

Kinetic study of the acetate-catalysed hydrolysis of phenyl acetate

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Received 11 June 1999; received in revised form 26 April 2000; accepted 12 May 2000

Abstract

The results of an investigation aimed at obtaining the kinetic characteristics of the hydrolysis reaction of phenyl acetate catalysed by sodium acetate are presented. The hydrolytic reaction giving phenol and acetic acid starting from phenyl acetate is particularly suitable to run in a microwave-irradiated environment. In fact, since the considered reaction is characterised by a very low rate, small variations occurring in an irradiated system can be detected. Furthermore, since this reaction runs in an aqueous environment, it can use the energy transmitted by microwave radiation efficiently, thanks to the high capacity of water absorbance at microwave frequencies. The reaction was run in a buffered aqueous solution of sodium acetate and acetic acid at equal concentrations (pH = 5). Kinetic constants were obtained in the 293–318 K temperature interval and at a concentration of both sodium acetate and acetic acid in the 0.4–0.06 mol dm⁻³ range. The derived activation energies decreased as the concentration of the sodium acetate/acetic acid increased. The kinetic study of the hydrolysis was carried out to obtain experimental data suitable for a fast comparison with the data that will be obtained from the development of this reaction in a microwave-irradiated environment. This paper also presents the analytical and experimental techniques suitable to run the experimental procedure in a microwave-irradiated reactor. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrolysis; Phenyl acetate; Microwave

1. Introduction

This study on the hydrolysis of phenyl acetate catalysed by sodium acetate was carried out using traditional techniques to obtain kinetic data suitable to be compared with those that will be obtained for the same reaction in a microwave-irradiated reactor.

The evolution of chemical reactions in microwave-irradiated environments (electromagnetic frequency in the field 3×10^8 – 300×10^8 Hz) has not been studied extensively so far, mainly because this type of radiation is difficult to produce and transmit, and also because cheap medium power generators working at frequencies other than 2.45 GHz are not easily available. For this reason kinetic data from microwave-irradiated environments are not easily available. But many new apparatus that use focused microwaves to run organic synthesis have become commercially available. Furthermore, several papers on the effect of microwave heating [1–7] and on chemical reactions in microwave-irradiated environments [8–13], have been reported recently. This testifies to an increasing interest in microwave-irradiated chemical reactions field.

In spite of this interest, a common accepted theory is far from being reached. Many authors have blamed the formation of hot spots in reacting molecules for the great acceleration that may be reached by the evolution velocity of a chemical reaction. For example, since at 150°C the ratio of the kinetic constants of the reaction between benzophenone tetracarboxylic acid dianhydride and 3-3'-diaminodiphenylsulphone in *N*-methylpyrrolidone running in a microwave heated environment or in a conventional heated environment is of about 30, reporting on the conclusions by Lewis et al. [15], Mingos and Baghurst [14] suggested that the observed rate acceleration may be explained by a very localised temperature rise (40–60°C), due to the absorption of the microwave radiation near the reaction sites. The hot spot formation theory is also proposed by Laurent et al. [16]. For heterogeneous catalytic reactions, Mingos [17] suggested that most research on catalytic reactions under microwave conditions had dwelled on kinetic aspects, and observed that reaction rates and product distributions are more consistent with a temperature 300–400 K higher than that measured for the bulk of the catalyst bed.

However, studying the evolution of the reaction between propan-1-ol and the ethanoic acid in an oven irradiated at 2.45 GHz and 650 W, Bond and co-workers [18] realised that “microwave radiation has no effect on the rate of reaction other than that of conventional heating”. This reaction

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Nomenclature

a, b	regression coefficients of the species in the equation $D=f(C)$
C	concentration of the species (mol dm^{-3})
D	optical density
E	activation energy (J mol^{-1})
k	rate constant (s^{-1})
k_0/k_{AcNa}	parameter in Eq. (12)
r	reaction rate ($\text{mol s}^{-1} \text{dm}^{-3}$)
t	time (s)
T	temperature (K)

Greek symbols

ΔD	difference of the optical density at two wavelengths 258 and 279.5 nm
λ	wavelength (nm)

Superscripts

λ	relative to the wavelength λ
0	initial condition

Subscripts

AcH	relative to acetic acid
AcNa	relative to sodium acetate
o	relative to other (non-reagent) compounds
P	phenol
PA	phenyl acetate
s	generic species
T	total

was run in a system with a total condenser using an experimental apparatus similar to that shown by Mingos and Baghurst [19], though, in my opinion, the experimental procedure could have the limitation of neglecting effects due to penetration depth. In fact, since the studied reaction runs in an aqueous environment and the penetration depth in distilled water is about 1 cm (this value greatly decreases on increasing the amount of dissolved salts), if the reactor can be assumed to be a sphere 10 cm in diameter, more than 50% of the volume is unaffected by the microwave. But the opinion that the evolution of chemical reactions is unaffected by electromagnetic radiation is also shared by other authors [20]. Unfortunately, from the description of the experimental procedures it is not possible to draw any conclusions, because the paper lacks fundamental information such as mixing data in the reaction apparatus. In fact, if one takes into account that agitation consistently alters the effect of radiation, it becomes impossible to reach any conclusion.

