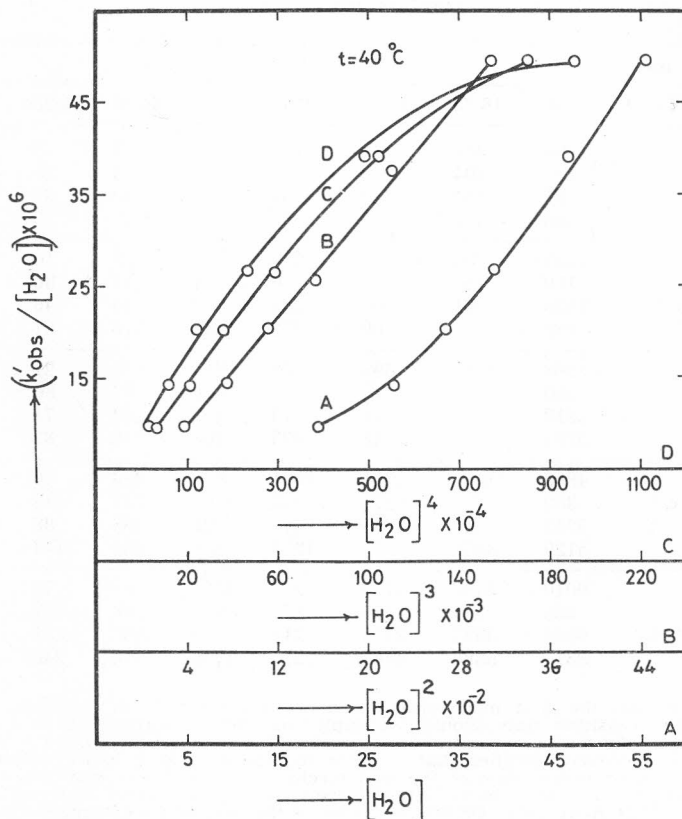
Calculated and Observed Rate Constants for the Overall, Unimolecular and Bimolecular Reactions

t/°C	$k' \cdot 10^6$ min ⁻¹	DMSO/wt %								
		0.00	16.25	31.82	42.05	52.04	66.83	81.28	90.72	95.55
30	k_1'	584	347	200	126	74	25	5	0.6	0.1
	k_2'	122	104	86	74	62	43	25	12.3	6.0
	$k_1' + k_2'$	706	451	286	200	136	68	30	12.9	6.1
	k'_{obs}	635	452	288	189	136	70	28	14	8
35	k_1'	1255	764	439	278	162	56	10	1.2	0.1
	k_2'	180	155	127	109	91	54	36	18.0	5.8
	$k_1' + k_2'$	1435	919	566	387	253	110	46	19.2	5.9
	k'_{obs}	1259	891	589	372	246	118	51	26	15
40	k_1'	2568	1563	898	568	331	114	21	2.6	0.3
	k_2'	250	212	176	151	126	88	50	25.1	12.0
	$k_1' + k_2'$	2818	1775	1074	719	457	202	71	27.7	12.3
	k'_{obs}	2754	1840	1043	685	400	188	82	38	19
45	k_1'	4893	2977	1711	1081	630	216	40	5.0	0.6
	k_2'	389	329	274	235	196	137	48	39.0	19.0
	$k_1' + k_2'$	5282	3306	1985	1316	826	353	88	44.0	19.6
	k'_{obs}	5129	3388	2138	1328	822	364	144	74	42
50	k_1'	9010	5483	3151	1992	1161	398	74	9	1
	k_2'	530	449	374	321	268	188	107	53	26
	$k_1' + k_2'$	9540	5932	3525	2313	1429	586	181	62	27
	k'_{obs}	8511	5888	3467	2335	1396	546	240	115	72

