Effect of Temperature and Microwave Power on the Hydrolysis of Phenyl Acetate

Renzo Carta and Laura Loddo
Dipartimento di Ingegneria Chimica e Materiali, Università di Cagliari, 09123 Cagliari, Italy

DOI 10.1002/aic.10135

A study of the influence of microwave radiation, at a frequency of 2.45 GHz on the evolution rate of the hydrolytic decomposition of phenyl acetate evolving in a radiated environment, is presented. The experimental data refer to temperatures of 25, 30, 35, 40, and 45°C at radiating powers of 500 and 1000 mW and to 35°C at the radiating powers of 50, 100, 200, 300, and 400 mW. Experimental data were obtained using the initial rate method and are correlated with a differential procedure. A comparison with the previously obtained results in a nonradiated environment is presented. From this comparison, the catalytic effect of microwave radiation with the reaction evolving in a nonradiated environment is proposed, replacing that running in a solution with catalytic acetate ions.

Keywords: microwave, kinetic, phenyl acetate, hydrolysis, catalysis

Introduction

The scientific community has largely accepted that many chemical reactions, running in a microwave-radiated environment, experience an increase in the evolution rate (Gabriel et al., 1998; Whittaker et al., 1994). Sometimes, this increase can be very high; for example, Gedye et al. (1988) report an increase 1200-fold greater than the rate of the same systems in a nonradiated environment.

Many theories have tried to explain this huge increase in the reaction rates and, in particular, two main theories have sparked the interest of members of the scientific community. The first theory addresses local hot spots close to the reaction sites (Baghurst, 1997, p. 24) or of a "specific bond activation" (Admek, 1992), which, as the authors highlighted, gives its contribution to rate enhancement in radiated environments with a thermal effect. The second theory addresses an "athermal effect," which is a specific effect linked to microwave radiation. For example, a specific nonthermal microwave effect was pointed out by Villa et al. (2001), while studying a solvent-free phase transfer catalysis for the synthesis of benzilidene cineole derivatives. Santagada et al. (2001) also found that the synthesis of dipeptides in microwave radiated environments gave the desired compounds in higher yields and in shorter reaction times than those obtained from conventional heating, working with nonboiling systems. Lewis et al. (1992) observed a reduction (from 105 to 55 kJ/mol for the imidization reaction) of the activation energy passing from nonradiated to radiated systems, but they modeled the rate enhancement using a nonuniform temperature profile on a molecular scale (that is, a hot spot–type model). The concept of localized excitation was also pointed out by Sun et al. (1988), who called this effect spectroscopic heating A reduction in the time needed to reach the equilibrium in the mutarotation reaction of α-D-glucose in a microwave heated run, with respect to that needed when using conventional heating, was observed by Pagnotta et al. (1993). They assumed that this was a consequence of a nonthermal effect, even though, in our opinion, the use of a microwave energy source of 1.2 kW may limit the value of this conclusion.

It is our view that the two different theories mentioned here are compatible with each other. Each gives an explanation for the increase in the reaction rates; the former, which speaks of hot spots, is compatible with a high radiating power that can support localized heating. The latter, which describes a specific microwave effect, can be compatible with a low radiating power so that the system can run thermostatically.

The theory describing hot spots, close to the molecular sites where the reaction takes place, is certainly of extreme interest

---

Correspondence concerning this article should be addressed to R. Carta at carta@dicm.unica.it.

and may explain the huge increases in the reaction rates reported in some of the literature; some authors have also quantified the temperature increase; for example, Chemat and Esved (2001) describe an increase of 40°C over the boiling temperature. Before drawing any conclusions, however, two main pieces of evidence must be taken into account:

(1) Some reactions do not show any significant increase in the reaction rates, even though they evolve in environments where the microwave radiation is absorbed well (such as in aqueous solutions).

(2) Microwave radiation in many solutions can penetrate in only a very low amount [for example, in an aqueous solution of NaCl with $C_{NaCl} = 0.5$ mol/L, the penetration depth at a frequency of 1 GHz is about 2 mm (Metaxas, 1993, pp. 31 and 80)]; overheating is thus a local phenomenon, but its results are applied over all the reactor volume.

Taking into account the above-mentioned observations, this fascinating principle is not completely acceptable from a cultural point of view.