On the contrary studying the hydrolysis of indometacin, Gattavecchia and Giovanardi [21] conclude that “it is possible to calculate that under MW (microwave) the Arrhenius activation energy is about 10 times lower than under conventional heating. This effect can be explained by assuming that the electromagnetic field generated by MW radiation

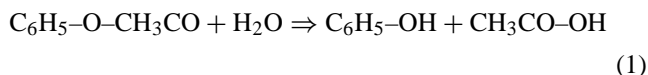
increases the polarisation of the carbonyl bond” giving rise to a possible non-thermal influence of microwave radiation on the evolution of the considered chemical reactions.

More experimental work appears necessary but also greater attention must be paid in designing experimental procedures to obtain significant kinetic data in irradiated environments [22,23]. In fact, many of the studies on this subject, and some of those quoted above, were run using energy amounts in the order of 10^6 Wh for reactions with quantities that need energies of about 10^3 Wh to evolve. It is evident that in such situations it is very difficult to tell whether the large increase in the reported yields and rates is due to the very large amounts of energy used or to the microwave radiation applied to the reacting environment. In fact, in the studied systems one can see a large increase in temperature, but this does not always justify the large increase in the rates of the studied chemical reactions; however, due to the large amounts of energy used, it is impossible to draw any conclusive considerations.

To overcome this limitation it would be appropriate to run the experiments with microwave generators that can give energies of about the same order of magnitude as those absorbed by the reaction. Furthermore the reaction should be run in a thermostatted environment, to eliminate all contributions due to temperature increase, and in a reactor of well-known fluidodynamics.

In order to understand the possible effect of electromagnetic waves propagating at frequencies in the field 0.3–30 GHz on the evolution of a chemical reaction, the data acquired in a radiated environment must be compared with the traditional kinetic data of the selected reaction. The selection of this reaction is of great importance, both because it must be of a low rate and because the power transmitted by the electromagnetic radiation must be used optimally.

Taking these points into account, the following reaction was selected:



The following are the most important among the advantages of the selected reaction catalysed from sodium acetate:

- The reaction runs in an aqueous environment; this allows the energy that can be given by the microwaves to be absorbed optimally [21]. In fact, it is well-known that, particularly at a frequency of 2.45 GHz, the energy transmitted by this radiation is well absorbed by water.
- Since the reaction runs at very low rates (at 25°C and with a concentration of sodium acetate of 0.40 mol dm^{-3} , we have a conversion of about 40% in about 30 days), also small variation occurring in irradiated environments can easily be highlighted.
- The reacting system can be analysed using the spectrophotometric method in the ultraviolet region. This entails a non-destructive analysis and the possibility of working with small quantities.

- The constant rate has already been obtained at 25°C [24]. Though the results presented in this reference are different from those obtained here (but of the same order of magnitude) a comparison could be helpful.

For the selected reaction, the kinetic parameters obtained in a non-irradiated environment are presented. The determinations were made at a temperature of between 293 and 318 K at 5 K intervals. For the same reaction the experimentation will also run at variable temperatures in an irradiated system. In fact it is necessary to check whether the high rate increases (if any) that one can have in microwave-irradiated systems [8–10,12,14,21] may be due to increase (even local increases) in temperature [25,26]. In this way any increase in the reaction rates in the irradiated system could be compared with those obtained in a non-irradiated environment working at a higher temperature. If so the extent of the link between activation energies in irradiated and non-irradiated environments must be found.

2. Experimental

The following chemical compounds were used throughout without further purification: phenyl acetate Carlo Erba RPE 99%; dioxane Carlo Erba RPE 99.8%; sodium acetate Carlo Erba RPE; acetic acid Carlo Erba RPE 99.8%; sodium chloride Carlo Erba RPE. The purity of the materials was always expressed in mass%.

The experimental procedure was designed to allow the determination of rate constants as simply as possible, not only to avoid the (non-negligible) difficulties related to the experimentation, but also to avoid too many complex operations which can cause even slight errors and limit the reading of the experimental data.

Since phenyl acetate is insoluble in water, a “master solution” was prepared by dissolving the ester in dioxane (0.5617 g of phenyl acetate + 9.7369 g of dioxane) and using this master solution as the source of phenyl acetate. To ensure that the dioxane is acting as co-solvent, the ratio “*q*” between the number of moles of phenyl acetate and that of dioxane must be greater than 15, but with the phenyl acetate concentrations used here, this ratio must not be greater than 35, so as not to have an excessively high dioxane concentration in the reacting solutions, which could cause excessive absorption of ultraviolet radiation in the sample analysis.