† The fact that the $A_{\text{AL}}1$ mechanism, by definition, contains no covalently bound water molecule in the transition state should not imply that the hydrolysis rate of this mechanism is independent of the water concentration, since this is an important kinetic requirement. The value of $n = 3$, however, signifies that 3 water molecules form a hydrogen-bound solvation sheath around the transition state of the $A_{\text{AL}}1$ mechanism. The reason why this does not apply to the $A_{\text{AC}}2$ mechanism is that the relatively more polar $A_{\text{AC}}2$ transition state will be preferentially solvated by the more polar DMSO molecules of the solvent components⁴. Evidence for this is given by the calculation of dipole moments of the two transition states, and is referred to later on. On the basis of this assumption, we applied the present treatment to the data on *tert*-butyl acetate reported by Yrjänä⁷ and Bunton and Wood⁸, who used other techniques in the separation procedure, and linear plots of $\log k_1'$ vs. $\log [\text{H}_2\text{O}]$ were obtained with slopes ranging between 2.5 and 3. It has to be concluded, therefore, that the water molecule necessary for the reaction via the $A_{\text{AC}}2$ mechanism is involved in the transition state, while for the $A_{\text{AL}}1$ mechanism it will be one of the three water molecules in the solvation sheath of the transition state.

TABLE I contin.

55	k_1'	16640	10130	5820	3680	2143	736	137	17	2
	k_2'	767	650	540	463	387	271	155	77	37
	$k_1' + k_2'$	17407	10780	6360	4143	2530	1007	292	94	39
	k'_{obs}	17780	12460	7450	4429	2412	987	417	182	121
60	k_1'	32100	19540	11230	7096	4134	1419	263	33	4
	k_2'	1058	898	745	640	534	374	213	106	42
	$k_1' + k_2'$	33158	20438	11975	7736	4668	1793	476	139	46
	k'_{obs}	33110	20150	12280	7586	4386	1536	640	288	159
65	k_1'	57060	34720	19950	12610	7348	2523	468	58	7
	k_2'	1461	1238	1029	883	738	516	295	417	71
	$k_1' + k_2'$	58521	35958	20979	13493	8086	3039	763	475	78
	k'_{obs}	57540	37690	19190	12290	6908	2512	1001	447	251

Figure 1. Trial plots of $\log k'_{obs}/[H_2O]$ against different powers of $[H_2O]$.

The activation energies E and the frequency factors A belonging to the three rate constants were obtained from the usual Arrhenius equation¹⁸. The entropies, enthalpies and free energies of activation were calculated using the thermodynamic

equations of the absolute reaction rate theory¹⁸. The values of the dielectric constant of DMSO-water mixtures were determined by interpolation from the results reported by Wolford¹⁹.

DISCUSSION

Agreement between Observed and Calculated Rate Constants

Examination of Table I shows that the sum of the individual rate constants ($k_1' + k_2'$) calculated by equation (3) agrees quite satisfactorily with the experimentally determined k'_{obs} . The equation is valid only in media containing less than 80% DMSO. Deviations are observed beyond this limit due to the sharp drop of the acidity function of the reaction mixtures²⁰ of high content of the organic solvent component. The contributions of each mechanism (cf. Table II), based on calculated rate constants were found to be concordant with the values determined experimentally by other investigators⁶⁻⁸ who used ¹⁸O tracer technique in other solvent mixtures of similar water contents.

TABLE II
Contribution of A_{AL1} Mechanism

DMSO wt %	% A _{AL1}							
	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C	60 °C	65 °C
0.00	83	88	91	93	94	96	97	98
16.25	77	81	88	90	92	94	96	97
31.82	70	78	84	86	89	91	94	95
42.05	63	75	79	82	86	87	92	94
52.04	45	64	72	76	81	85	89	91
66.83	37	51	56	61	68	73	79	83
81.28	16	22	29	45	41	47	55	61
90.72	5	7	9	11	15	18	23	12
95.55	1	2	2	3	4	5	8	9

TABLE III
Activation Energies and Frequency Factors for the Overall, Unimolecular and Bimolecular Reactions

