# MEDIUM EFFECTS ON THE KINETICS AND MIXED MECHANISM OF THE ACID HYDROLYSIS OF TERT - BUTYL BENZOATE

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## SUMMARY

The rates of acid hydrolysis of tert-butyl benzoate in dioxane-water mixtures were measured. The activation energy decreases considerably with increase in dioxane content due to the change of the reaction mechanism from $A_{AL}1$, which predominates in water, to $A_{AC}2$, which prevails in dioxane-rich solvents. The rate constant in water is represented by $k'_{obs} = 10.7e^{-97500/RT}$ min$^{-1}$, as compared to $k'_{obs} = 4.5e^{-66500/RT}$ min$^{-1}$ in 80 % dioxane-water mixture. The proportion of the $A_{AC}2$ mechanism decreases both with increasing temperature and decreasing dioxane content. The relative amount of this mechanism, compared to the $A_{AL}1$ mechanism, is largely determined by temperature and solvation requirements of the two transition states in the respective media. The separated rate constants, and the corresponding activation, as well as Arrhenius, parameters were calculated and discussed.

## INTRODUCTION

A great deal of current research in the field of reaction kinetics is devoted to the elucidation of solvent effects on the kinetics of organic reactions, in binary mixtures of water with organic solvents[1-4]. The hydrogen-bonded structure of water in a mixed solvent can be changed by gradually changing the composition of the medium. Consequently, the changes in the solvation properties of the binary solvent mixture, in the immediate vicinity of the reactants and transition states, are reflected in the effects on reaction rates and mechanism[5]. The acid hydrolysis of simple carboxylic esters is generally known to involve acyl-oxygen bond fission $A_{AC}2$. However, exceptions to this behaviour are mostly exhibited by esters of tertiary alcohols which hydrolyse by the alkyl-oxygen bond fission[6]. Thus, the continuous addition of an organic cosolvent to water produces significant changes in the mechanism of hydrolysis of tert-butyl esters from $A_{AL}1$ in pure water to $A_{AC}2$ in slightly aqueous media[7,8]. The rate and thermodynamic activation parameters of the reaction are then expected to change to an extent

depending on the change in the solvent composition. The present paper reports this study as applied to the acid hydrolysis of tert-butyl benzoate in dioxane-water mixtures.

## EXPERIMENTAL

Tert-butyl benzoate was prepared as previously described[9]. The purity, calculated from the titre, after complete hydrolysis, was 99.5%. Symmetrical 1,4 dioxane was purified by refluxing with dilute HCl under nitrogen atmosphere, treatment with KOH pellets, distillation, drying over sodium metal and distillation from stannous chloride. The pure solvent boiled at 101.5°C under 1 atmosphere[10]. The water used in the preparation of solutions and in the kinetic runs was freshly distilled from alkaline potassium permanganate. The rate of reaction was determined using 0.02M tert-butyl benzoate and 0.05 M HCl in a series of water-dioxane mixtures ranging from 0 to 80% (w/w). The procedure involved a volumetric analysis of the acid produced during the course of the reaction[11].

## RESULTS AND CALCULATION

Table (1) contains the rate constants at several temperatures and in the whole range of solvent composition, as calculated from a first-order rate law. Kinetically, the reaction was found to follow the first-order course up to about 70% completion. The observed rate constant, $k'_{obs}$, includes two specific rates, $k'_1$ and $k'_2$, due to the unimolecular, and bimolecular mechanisms, respectively. Table (2) compiles the two separate rate constants as calculated by our previous analysis of the kinetic data[5]. A statistical least squares treatment[12] of the Arrhenius equation was used to calculate the activation energies, $E_{obs}$, $E_1$ and $E_2$, based on the rate constants $k'_{obs}$, $k'_1$ and $k'_2$ respectively. The entropies, enthalpies and free energies of activation were calculated using the thermodynamic equations of the absolute rate theory[13]. The values of the dielectric constant of dioxane-water mixtures were determined by interpolation from the results reported by Akerlof[14].