The reactions were initiated by addition of 0.10/0.20/0.30 cm³ of the master solution of ester in dioxane to 25 cm³ of the appropriate aqueous buffer solution. The buffer solutions used to dilute the master solution were prepared by dissolving sodium acetate and acetic acid in bi-distilled air-free water until the concentration of the acid was equal to that of its conjugate base, hence pH = 5.00 ± 0.10. Sufficient amounts of sodium chloride were added to all buffer solutions so as to maintain a constant ionic strength of 0.5 mol dm⁻³, and to have an equal secondary salt effect on

Table 1

Slopes of the curves of optical density vs. concentration at 258 and 279.5 nm (P: phenol; PA: phenyl acetate)

Species	C_s (mol dm ⁻³)	$dD/d\lambda$	
		258 nm	279.5 nm
P	154.8×10^{-4}	-0.213	0.086
P	38.7×10^{-4}	-0.043	0.017
PA	49×10^{-4}	-0.008	0.003
PA	24.5×10^{-4}	0.003	0.003

the rate constant in all buffer solutions, whatever the amount of dissolved sodium acetate and acetic acid.

Two equal amounts of these buffer solutions with C_{AcNa} = 0.06, 0.12, 0.2, 0.3, and 0.4 mol dm⁻³ (and with equal concentrations of acetic acid) plus the added amount of the master solution were poured into a water thermostatic bath (temperature controlled at ±0.1°C) at temperatures of 293.0, 298.0, 303.0, 313.0, and 318 K. The reacting solutions in the two flasks were shaken continuously using a magnetic stirrer at 300 rpm.

The experimental determination was carried out until a conversion of about 40% was reached. This was assumed as a limit because higher phenol concentrations in the reacting solution lead to a greater number of errors in optical density measurements. This situation is presented in Table 1, which shows a fivefold increase in the slope of the curves of the spectrum on increasing the concentration of phenol from 38.7×10^{-4} to 154.8×10^{-4} mol dm⁻³. Thus, when the concentration of phenol in the reaction solution increases, small wavelength differences due to mechanical imprecision in the spectrophotometric apparatus (Shimadzu 160A) may affect optical density differences by an amount that, although not too large as an absolute value, may cause errors that could not be compatible with the desired results. These different values in the optical densities taken to calculate the phenyl acetate concentration in the reacting solution, for a conversion greater than 40%, cause incorrect concentrations which may also lead to errors in the evaluated rate constant. As a security measure, with a catalytic compound concentration of 0.40 and 0.30 mol dm⁻³, the reaction (1) was left to run up to a conversion of about 80%. The data obtained, though incorrect, led to the conclusion that no variation occurs in the evolution mechanism of the reaction.

About every 12 h, three samples of about 3.5 ml each were withdrawn from each of the two flasks containing the reacting solution and the optical density measured; the average between these values was then used as an optical density value for the solution in further calculations. Analyses were made reading the optical absorption at the two wavelengths, 258 and 279.5 nm. The data thus acquired were processed using the two-wavelength method. The concentration of the reagent can be obtained from the difference of the average value of the optical densities at 258 and 279.5 nm using the

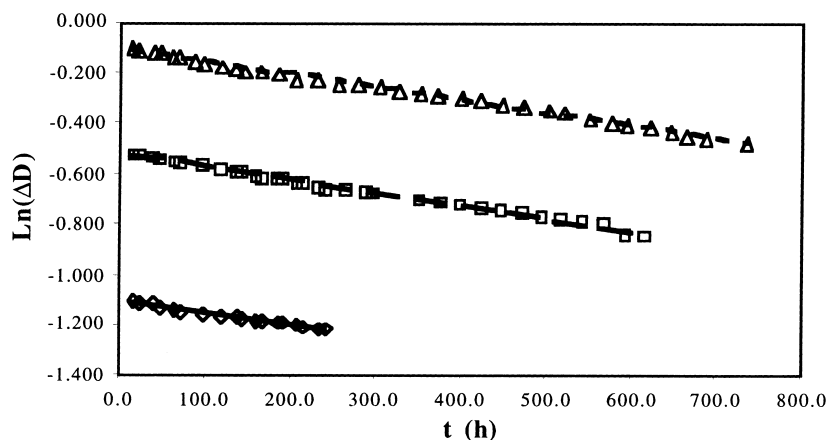


Fig. 1. Comparison between experimental data: (a) $C_{PA}^0 = 1.6 \times 10^{-3}$ (\diamond) mol dm^{-3} regression straight line (—) $\ln(\Delta D) = -4.69E-4t - 1.10$; (b) $C_{PA}^0 = 3.2 \times 10^{-3}$ (\square) mol dm^{-3} regression straight line (—) $\ln(\Delta D) = -5.13E-4t - 0.521$; (c) $C_{PA}^0 = 4.9 \times 10^{-3}$ (Δ) mol dm^{-3} regression straight line (- -) $\ln(\Delta D) = -4.99E-4t - 0.107$.

equation

$$C_{PA} = 5.218 \times 10^{-3} \Delta D + 3.938 \times 10^{-5} \quad (2)$$

the squared correlation coefficient of this equation with data in the field $C_{PA} = 3.37E-3 - 7.85E-3 \text{ mol dm}^{-3}$ was 0.99981.