E/(kcal/mol)	DMSO/wt %								
	0.00	16.25	31.82	42.05	52.04	66.83	81.28	90.72	95.55
	a) Overall								
E_{obs}	26.62	25.76	25.13	24.24	23.03	20.60	19.96	19.64	18.42
log A	14.3	13.5	12.9	12.0	11.0	8.9	8.1	7.6	6.4
	b) Unimolecular								
E_1	26.80	27.16	26.54	26.10	26.32	26.32	—	—	—
log A	14.4	14.4	13.8	13.3	13.2	12.7	—	—	—
	c) Bimolecular								
E_2	14.33	14.55	14.42	14.42	14.55	14.33	—	—	—
log A	4.7	4.7	4.6	4.4	4.5	4.2	—	—	—

Arrhenius Parameters and the Reaction Mechanism

In Table III it is readily seen that the overall activation energy E_{obs} decreases with decreasing water content in the mixed solvent; the decrease is about 9 kcal/mol* for a solvent change of 0—95% by wt. of DMSO. Such a phenomenon was reported before in few cases of the acid hydrolysis of some esters of tertiary alcohols^{3,7,21}. This pronounced change of E with solvent composition is far beyond the one to be expected in cases of, e. g., esters hydrolysing via pure single mechanism²². The E values assigned for the latter hydrolyses range from 14 to 20 kcal/mol and from 26 to 33 kcal/mol for the $A_{\text{AC}2}$ and $A_{\text{AL}1}$ mechanisms, respectively, of the Ingold classification.^{8,10} The fact that the activation energy of the present reaction depends strongly on solvent composition and that its values lie somewhere between the two ranges mentioned above confirms that the reaction proceeds via a mixed mechanism comprising both $A_{\text{AC}2}$ and $A_{\text{AL}1}$ simultaneously. The relative contribution of each mechanism is very sensitive to changes in temperature and reaction medium. Thus, at higher temperatures in water or highly aqueous media, the $A_{\text{AL}1}$ mechanism prevails while the reverse is true for the $A_{\text{AC}2}$ mechanism (cf. Table II). The calculated rate constants for each type of mechanism gave good Arrhenius plots and the corresponding activation energies were found to be typical for those experimentally determined for the two mechanisms independently. The frequency factor, A , decreases in a manner parallel to the decrease of E with addition of DMSO. For the overall reaction, the value of $\log A$ changes from 14 to 6 whereas for the unimolecular and bimolecular reactions it lies round 14 and 4, respectively. These values agree very well with the ranges 14—16 for the $A_{\text{AL}1}$ mechanism and 4—8 for the $A_{\text{AC}2}$ mechanism normally obtained for most esters²³⁻²⁶.

Role of Solvation Properties of the Medium

The reaction rate is largely retarded as the content of the organic cosolvent in the reaction mixture is increased. Thus, at 30 °C the rate in 95% DMSO is 80 times lower than in pure water. On the other hand, the relative proportions of the two concurrent mechanisms are dependent on the precise nature of the medium. The interchange of these mechanisms can thus be rationalised as due to a difference in the response of the transition states of the two mechanisms towards changes in the solvation properties of the reaction medium. Evidence for this finds support in the work of Cox and McTigue⁴ based on activity-coefficient measurements for *tert*-butyl acetate as well as other carbonyl compounds which hydrolyse typically via pure $A_{\text{AC}2}$ and $A_{\text{AL}1}$ mechanisms. One might expect that as the DMSO content of the solvent mixture increases, the H_2O molecules in the solvation sheaths of H_3O^+ and the transition state of the bimolecular mechanism will be gradually replaced by DMSO. Hence, at high DMSO contents, the water molecules in the medium will be mostly captured by DMSO molecules into the well-known 2:1 association complexes²⁷⁻²⁹, and the $A_{\text{AC}2}$ transition state will be almost entirely solvated by the excess DMSO molecules, and will thus be more stabilised and facilitated. This is quite evident in Table II where the $A_{\text{AC}2}$ proportion increases at 30 °C from 17 to 99% as the DMSO content increases from 0 to 95.6%