Specific microwave effects are also lacking in justifications. It is indeed well known that radiation at 2.45 GHz promotes the transformation of the nonreactive triplet radical pair ($[\dot{R}_1\dot{R}_2]^T$) into the reactive singlet pair ($[\dot{R}_1\dot{R}_2]^S$) (Buchachenko, 1994, pp. 25–27); for nonradical reactions, however, no theoretical deduction justifies the increase in the reaction rate. Also, the large amount of experimental data can hardly be used to support this interpretation because many of the reaction systems are not thermostated and the reactions have been run using huge amounts of energy; in this situation it is very difficult to eliminate the thermal effects.

We have already presented a study to the scientific world in which we demonstrated at a constant temperature of 25°C, a modest increase in the reaction rate of phenyl acetate hydrolysis running in a radiated environment with respect to that running in a nonradiated environment (Carta, 2002). In the same work, we suggested the possibility that the increase could be attributed to a sort of catalytic effect of the microwave radiation. This latter consideration was justified by the fact that the kinetic constant obtained in a radiated environment does not depend on the catalytic acetate ion concentration in the reacting solution. However, as we indicated in the same article, for this conclusion to be confirmed there is a need for further data to be obtained at different temperatures and at different radiation powers for the same system. In fact, a decrease in the activation energy, with respect to that of the same reaction running in a nonradiated system, will provide further confirmation of the "catalytic" effect of the radiation. We also think that the study of the same system with different powers of microwave radiation could be of significant importance in highlighting the influence of the radiation on this hypothetical catalytic effect. In our view, the investigation should also be extended to other systems, particularly those running with different kinetic mechanisms.

In this work we present new experimental data on the hydrolysis of phenyl acetate in aqueous solutions of sodium acetate in a microwave-radiated environment. The evolution of the reaction will take place at temperatures of 25, 30, 35, 40, and 45°C at radiating powers of 500 and 1,000 mW, and at 35°C in environments radiated with a microwave radiation of 50, 100, 200, 300, 400, 500, and 1000 mW. At radiating powers of 500 and 1,000 mW, activation energies were also obtained. The catalytic acetate ion concentration was also varied; the values $C_{AcNa} = 0.06, 0.12, 0.2, 0.3,$ and 0.4 mol/L were imposed.

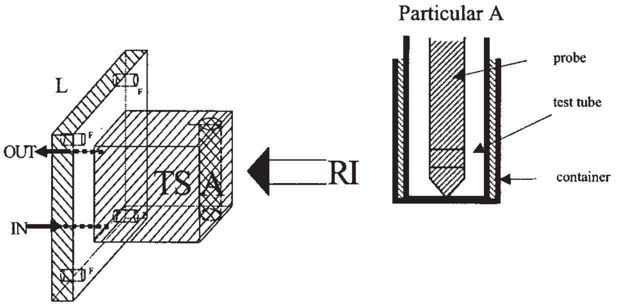

Figure 1. Experimental reactor.

TS: thermostatic fluid container; A: reagent solution container; L: stainless steel reflecting plate; RI: incident radiation sent through a wave guide of the type R22; IN/OUT: input and output of the thermostatic fluid; F: holes to connect the structure the wave guide; test tube ID 10 mm; probe diameter 6 mm; container ID 12 mm; tube test wall thickness 0.5 mm; container wall thickness 1 mm; volume of the reacting solution used 2 cm^3.

Experimental Procedure and Elaboration of Experimental Data

The radiating apparatus was presented in a previous work by the same authors (Carta, 2002). Particular attention was paid to the design of the reactor. In fact the container where the reaction takes place must allow irradiation but at the same time also keep the reacting mixture at a constant temperature. Water cannot be used as the fluid for maintaining the temperature of the reacting mixture at a constant level because only a few millimeters completely absorbs radiation at 2.45 GHz; thus we used carbon tetrachloride, a compound that is transparent to radiation at 2.45 GHz [the loss factor at 3 GHz and at 25°C is less than 2.17×10^{-4} F/m, in the same conditions as for distilled water, 12.04 F/m (von Hippel, 1954)]. In Figure 1 a sketch of the apparatus is shown; the reacting mixture contained in a test tube is placed in the part indicated by the letter A. The reacting fluid was shaken manually so as to justify the assumption of a perfectly mixed reaction system. The fluid used to keep the temperature constant was introduced into the compartment TS through the two tubes marked IN and OUT (Figure 1). The reactor was contained inside a wave-guide type R22 (European Standard Designation) designed for this purpose. A short circuit, which could be tuned, was used to modify the power sent to the reactor. A directional coupler (−30 dB, isolation −48 dB), is inserted between the radiating slot and the end of the guide where the reactor is placed, making it possible to separate the directed from the reflected radiation. The difference between these two signals was supposed as being absorbed by the reacting solution (this being the only possible absorption source); the two signals were transferred through two N connectors to two Schottky diodes (DZM124NB, Herotek, Inc. San Jose, CA), which issued a continuous tension signal proportional to the power of the radiation; the tension was acquired with a data acquisition board (NI PCI-MIO-16E4) and stored for further elaboration.