The three measured optical densities obtained for each reacting solution were averaged and the two obtained values compared. If the difference was lower than 0.1%, the average value was assumed to be the correct measurement. If the difference was greater, then it was assumed to be due to experimental errors. The contents of the two flasks were mixed together and the resulting mixture was divided into two parts, and placed into a thermostatic bath to react for another 2 h, after which the measurements were repeated. This alternating procedure had to be used about 5% of the total number of times.

In order to see whether the initial reagent concentration has any effect on the reaction evolution, e.g. by modifying the order of the reaction, experimental runs were made starting from various concentrations of phenyl acetate.

The runs were made using the initial concentrations $C_{PA}^0 = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$, $C_{PA}^0 = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$, $C_{PA}^0 = 6.5 \times 10^{-3} \text{ mol dm}^{-3}$ and the normally used concentration $C_{PA}^0 = 4.9 \times 10^{-3} \text{ mol dm}^{-3}$. Fig. 1 shows experimental $\ln(\Delta D)$ vs. t data obtained using $C_{PA}^0 = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$, $C_{PA}^0 = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$, $C_{PA}^0 = 4.9 \times 10^{-3} \text{ mol dm}^{-3}$. These data refer to a temperature of 298.0 K and a sodium acetate and acetic acid concentration of 0.12 mol dm^{-3} . With respect to the kinetic constant (the absolute value of the slope of the regression straight line) obtained starting from $C_{PA}^0 = 4.9 \text{ mmol dm}^{-3}$, the percentage differences starting with $C_{PA}^0 = 3.2 \text{ mmol dm}^{-3}$ and $C_{PA}^0 = 1.6 \text{ mmol dm}^{-3}$ are, respectively, 2.34 and 6.01%, i.e. of the same order of magnitude as the experimental errors. Difference values of the same order were

also obtained by repeating the experiment at 303.0 K and $C_{PA}^0 = 6.5 \text{ mmol dm}^{-3}$. Thus all experimental work was carried out using $C_{PA}^0 = 4.9 \text{ mmol dm}^{-3}$. In fact with this initial phenyl acetate concentration, interferences with optical densities readings of the reacting solutions due to an excessively high concentration of the co-solvent dioxane were avoided, and an adequate signal level was given so as to reduce the effect of casual errors in optical absorbance.

3. Discussion

The considered reaction has already been studied at 25°C by Gold et al. [24]. Even if Gold, as in this paper, uses a spectrophotometric apparatus to make its measurements, the procedure here is different. Since this paper is a presentation of the experimental results obtained and of the experimental method used, the previously used methodologies have been reported so that the comparison with the method used here may point out any possible theoretical or procedural errors.

The rate constants of the hydrolytic reaction of phenyl acetate were evaluated by Gold et al. [24] by following the increment in optical density at 270 nm obtained in the solution when phenyl acetate is replaced by phenol, and by applying a least-square procedure to the experimental data $\ln[\bar{D} - D(t)]$ vs. time t . In this equation \bar{D} is the optical density when the total conversion of phenyl acetate, which is initially present in the reaction environment, is achieved. \bar{D} was obtained by measuring the optical density of the system derived by performing hydrolysis of the ester in a 0.1 N sodium hydroxide solution, followed by acidification with 2 N sulphuric acid to give a unionised phenol solution of the same concentration as the initial concentration of ester in the kinetic experiment.

In this work, due to the technological advances achieved in the construction of spectrophotometric apparatus since 1968, the well-known two-wavelength method has been used. This

was necessary because both phenyl acetate and phenol absorb the radiation in the ultraviolet field (200–300 nm). The two-wavelength method is useful because it allows to calculate the unknown concentration of a compound of interest in a mixture that also contains an interfering component. This can be done by calculating the absorbance difference between two points on the mixture spectra, which is directly proportional to the concentration of the component of interest, whatever the interfering component.

The two selected wavelengths were 258 and 279.5 nm. They were selected because the absorbance spectrum of phenyl acetate has a maximum value at 258 nm, while at 279.5 nm the phenol solutions have the same optical density values as at 258 nm. This same optical density value at 258 and 279.5 nm is shown by the phenol solutions at different phenol concentrations.

Thus in a solution containing both phenyl acetate and phenol, the optical density is

$$D_T^{258} = D_{PA}^{258} + D_P^{258} + D_o^{258} \quad (3)$$

$$D_T^{279.5} = D_{PA}^{279.5} + D_P^{279.5} + D_o^{279.5} \quad (4)$$

Thus

$$\begin{aligned} \Delta D &= D_T^{258} - D_T^{279.5} = [D_{PA}^{258} - D_{PA}^{279.5}] - [D_P^{258} - D_P^{279.5}] \\ &+ [D_o^{258} - D_o^{279.5}] = [D_{PA}^{258} - D_{PA}^{279.5}] \\ &+ [D_o^{258} - D_o^{279.5}] = [a_{PA}^{258} - a_{PA}^{279.5}] C_{PA} \\ &+ [b_{PA}^{258} - b_{PA}^{279.5} + D_o^{258} - D_o^{279.5}] \end{aligned} \quad (5)$$

where $D_{PA}^{258} = a_{PA}^{258} C_{PA} + b_{PA}^{258}$ and $D_{PA}^{279.5} = a_{PA}^{279.5} C_{PA} + b_{PA}^{279.5}$. Then the difference between the values of optical densities at these two wavelengths is proportional to the concentration of the reagent.