(w/w). On the other hand, the solvation requirements of the A_{AL1} mechanism is quite different in the sense that the transition state is smaller in volume and thereby leading to a lower solvation and less stabilisation relative to that of the A_{AC2} mechanism. In other words, solvation of the A_{AC2} transition state with DMSO is stronger, and hence predominating, than solvation of the A_{AL1} with water. The net result will be a large drop in the contribution of A_{AL1} mechanism as the DMSO content is increased. This is in fact found experimentally as seen in Table II. In a highly associated solvent system such as the one under investigation, it is quite reasonable to assume that temperature will have a different effect on the solvation requirements of the two transition states. In Table II it is seen that at a fixed solvent composition the percentage contribution of the A_{AL1} mechanism increases with increased temperature. Supporting this argument is the fact that the stability of the internal structure of the binary DMSO- H_2O solvent system is affected largely by temperature; there is even an association decomposition¹⁰ of the 2:1 complex between 40 and 60 °C.

Effect of the Dielectric Constant

An alternative aspect of the solvent effect can be tested by considering the influence of changes in the dielectric constant, D , on the reaction rate. Thus, an increase in D causes a consequent increase of the rate. The present results, based on an ion-dipole interaction theory³⁰, were found to give good linear plots of $\log k'_{obs}$ versus $1/D$, though deviating from linearity at low dielectric constants (Figure 2). Such deviations are very often observed in binary solvent mixtures, whose components differ in their dielectric constants, and are attributed to specific solvation phenomena.¹⁸ The negative slopes of the linear parts of these plots gave, according to the Laidler-Landskroener treatment³⁰, a reasonable value for the radius of the transition state, r^* , amounting to 320 pm.

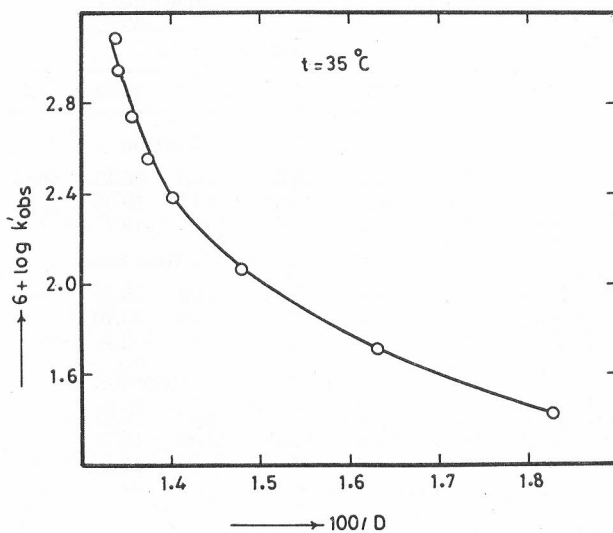


Figure 2. Dependence of $\log k'_{obs}$ on the dielectric constant of the solvent.

An approach to the relative polarities of the transition states of the $A_{AL}1$ and $A_{AC}2$ mechanisms can be presented using the Laidler's equation³¹ for ion-dipole interactions as applied to both unimolecular and bimolecular rate constants. The equation gives values of about 30 and 38 debye for μ^* , for the dipole moment of the $A_{AL}1$ and $A_{AC}2$ transition states, respectively. These values, though higher than those reported by Laidler³¹ (26.1 debye) support our assumption that the more polar $A_{AC}2$ transition state will be preferentially solvated with DMSO molecules ($\mu = 3.9$ debye*)³² rather than with water molecules ($\mu = 1.85$ debye)³³; and the reverse is true for the less polar $A_{AL}1$ transition state.

Thermodynamic Functions of Activation

Table IV contains the values of the activation parameters for the overall, unimolecular and bimolecular reactions. All parameters are strongly dependent on solvent composition. The enthalpy of activation, ΔH^\ddagger , for the overall reaction decreases by about 10 kcal/mol on passing from water to 95% DMSO. This change is accompanied by a change in mechanism, and therefore the values is more or less constant for the separated unimolecular and bimolecular reactions. For the overall reaction the entropy of activation, ΔS^\ddagger , requires the values between +4.9 and -31.2 e. u.** This strong decrease of ΔS^\ddagger , is also indicative of a decrease in the $A_{AL}1$ mechanism and a subsequent increase in the $A_{AC}2$ mechanism as the medium becomes enriched in DMSO. However, the values of ΔS^\ddagger for the separated unimolecular and bimolecular reactions vary, from 5 to -2 and from -38 to -41 e. u., respectively. Generally, carboxylic esters following the $A_{AL}1$ mechanism during hydrolysis should be characterised by more positive entropies of activation relative to those hydrolysing by the $A_{AC}2$ mechanism, and a particularly large entropy differential