The transformation from the tension signal to the corresponding power was made using a tuning curve provided by Herotek.

The following chemical compounds were used throughout without further purification: phenyl acetate (PA), RPE 99% (Carlo Erba Reagenti, Milan, Italy); phenol (P), ACS 99% (Aldrich, Milwaukee, WI); dioxane (Dx), RPE 99.8% (Carlo Erba); sodium acetate (AcNa), RPE 99.5% (Carlo Erba); acetic acid (AcH), RPE 99.8% (Carlo Erba); sodium chloride, RPE 99.5% (Carlo Erba). The purity of the materials was always expressed in mass%.

Because phenyl acetate is insoluble in water, a "master solution" was prepared by dissolving the ester in dioxane, which acts as a cosolvent (about 0.5000 g of phenyl acetate brought to 10 cm^3 with dioxane) and this master solution was used as the phenyl acetate source.

Reactions were initiated by adding 0.57/0.63/0.69/0.75 cm^3 of the master solution of ester in dioxane to 15 cm^3 of the appropriate aqueous buffer solution (sodium acetate + acetic acid pH = 5 ± 0.1), with catalytic sodium acetate concentrations C_{AcNa} = 0.06/0.12/0.2/0.3/0.4 mol/dm^3; an amount of sodium chloride able to bring the ionic strength of the solution to 0.4 mol/L was also added. The volumetric quantities of the master solutions were weighed (Sartorius Research Balance R200D) to reduce the errors connected with these small amounts. Each run was repeated three times, and the experimental values reported here were obtained by averaging the three experimental values.

For safety reasons the carbon tetrachloride, used to keep the temperature of the reacting solution constant, was circulated in a closed circuit using a centrifugal pump. To avoid any superheating effect, the flow rate of the carbon tetrachloride was set so that the retention time in the radiated section of the circuit was less than 15 s; the carbon tetrachloride was charged to a 200-cm^3 container placed in a thermostat (B LAUDA 1.6 kW), for safety purposes the temperature of this fluid was read every 10 min (Hanna HI Digital Thermometer 92710C). The solution containing the acetate ions and the "master" solution was kept a at constant temperature using the same thermostat.

The reacting mixture was exposed to radiation for 120 min and the optical density of this solution was read locally at 258 and 279.5 nm, using a sensor linked to the spectrophotometer (Varian Carry 50) by a 2.50 m long optical-fiber cable. The optical-fiber cable absorbed a large part of the radiation power from the spectrophotometer, thus reducing data precision, but in this way it was possible to follow the variations of the PA concentration in real time. The values of the optical density were read every 10 min. The procedure and the experimental apparatus are better described in a previous work by Carta and Loddo (2002). The data reported were obtained by averaging the three values read at intervals of 30 s; these three values were taken as being obtained at the same time because the reaction rate was very small. The errors connected with the whole system were checked by reading the optical densities of five solutions of hydrochloric acid. The error was ±0.002 at 258 nm without regard to the absolute value; at 279.5 nm it was slightly lower.

These data were processed using the two-wavelength method. With this method the concentration of the reacting phenyl acetate can be obtained from the difference ΔD of the given values of the optical densities at 258 and 279.5 nm, regardless of the amount of phenol generated during the evolution of the reaction

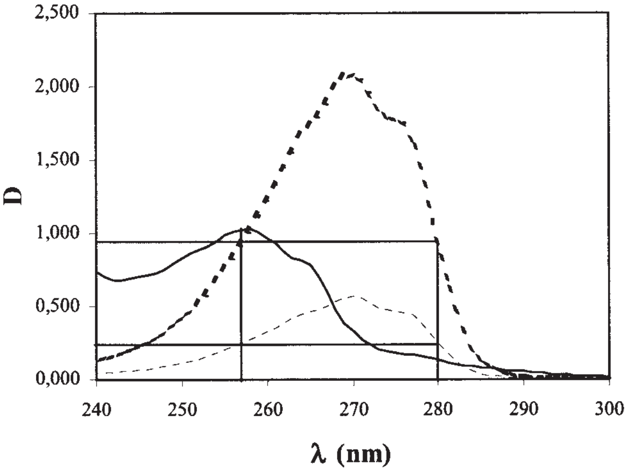

Figure 2. Spectra of phenyl acetate with C_{PA} = 49 × 10^{-3} mol/dm^3 (—) and of phenol C_P = 38.7 × 10^{-4} mol/dm^3 (----) and C_P = 154.8 × 10^{-4} mol/dm^3 (----).