Differentiating the previous equation vs. time (t), the following equation can be written:

$$\frac{dC_{PA}}{dt} = \frac{1}{a_{PA}^{258} - a_{PA}^{279.5}} \frac{d\Delta D}{dt} \quad (6)$$

If, as shown by Gold et al. [24], the order of reaction (1) with respect to phenyl acetate is 1 and since in this case b_{PA}^{258} and $b_{PA}^{279.5}$ are negligible compared to the products $a_{PA}^{258} C_{PA}$ and $a_{PA}^{279.5} C_{PA}$, then

$$\frac{dC_{PA}}{dt} = -kC_{PA} = \frac{k}{a_{PA}^{258} - a_{PA}^{279.5}} [\Delta D - (D_o^{258} - D_o^{279.5})] \quad (7)$$

At this concentration the contribution to the total optical density difference of the reacting solution ΔD given by the other components in the reacting environment (acetic acid, sodium acetate, dioxane) was found to be so small that it could be neglected. For example, the optical density of dioxane (the non-reagent component that shows the highest light absorption in the conditions used here) at a concentration of 2.2×10^{-1} (about double that of the reacting environment) and at 258 nm is 10.0×10^{-3} , while at 279.5 nm it is 9.0×10^{-3} . The absolute difference is 1.0×10^{-3} . Hence, comparing this contribution with the recorded values of the optical densities ($1200 \times 10^{-3} / 700 \times 10^{-3}$), we have an average percentage difference of 0.1%, and since this is much smaller than other experimental errors, it has been duly neglected. Thus from Eqs. (5)–(7), and taking into account the above conclusions

$$\frac{d\Delta D}{dt} = -k\Delta D \quad (8)$$

From the integration of Eq. (8), the constant rate of the reaction (1) can be obtained from the slope of the regression straight line of experimental $\ln(\Delta D / \Delta D^0)$ (ΔD^0 being the difference of the optical density of the reacting solution at $t = 0$) vs. time data. Figs. 2–7 present experimental $\ln(\Delta D)$ vs. t (time). The kinetic constants have been derived from

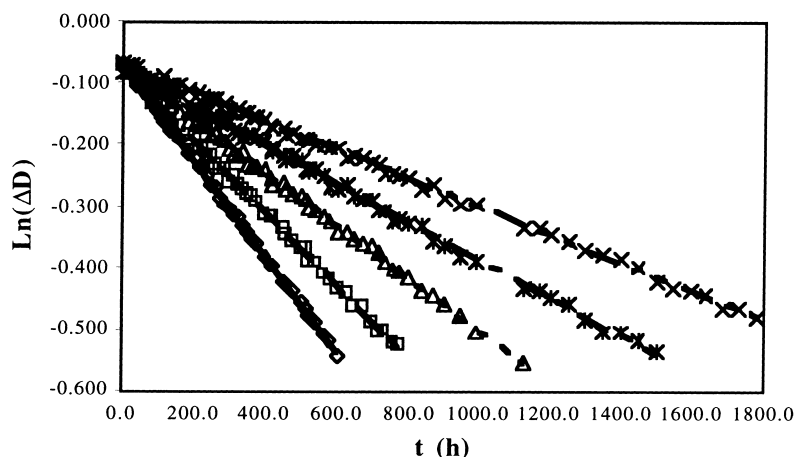


Fig. 2. Determination of the kinetic constant for the reaction (1) at 293 K. Regression curves: $C_{AcNa} = 0.4 \text{ mol dm}^{-3}$ (—); $C_{AcNa} = 0.3 \text{ mol dm}^{-3}$ (---); $C_{AcNa} = 0.2 \text{ mol dm}^{-3}$ (- · -); $C_{AcNa} = 0.12 \text{ mol dm}^{-3}$ (· · ·); $C_{AcNa} = 0.06 \text{ mol dm}^{-3}$ (- · · ·). Experimental data: $C_{AcNa} = 0.4 \text{ mol dm}^{-3}$ (\diamond); $C_{AcNa} = 0.3 \text{ mol dm}^{-3}$ (\square); $C_{AcNa} = 0.2 \text{ mol dm}^{-3}$ (Δ); $C_{AcNa} = 0.12 \text{ mol dm}^{-3}$ (\times); $C_{AcNa} = 0.06 \text{ mol dm}^{-3}$ (\times).