TABLE IV
Thermodynamic Parameters of Activation at 40 °C

Parameter	DMSO/wt %								
	0.00	16.25	31.82	42.05	52.04	66.83	81.28	90.72	95.55
a) Overall Reaction									
ΔG^\ddagger /(kcal/mol)	24.47	24.73	25.03	25.35	25.68	26.15	26.67	27.13	27.56
ΔH^\ddagger /(kcal/mol)	26.00	25.14	24.51	23.62	22.41	19.98	19.34	19.02	17.80
ΔS^\ddagger /(cal/mol K)	4.9	1.3	-1.7	-5.6	-10.5	-19.7	-23.4	-25.9	-31.2
b) Unimolecular Reaction									
ΔG^\ddagger /(kcal/mol)	24.52	24.83	25.18	25.46	25.78	26.46	—	—	—
ΔH^\ddagger /(kcal/mol)	26.18	26.54	25.92	25.48	25.70	25.70	—	—	—
ΔS^\ddagger /(cal/mol K)	5.3	5.4	2.4	0.1	-0.3	-2.4	—	—	—
c) Bimolecular Reaction									
ΔG^\ddagger /(kcal/mol)	25.90	26.07	26.19	26.27	26.32	26.62	—	—	—
ΔH^\ddagger /(kcal/mol)	13.71	13.93	13.80	13.80	13.93	13.71	—	—	—
ΔS^\ddagger /(cal/mol K)	-38.94	-38.79	-39.59	-39.84	-39.59	-41.25	—	—	—

* 1 D = $3.34 \cdot 10^{-30}$ C m.

** 1 e. u. = $4.184 \text{ JK}^{-1} \text{ mol}^{-1}$.

between the two mechanisms should be observed¹¹. These requirements are amply fulfilled by the data in Table IV indicating good consistence between the values calculated according to our separation procedure and those generally assigned for the respective mechanisms. The values of ΔG^\ddagger , the free energy of activation, for the overall reaction varies much less than does ΔH^\ddagger or ΔS^\ddagger . This weak dependence is due largely to the linear compensation between ΔH^\ddagger and ΔS^\ddagger .

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SAŽETAK

**Kinetika, aktivacijski parametri i mehanizam kisele hidrolize
tert-butilacetata u vodenoj otopini DMSO***F. Y. Khalil i M. T. Hanna*

Kisela hidroliza *tert*-butilacetata proučavana je u smjesama DMSO-H₂O različita sastava. Poznato je da u tim okolnostima *tert*-butil hidrolizira istovremeno i monomolekularnim i bimolekularnim mehanizmom. U ovom radu izračunan je doprinos svakoga od tih mehanizama i to jedino na temelju kinetičkih podataka. Izračunane vrijednosti slažu se s eksperimentalnim vrijednostima, koje su odredili drugi autori pomoću ¹⁸O-obilježivačke tehnike. Nađeno je da su doprinosi pojedinih mehanizama jako ovisni o temperaturi reakcijskog medija. Udjel mehanizma A_{A1} povećava se s porastom temperature i smanjenjem udjela DMSO, a obrnuti odnos vrijedi za mehanizam A_{AC2}. Energija aktivacije i termodinamički parametri za ukupnu reakciju kao i za pojedinačne A_{A1} i A_{AC2} reakcije izračunani su i razmotreni.

KEMIJSKI ODJEL
FAKULTET PRIRODNIH ZNANOSTI
ALEKSANDRIJSKO SVEUČILIŠTE
ALEKSANDRIJA, EGIPAT

Prispjelo 12. prosinca 1978.