## DISCUSSION

Dioxane lowers the rates of the overall, unimolecular and bimolecular reactions (Figure (1)). The coexistence of the two mechanisms $A_{AL}1$ and $A_{AC}2$, in the present reaction, with the former largely sensitive to the ionising power of the solvent, causes the three rate constants to decrease to different extends, with progressive addition of dioxane. This decrease takes place in the manner shown in Figure (1), plotted using the data at 50°C, as a representative temperature. The curves have the same features, but not the same extent of decrease of the rate constant with increasing dioxane content of the medium. Moreover, the unimolecular rate constant, $k'_1$, is higher than the bimolecular one, $k'_2$, in the same medium, over a range of solvent composition, varying from 0-30% (w/w) dioxane. Beyond this point, the trend is reversed, and $k'_1$ becomes lower than $k'_2$, until about 80% dioxane. The difference in rates on both sides of this point is solvent-dependent, being lowest as the solvent becomes rich in dioxane, although the relative magnitudes of the two rate constants are reversed after the inflection point. Thus, the ratio $k'_1/k'_2$ decreases from 1.4 to 0.1, in 0% to 80% dioxane Table (2). Consequently, the relative proportions of the two concurrent mechanisms will depend on the precise nature of the medium, and the interchange of these mechanisms will be 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. As the dioxane content of the solvent mixture increases sufficiently, the water molecules in the solvation sheaths of $H_3O^+$ and the $A_{AC}2$ transition state will be gradually replaced by dioxane molecules. Hence, at low water concentrations, the $A_{AC}2$ transition state will be almost entirely solvated by dioxane molecules, and will thus be more stabilised[15]. In other words, solvation of the $A_{AC}2$ transition state with dioxane is stronger, and hence more predominating than solvation of the $A_{AL}1$ mechanism with water. The solvation requirements of the latter mechanism is quite different in the sense that the transition state is smaller in volume[15] and thereby leading to lower solvation, and less stabilisation, relative to that of the $A_{AC}2$ mechanism. This is quite evident in Table (2), where the $A_{AC}2$ proportion increases at 50°C from 44 to 91%, as the dioxane increases from 0 to 80% (w/w).

The overall activation energy, $E_{obs}$, varies from 97.5 to 66.5 kJ mol$^{-1}$, as the dioxane content of the solvent increases from 0-80% (w/w). For esters generally hydrolysed by the pure $A_{AL}1$ mechanism, the activation energy equals 100 to 140 kJ mol$^{-1}$, while for those hydrolysing by the pure $A_{AC}2$ mechanism, the values are 50 to 80 kJ mol$^{-1}$, and are independent of temperature and solvent composition[6]. In the light of these findings, and the data in Table (1), 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 The values of $E_1$ and $E_2$ for the unimolecular and bimolecular reactions, respectively, are about 108 and 64 kJ mol$^{-1}$, and are consistent with the ranges assigned for the respective pure mechanisms.[6].

**Table 1.** First–order rate constants $k'_{obs}$ and activation energies $E_{obs}$ for the acid hydrolysis of tert–butyl benzoate in dioxane–water mixtures.

| Solvent Composition | | $k'_{obs} \times 10^6$ min$^{-1}$ | | | | $E_{obs}$, kJ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| Dioxane, wt % | [H$_2$O] Moles/1 | 50°C | 55°C | 60°C | 65°C | |
| 0.00 | 55.52 | 423 | 750 | 1246 | 2147 | 97.5 |
| 10.27 | 50.24 | 333 | 576 | 981 | 1660 | 95.0 |
| 20.46 | 44.65 | 267 | 434 | 749 | 1224 | 92.8 |
| 30.50 | 39.29 | 184 | 329 | 500 | 835 | 90.0 |
| 40.29 | 34.90 | 161 | 289 | 427 | 658 | 83.7 |
| 51.79 | 28.62 | 103 | 251 | 302 | 430 | 81.6 |
| 59.99 | 23.06 | 77 | 166 | 209 | 300 | 78.2 |
| 69.80 | 17.41 | 53 | 77 | 124 | 166 | 71.1 |
| 79.75 | 11.67 | 32 | 40 | 73 | 90 | 66.4 |

**Table (2).** Measured and calculated rate constants at 50°C

| Dioxane, wt % | $k' \times 10^6$, min$^{-1}$ | | | $k'_1/k'_2$ | % $A_{AC}2$ |
|---|---|---|---|---|---|
| | $k'_{obs}$ | $k'_1$ | $k'_2$ | | |
| 0.00 | 423 | 244 | 178 | 1.4 | 42 |
| 10.27 | 333 | 185 | 145 | 1.3 | 44 |
| 20.46 | 267 | 147 | 124 | 1.2 | 46 |
| 30.50 | 184 | 92 | 102 | 0.9 | 53 |
| 40.29 | 161 | 70 | 85 | 0.8 | 55 |
| 51.79 | 103 | 39 | 62 | 0.6 | 61 |
| 59.99 | 77 | 20 | 57 | 0.4 | 74 |
| 69.80 | 53 | 9 | 43 | 0.2 | 83 |
| 79.75 | 32 | 3 | 29 | 0.1 | 91 |