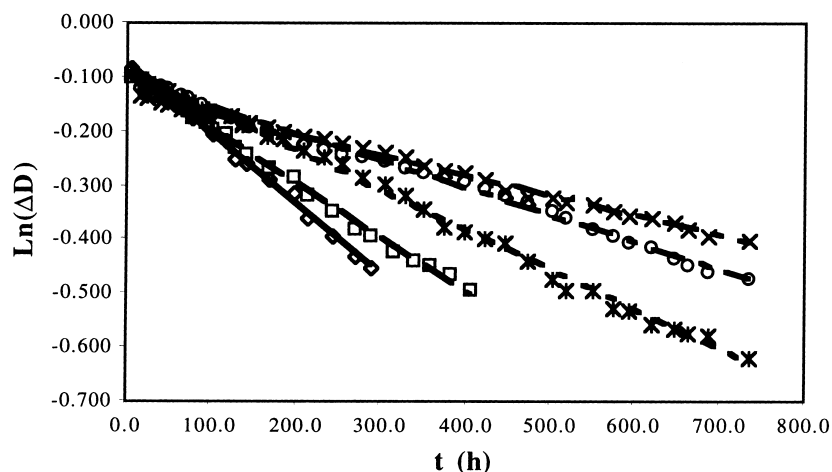


Fig. 3. Determination of the kinetic constant for the reaction (1) at 298 K. Regression curves: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (—); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (---); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (- · -); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (- · · -); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (- · · ·). Experimental data: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (\diamond); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (\square); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (\ast); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (\circ); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (\times).

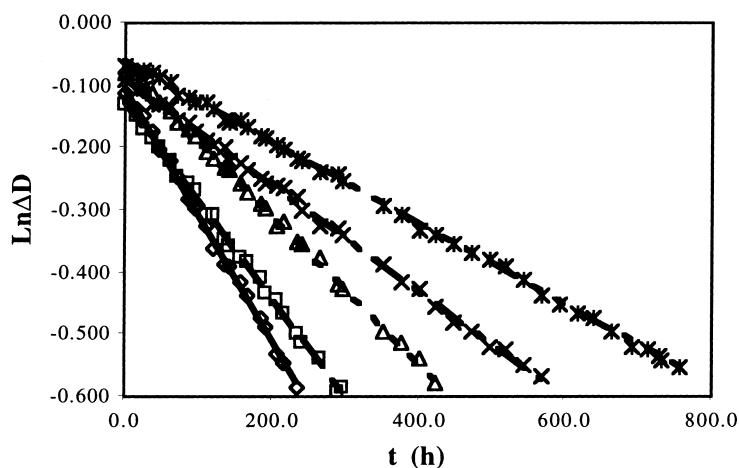


Fig. 4. Determination of the kinetic constant for the reaction (1) at 303 K. Regression curves: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (—); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (---); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (- · -); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (- · · -); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (- · · ·). Experimental data: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (\diamond); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (\square); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (Δ); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (\ast); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (\times).

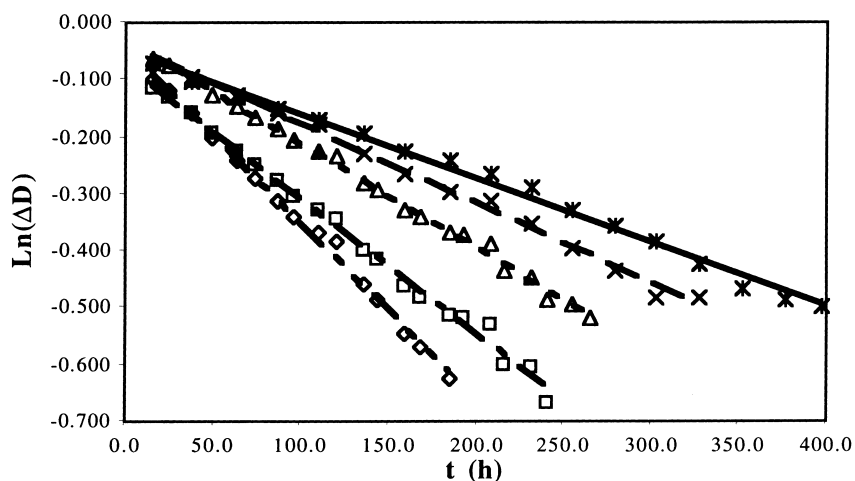


Fig. 5. Determination of the kinetic constant for the reaction (1) at 308 K. Regression curves: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (—); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (---); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (- · -); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (- · · -); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (- · · ·). Experimental data: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (\diamond); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (\square); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (Δ); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (\ast); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (\times).