$$C_6H_5\text{—O—Ac} + H_2O \rightarrow C_6H_5\text{—OH} + \text{AcOH} \qquad (1)$$

In fact, as highlighted in Figure 2, solutions of phenyl acetate showed an absorption maximum at a wavelength of 258 nm; on the other hand, phenol has the same absorption at 258 and at 279.5 nm, regardless of the concentration of phenol in the solution. Thus, if there is no interaction in the absorption between the two components, the difference between the light absorption at 258 and 279.5 nm can depend only on the phenyl acetate concentration; the other component (acetic acid) present in the reacting solution (the effect of the water is eliminated during the zeroing) does not cause any interference.

The concentration of PA used in all the reacting solutions was so high that any fractional errors were small enough so as to not affect the results, although the maximum value reported by Carta (2002) was respected. Because of this, the given optical densities were in the interval 0.24–0.50.

Experimental data of the evolution of reaction 1 were interpreted by using the initial rate method. This method was used because the measured rates were so small that the fractional conversion achieved in 120 min of evolution of reaction 1 was 0.25. With these low variations in the concentrations of the phenyl acetate in the reacting system as a function of the given ΔD, values can be given from the following linear equation:

$$C_{\mathrm{PA}} = a\Delta D + b \qquad (2)$$

The generation velocity of the phenyl acetate can be obtained from the numerical differentiation of experimental ΔD vs. t data through the following expression

$$R_{\mathrm{PA}} = \frac{dC_{\mathrm{PA}}}{dt} = a\frac{d\Delta D}{dt} \qquad (3)$$

Table 1. Experimental Generation Rates of Phenyl Acetate at a Radiating Power of 500 mW

	Temperature (°C)									
	25		30		35		40		45	
C_{AcNa} (mol/L)	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})
0.4	1.00	2.49	1.33	7.77	1.41	17.50	1.50	26.15	1.35	24.48
	1.15	3.49	1.49	7.77	1.54	17.54	1.59	27.38	1.49	37.79
	1.32	3.94	1.58	9.67	1.68	18.99	1.60	30.92	1.63	35.62
	1.50	3.76	1.69	10.91	1.81	20.65	1.75	31.16	1.74	40.45
	1.74	5.04	1.99	16.26	1.98	23.89	2.02	58.08	2.02	52.57
0.3	1.03	2.97	1.35	8.29	1.41	18.02	1.49	28.87	1.36	25.67
	1.17	3.18	1.47	8.29	1.56	17.95	1.60	31.21	1.49	33.16
	1.34	3.59	1.60	10.15	1.71	18.09	1.61	24.20	1.64	35.80
	1.45	3.80	1.72	10.56	1.82	20.20	1.74	31.86	1.74	39.44
	1.73	4.04	1.93	13.78	2.01	24.69	2.01	46.05	1.91	38.26
0.2	1.03	2.90	1.30	7.87	1.39	16.50	1.35	16.20	1.28	22.11
	1.16	3.18	1.50	8.60	1.56	17.92	1.46	26.09	1.48	29.67
	1.30	3.21	1.57	9.81	1.68	19.30	1.59	26.05	1.61	35.42
	1.43	3.66	1.79	11.39	1.83	19.68	1.78	31.46	1.72	35.81
	1.73	4.18	1.86	10.91	2.00	25.10	1.99	40.01	1.91	39.41
0.12	1.03	2.76	1.32	7.32	—	—	1.34	15.72	1.32	24.31
	1.15	3.07	1.41	9.49	1.56	18.06	1.36	15.68	1.50	29.86
	1.26	3.31	1.59	9.49	1.53	17.57	1.47	23.01	1.62	38.00
	1.65	4.21	1.70	10.70	1.71	19.06	1.75	31.81	1.71	37.18
	1.70	4.18	1.89	10.50	1.99	26.93	2.02	47.42	1.81	38.14
0.06	1.01	2.49	1.39	8.29	—	—	1.35	14.68	1.35	25.61
	1.17	3.45	1.49	9.01	1.56	18.71	1.36	15.64	1.49	32.66
	1.33	3.73	1.61	10.05	1.70	18.47	1.51	27.67	1.63	36.33
	1.37	3.66	1.68	10.49	1.85	20.47	1.74	31.41	1.79	34.66
	1.49	4.11	1.87	10.57	1.99	26.27	1.99	41.70	1.89	37.36