**Table 3.** Free energies, enthalpies and entropies of activation for the overall reaction.

| Parameter | Dioxane, wt % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.00 | 10.27 | 20.46 | 30.50 | 40.29 | 51.79 | 59.99 | 69.80 | 79.75 |
| $\Delta G^\circ$ kJ mol$^{-1}$ | 110.9 | 111.3 | 112.1 | 113.0 | 113.4 | 114.6 | 115.5 | 116.3 | 117.6 |
| $\Delta H^\circ$ kJ mol$^{-1}$ | 95.0 | 94.1 | 89.0 | 87.0 | 80.8 | 79.1 | 75.7 | 68.6 | 64.0 |
| $- \Delta S^\circ$ J mol$^{-1}$ deg$^{-1}$ | 49.3 | 53.1 | 68.2 | 80.3 | 100.4 | 110.5 | 123.0 | 148.1 | 166.5 |

The reaction rate decreases as the dielectric constant is lowered. According to the ion–dipole interaction theory[17], the plot of log k' vs, 1/D should be linear. The present results give a straight line which deviates from linearity at low dielectric constants. Such deviations are frequently observed in binary solvent mixtures, the components of which differ in their dielectric constants, and are attributed to specific solvation phenomena[13] in which the activated complexes are preferably solvated by the higher dielectric component of the solvent mixture.

The effect of solvent composition, expressed in dielectric constant, on the activation energy of the reaction is also a point of interest. Table (1) shows that the overall $E_{obs}$ decreases gradually as the dielectric constant is decreased from 69.8 to 9.5 at 50°C. Since the participation of the $A_{AL}1$ mechanism, with the higher activation energy, decreases while that of the $A_{AC}2$, with the lower one, increases as the dielectric constant is decreased, the overall $E_{obs}$ will be expected to decrease considerably.
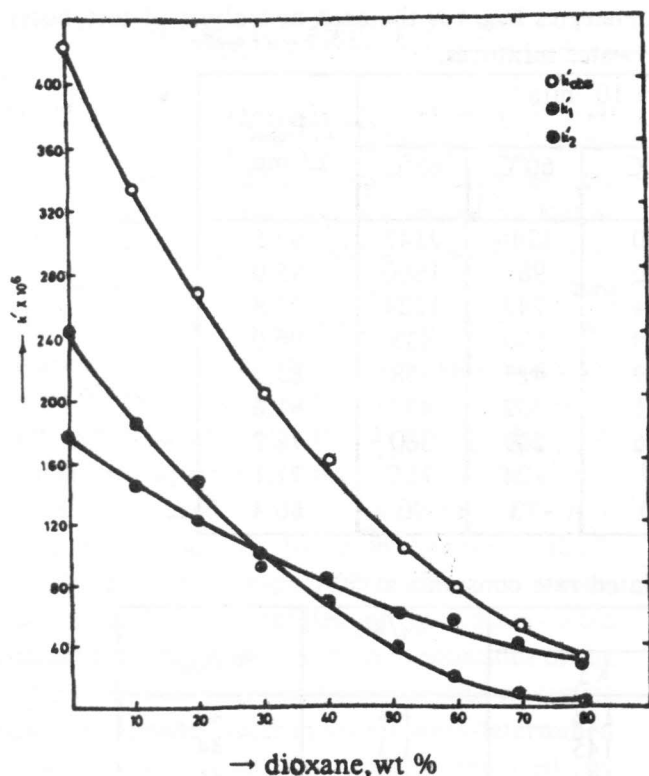
→ dioxane, wt %

**Figure 1.** Comparative representation of the reaction rate as a function of the wt% of dioxane at 50°C.

Table (3) contains the values of the free energies $\Delta G^*$, enthalpies $\Delta H^*$, and entropies $\Delta S^*$, of activation, for the overall reactions, at 50°C. It is noticed that $\Delta G^*$ increases regularly with increasing dioxane content of the medium for the unimolecular and bimolecular reaction. The $\Delta H^*$ values for the overall reaction decrease with increasing dioxane content, due to the continuous change in mechanism. This is evidenced by the fact that the $\Delta H^*$ value, for the separated unimolecular 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 -11.8 to -39.8 J mole$^{-1}$deg$^{-1}$ as the dioxane content increases. This is a direct consequence of the decrease in the contribution of the $A_{AL}1$ mechanism, and a parallel increase in the $A_{AC}2$ mechanism, as the medium becomes enriched in dioxane. The values of $\Delta S^*$, for the separated unimolecular and bimolecular reactions, are all in good agreement with the ranges assumed for each mechanism[18], and are in favour of the present procedure of resolving the rate into the two concurrent mechanisms.

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