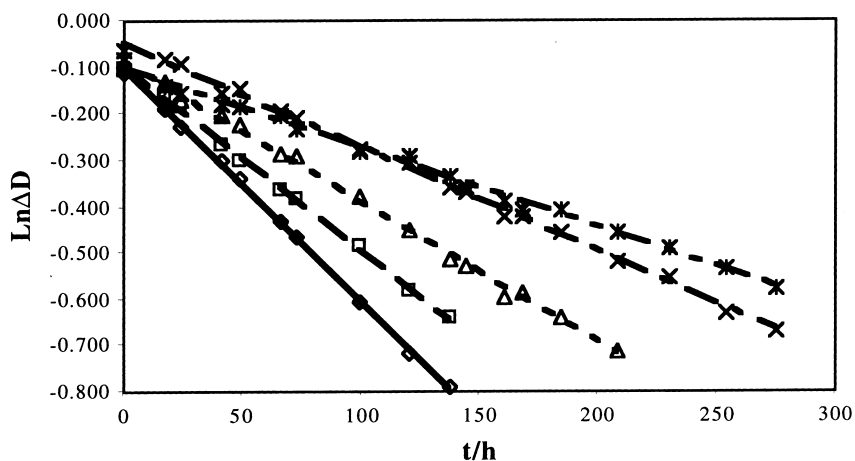


Fig. 6. Determination of the kinetic constant for the reaction (1) at 313 K. Regression curves: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (—); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (---); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (- - -); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (- · - ·); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (- - -). Experimental data: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (\diamond); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (\square); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (Δ); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (\ast); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (\times).

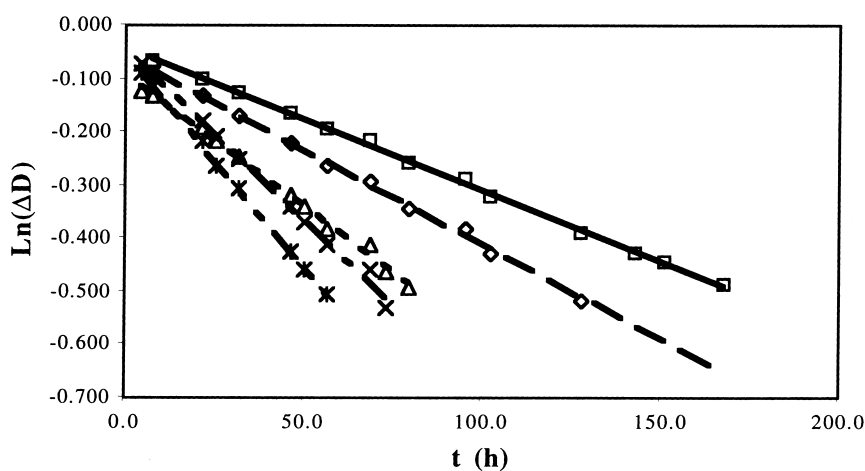


Fig. 7. Determination of the kinetic constant for the reaction (1) at 318 K. Regression curves: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (—); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (---); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (- - -); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (- · - ·); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (- - -). Experimental data: $C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$ (\diamond); $C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$ (\square); $C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$ (Δ); $C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$ (\ast); $C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$ (\times).

$\ln(\Delta D)$ data and not from $\ln(\Delta D/\Delta D^0)$, because ΔD^0 values can sometimes be imprecise, due to difficulties mixing the components of the reagent solutions. The linearity of data $\ln(\Delta D)$ vs. t (squared correlation coefficients of all data greater than 0.993) confirm the goodness of this

assumption. The kinetic constants obtained performing a linear regression of the experimental data are shown in Table 2; the squared correlation coefficients are also shown in brackets; values approaching 1 show the validity of these assumptions.

Table 2
Kinetic constant derived from linear regression of experimental $\ln(\Delta D)$ vs. t data

T (K)	k (h^{-1}) (R^2)				
	$C_{\text{AcNa}} = 0.4 \text{ mol dm}^{-3}$	$C_{\text{AcNa}} = 0.3 \text{ mol dm}^{-3}$	$C_{\text{AcNa}} = 0.2 \text{ mol dm}^{-3}$	$C_{\text{AcNa}} = 0.12 \text{ mol dm}^{-3}$	$C_{\text{AcNa}} = 0.06 \text{ mol dm}^{-3}$
293	7.80E-4 [1.000]	5.91E-4 [0.998]	4.30E-4 [0.998]	3.12E-4 [0.998]	2.32E-4 [0.999]
298	1.30E-3 [0.997]	1.00E-3 [0.997]	7.37E-4 [0.994]	4.99E-4 [0.997]	3.78E-4 [0.997]
303	2.03E-3 [0.998]	1.57E-3 [0.998]	1.18E-3 [0.999]	8.49E-4 [0.998]	6.52E-4 [0.999]
308	3.09E-3 [0.995]	2.36E-3 [0.994]	1.82E-3 [0.996]	1.39E-3 [0.994]	1.12E-3 [0.992]
313	5.03E-3 [0.999]	3.95E-3 [0.999]	3.03E-3 [0.997]	2.24E-3 [0.997]	1.71E-3 [0.994]
318	7.98E-3 [0.999]	7.38E-3 [0.995]	4.92E-3 [0.995]	3.53E-3 [0.997]	2.66E-3 [0.998]

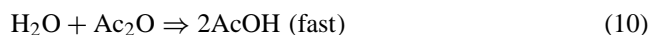
Table 3
Activation energies as a function of sodium acetate concentration

C_{AcNa} (mol dm ⁻³)	E (J mol ⁻¹)
0.4	71 289
0.3	72 696
0.2	74 643
0.12	75 465
0.06	76 510

The activation energies of the reaction were obtained plotting $\ln(k)$ against $1/T$. The values are reported in Table 3.