The generation rate R_{PA} can be obtained by scaling up the slope of the linear interpolation of ΔD vs. t of experimental data with the extinction coefficient. The values thus obtained are reported in Tables 1, 2, and 3 at powers of 500 and 1,000 mW at temperatures of 25, 30, 35, 40, and 45°C and at radiating powers of 50, 100, 200, 300, and 400 mW at a temperature of 35°C.

Table 2. Experimental Generation Rates of Phenyl Acetate at a Radiating Power of 1,000 mW

	Temperature (°C)									
	25		30		35		40		45	
C_{AcNa} (mol/L)	$C_{PA} \times 10^3$ (mol/l)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})
0.4	1.66	8.47	1.33	12.02	1.33	16.95	1.69	30.69	1.39	33.14
	1.79	11.24	1.49	13.05	1.50	21.53	1.87	36.72	1.50	38.35
	1.82	10.66	1.61	12.66	1.61	23.94	2.00	34.67	1.61	36.19
	1.87	10.71	1.75	14.35	1.74	25.87	2.11	40.45	1.74	41.37
	2.00	11.73	1.90	14.81	1.99	34.64	2.28	44.70	1.89	39.76
0.3	1.63	8.47	1.32	10.43	1.34	18.31	1.66	31.48	1.35	32.19
	1.84	10.26	1.46	11.49	1.47	20.94	1.82	36.43	1.49	33.94
	1.87	10.45	1.61	14.11	1.60	24.90	1.98	37.05	1.62	35.96
	1.99	11.92	1.74	14.20	1.77	23.44	2.19	38.34	1.76	40.18
	2.17	11.80	1.80	18.74	1.91	30.21	2.39	45.99	1.89	41.14
0.2	1.67	9.57	1.36	10.99	1.35	17.54	1.65	31.24	1.36	35.34
	1.82	9.84	1.46	13.36	1.50	21.31	1.79	37.83	1.50	36.72
	1.89	10.99	1.60	13.57	1.62	23.83	1.97	35.92	1.57	35.78
	1.99	12.23	1.78	15.27	1.77	25.68	2.13	40.85	1.77	40.09
	2.00	12.12	1.81	17.72	1.89	28.15	2.28	44.52	1.83	39.39
0.12	1.67	10.21	1.31	10.49	1.33	18.31	1.64	29.96	1.37	32.88
	1.82	11.30	1.46	12.29	1.49	20.90	1.80	37.43	1.49	36.28
	1.89	10.61	1.60	13.69	1.61	23.18	1.96	35.16	1.62	38.82
	2.01	11.85	1.73	13.93	1.79	26.20	2.10	37.16	1.78	40.23
	2.17	12.36	1.83	19.01	1.87	26.86	2.35	44.70	1.89	41.45
0.06	1.72	9.69	1.39	11.26	1.33	18.34	1.67	30.21	1.36	34.37
	1.85	10.64	1.59	14.77	1.42	19.93	1.80	35.69	1.49	34.74
	1.88	10.87	1.62	13.58	1.63	22.59	1.98	37.31	1.64	39.61
	2.00	11.28	1.70	13.16	1.67	22.89	2.15	39.68	1.76	40.49
	2.30	15.91	1.87	19.12	1.92	30.96	2.36	43.84	1.79	39.14

Table 3. Experimental Generation Rates of Phenyl Acetate at 35°C and at Various Radiating Powers