4. Conclusions

Two types of mechanism have been proposed for the aqueous acetate-catalysed hydrolysis of ring-substituted phenyl acetates (ArOAc). One was proposed by Bender [27,28] and accepts that the reaction runs by the nucleophilic catalysis mechanism represented by the following stepwise process:



The other mechanism suggests that the considered reaction runs as a general base catalysis. This mechanism probably involves a transition component where ester, base, and a water molecule are all joined together [29]. The precise structure of this transition compound has been written in different ways [30,31] but the examination of the problems connected with the mechanism is not within the aim of this paper. It is sufficient to point out that both proposed mechanisms arrive at the conclusion that the reaction runs following a first order kinetics with respect to the reagent.

Table 4
Parameters of the Eq. (12)

T (K)	k_0 (h ⁻¹)	k_{AcNa} (h ⁻¹ dm ³ mol ⁻¹)
293	1.22E-4	1.61E-3
298	1.92E-4	2.74E-3
303	3.78E-4	4.07E-3
308	6.30E-4	5.90E-3
313	1.09E-3	9.72E-3
318	1.71E-3	1.57E-2

Since all the above conclusions are compatible with a first order kinetics of the considered reaction, the rate can be written as

$$r = k(C_{\text{AcNa}})C_{\text{PA}} \quad (11)$$

On the other hand, according to the mechanisms proposed for the evolution of the reaction

$$k(C_{\text{AcNa}}) = k_0 + k_{\text{AcNa}}C_{\text{AcNa}} \quad (12)$$

Fig. 8 shows the kinetic constants as a function of sodium acetate concentrations. The obtained value can be represented by Eq. (13). The parameters of this equation, which have already been used at 25°C by Gold et al. [24], have been obtained by a linear regression of the data k vs. C_{AcNa} . The results are shown in Table 4.

As highlighted in Fig. 8, the obtained rate constants show a linear dependence on the catalyst concentration, confirming the theoretical results shown in Eq. (13).

The evolution of the reaction (1) has been examined carefully. Considering the final purpose of this work the following results should be highlighted:

- The rate is very low, at 293 K a 37% conversion can be performed at the highest catalyst concentration in more than 25 days. Thus any small variations in an irradiated environment can easily be detected.

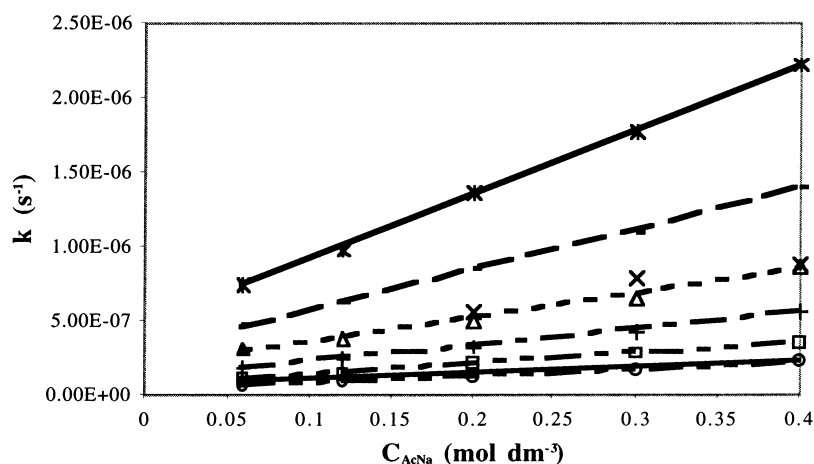


Fig. 8. Kinetic constants vs. sodium acetate concentration. $T = 318$ K: regression curve (—), data (✕); $T = 313$ K: regression curve (— —), data (x); $T = 308$ K: regression curve (· · ·), data (Δ); $T = 303$ K: regression curve (- · - ·), data (□); $T = 293$ K: regression curve (- - -), data (○).

- Table 3 shows the influence that the concentration of sodium acetate and acetic acid may have on the evolution of the reaction. This will be useful because a point to be investigated in the near future with experiments in an irradiated environment is whether microwave radiation can modify this influence, and if it does, by how much.
- Table 4 shows the influence of temperature on the evolution of the reaction. The experiment in an irradiated environment must fulfil two objectives:
 - First, can the reaction rate increment (if any) be considered an effect of temperature?
 - Second, do microwaves modify the influence of temperature on the evolution of the reaction?

About the present reaction, we can say that activation energies decrease as the sodium acetate concentration increases. This obvious fact confirms the catalytic action of the buffer mixture of sodium acetate and acetic acid. The value of the activation energy as a function of sodium acetate concentration can be obtained from the empirical equation

$$E = 15.359C_{\text{AcNa}} - 77.444 \quad (13)$$

In this very good linear relation (squared correlation coefficient $R^2 = 0.9941$), activation energy is given in J mol^{-1} and the sodium acetate concentration in mol dm^{-3} . The equation is valid in the $0.06\text{--}0.4 \text{ mol dm}^{-3}$ sodium acetate concentration field.

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