	Power (mW)									
	50		100		200		300		400	
C_{AcNa} (mol/L)	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})	$C_{PA} \times 10^3$ (mol/L)	$-R_{PA} \times 10^6$ (mol L^{-1} h^{-1})
0.4	1.66	21.49	1.64	18.09	1.65	18.9	1.66	19.09	1.69	23.20
	1.80	25.29	1.80	23.91	1.80	24.99	1.82	25.20	1.88	26.34
	1.98	26.17	1.96	28.58	1.97	21.84	1.98	27.84	2.00	29.94
	2.15	30.37	2.10	30.43	2.13	31.19	2.19	26.75	2.11	29.78
	2.36	43.76	2.24	29.85	2.28	30.05	2.39	31.73	2.38	36.29
0.3	1.70	21.55	1.69	20.00	1.64	19.40	1.66	21.57	1.67	22.50
	1.86	26.18	1.85	25.05	1.81	23.59	1.82	21.86	1.84	21.65
	2.02	28.50	1.98	29.60	1.96	24.36	1.99	26.66	1.98	26.89
	2.17	34.55	2.16	28.63	2.14	27.29	2.14	25.31	2.12	31.69
	2.29	48.09	2.28	29.63	2.27	29.63	2.32	32.13	2.32	33.04
0.2	1.68	23.10	1.68	18.08	1.70	21.02	1.69	20.69	1.69	22.28
	1.76	21.93	1.84	20.53	1.85	22.83	1.82	22.90	1.85	24.95
	2.01	32.67	1.99	24.28	2.00	26.70	2.01	28.71	2.20	27.20
	2.16	26.52	2.17	26.95	2.18	30.59	2.23	27.73	2.32	31.59
	2.34	37.66	2.34	35.23	2.33	32.76	2.35	34.26	—	—
0.06	1.65	17.15	1.69	19.77	1.69	21.55	1.70	20.68	1.69	22.09
	1.83	25.98	1.86	23.67	1.82	25.07	1.83	24.53	1.86	22.09
	1.99	23.93	1.98	23.69	1.99	23.37	2.02	25.95	2.01	25.32
	2.15	28.29	2.14	24.12	2.25	31.13	2.18	24.60	2.16	28.34
	2.29	34.39	2.32	35.94	2.27	39.90	2.42	33.50	2.37	32.25

Figure 3 shows experimental data of $\ln(-R_{PA})$ vs. $\ln(C^0_{PA})$ at powers of 500 and 1,000 mW and at a temperatures of 30°C; similar curves were also obtained at the other four temperatures studied. From the slope of the regression line of these data, the kinetic constants at 25, 30, 35, 40, and 45°C were obtained; these data and those obtained for the radiated powers of 50, 100, 200, 300, and 400 mW at 35°C are shown in Table 4.

The extinction coefficient "*a*" in Eq. 2 was evaluated by a calibration curve that was made by using a solution containing phenyl acetate (concentration in the field 0e-3 ÷ 3e-3 mol/L) and phenol (concentration in the field 3e-3 ÷ 0e-3 mol/L) so that $C_{PA} + C_P = 3e\text{-}3$. With this procedure $a = 6.33e\text{-}3$ and $b = 9.495e\text{-}5$ ($R^2 = 0.998$) were obtained.

For the systems radiated with a radiation of 500 and 1000 mW an Arrhenius diagram was made (Figure 4); from the linear regression of these data the activation energies at 500 and 1000 mW were obtained: 71,348 and 69,666 J/mol, respectively (Table 5).

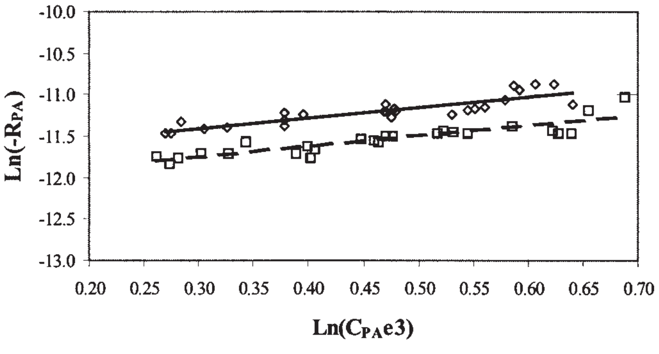

Figure 3. Initial generation velocity of phenyl acetate at 30°C with radiating power of 500 mW (----, regression coefficient 0.7956) and 1,000 mW (—, regression coefficient 0.7687).

Comments and Discussion

On considering the analysis of the experimental data a fundamental fact can be deduced. At all the temperatures examined and at all radiation powers used, the kinetic constant does not depend on the catalytic acetate ion concentration. In fact, by observing Figure 3, it is possible to see that experimental $\ln(-R_{PA})$ vs. $\ln(C^0_{PA})$ data can be well correlated (regression factor > 0.80) without taking the acetate ion concentration into account. Experimental data have been plotted as $\ln(-R_{PA})$ vs. $\ln(C^0_{PA})$ to control the order of the reaction, which, in previous works, was found to be 1. Analysis of these data also confirms these results [obtained values of the slope of the line $\ln(-R_{PA})$ vs. $\ln(C^0_{PA})$ in the field ranged from 0.98 to 1.30]. In effect the regression coefficients are not so significant as to warrant the previous deduction, but it is necessary to indicate that the reported data are not the measured ones (the real measured data are ΔD vs. *t*) but are data obtained with an analytical procedure.

The observation that the kinetic constant does not depend on the concentration of the catalytic ion can bring us to two possibilities:

(1) The catalytic ions do not give their action in radiated systems.

(2) The catalytic action of acetate ions is "replaced " by an

Table 4. Kinetic Constants (min^{-1}) at 25, 30, 35, 40, and 45°C for Radiating Power of 500 and 1,000 mW; and at 35°C for Radiating Power of 50, 100, 200, 300, 400, 500, and 1,000 mW

	Power (mW)						
T (°C)	50	100	200	300	400	500	1000
25						2.76e-3	5.59e-3
30						5.38e-3	7.49e-3
35	7.89e-3	8.64e-3	9.94e-3	11.4e-3	11.7e-3	11.3e-3	12.1e-3
40						12.3e-3	19.3e-3
45						17.4e-3	27.7e-3

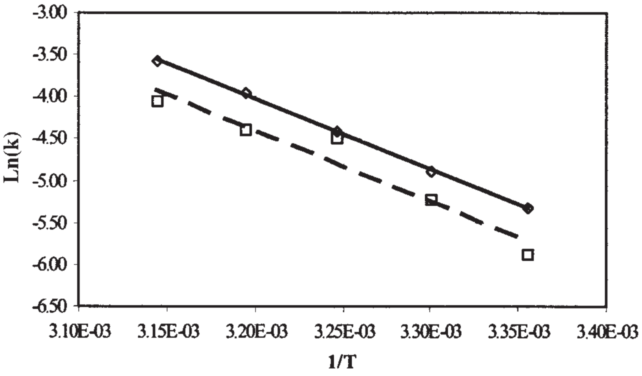

Figure 4. Arrhenius diagram for the system radiated with 500 mW (– – –, activation energy 71,348 J/mol, regression coefficient 0.9335) and with 1,000 mW (—, activation energy 69,666 J/mol, regression coefficient 0.9986).

action, which is also a catalytic action, given by the radiation, and because this action is stronger than that given by the acetate ions, the latter is hidden.

In effect, conclusion (1) can be easily denied by observing the data reported in Figure 5. The diagram shows the ratio between the kinetic constant in both a radiated and a nonradiated environment; at the temperature of 35°C this ratio becomes about 1 for $C_{AcNa} \approx 0.6$ mol/L. This fact means that the catalytic effect of acetate ions, given by the equation (Carta, 2001)

$$k^* = k_0 + k_{AcNa} C_{AcNa} \tag{4}$$

for $C_{AcNa} = 0.6$ mol/L, becomes about equal to that given by the microwave radiation, so the catalytic effect is still active.

Figure 6 highlights the fact that the ratio k/k^*, as a function of the radiated power, is very high even for the lower radiating power used. This fact suggests that the conclusion reported in point (2) is valid. In fact, as the radiating power increases, the ratio between the kinetic constant increases but with a velocity that becomes smaller as the radiating power increase. In fact we have larger increases going from a nonradiated environment to an environment radiated with a microwave of 50 mW. Then we can have a catalytic-like microwave effect at a small power; in fact at 35°C as the radiating power goes from 0 to 50 mW the kinetic constant increases 16-fold, but if the radiating power goes from 500 to 1000 mW the kinetic constant increases only 1.16-fold.

Table 5. Activation Energies at Three Levels of Radiating Power

Radiation Power (mW)	Activation Energy (J/mol)
0	76,610*
500	71,348
1000	69,666

*k^* from Carta (2001) with $C_{AcNa} = 0.06$ mol/L.

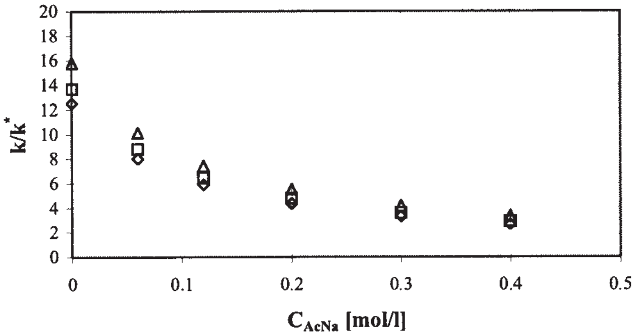

Figure 5. Ratio of kinetic constant in radiated environment (power of the radiation: ◇, 50 mW; □, 100 mW; △, 200 mW) to the kinetic constant in nonradiated system as a function of the acetate ions concentration.

Furthermore, the fact that we have larger increases in the kinetic constant as the irradiated power goes from 0 to 50 mW demonstrates that the radiation gives a specific microwave effect that impinges all thermal effects: in fact if the thermal effects are greater than the nonthermal effects, one has to wait for a greater influence of the radiating power as the transmitted power increases.

Figure 4 shows ln(k) vs. $1/T$ for systems radiated with a microwave of 500 and 1,000 mW of power, respectively. The activation energy decreases by 2.4% as the radiating power goes from 500 to 1,000 mW and both these values are lower than those obtained from the kinetic constants already obtained (Carta, 2001) in nonradiated environments. A reduction of the activation energies in radiated environments, with respect to that in nonradiated environments, was also obtained in other research (Gattavecchia, 1997; Lewis, 1992). Lewis et al. obtained a reduction from 105,000 J/mol for thermal imidization to 57,000 J/mol for microwave imidization; in a clever analysis they proposed that the energy of the dipole moments on a local scale was higher than that for nonpolar bond. This higher localized energy gives an apparent reduction in the activation energy, given that the overall energy of the reactants was greater than that predicted from the observed temperature.

The physical effect observed by Lewis et al. and ourselves is the same but brings us to different and—in some terms—quite different conclusions. Lewis et al. reported of a thermal effect, although we think that the reductions we have are not compatible with a thermal effect, given that the power used is so low

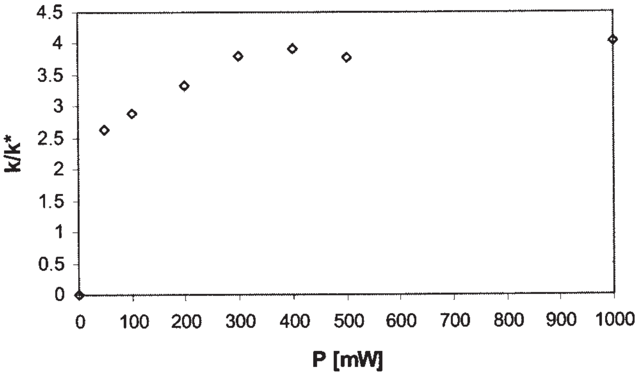

Figure 6. Variation of the kinetic constant in radiated (*k*) and in nonradiated (k^* at $C_{AcNa} = 0.4$ mol/L) environment at different radiating powers and at a temperature *T* = 35°C

as to make us think that a thermal effect cannot take place. In fact both Lewis's experiment and the one reported here are similar, but the differences in the amount of power used (0.5–1 W with a volume of 2 cm^3 of radiated reacting solution for us, compared to 10–25 W with a volume of 2.5 cm^3 of radiated reacting solution for Lewis et al.) allow each conclusion to be justified.

On the other hand, because the decrease is so low that it can be induced (at least for an important fraction of the whole variation) by experimental errors, it is not possible to draw any important conclusion from these results. What is clear, however, is that microwave radiation does have important effects on this homogeneous catalyzed reaction and that these effects are of an athermal type. Indeed, both the increases in the kinetic constants and the linked reduction in the activation energy, together with the fact that we have these effects independently of the catalytic species concentrations even at low amounts of transmitted energy (0–0.5 W/cm^3), lead us to conclude that the microwave effect is of an athermal type.

Other information provided by these data, which should be highlighted, is that given by the analysis of Figures 5 and 6. In Figure 5 the ratio k/k^* between the kinetic constants in radiated and nonradiated environments decreases as the concentration of the acetate ions increases and this also happens when the radiated power increases. The reported values of the ratios change 1.6 times as the power of the striking radiation increases 20-fold. This brings us to the conclusion that there certainly exists an effect linked to the increase in the radiated power, but that this effect is poor compared to that given by the radiation at lower powers (for $P = 50$ mW, $k/k^* \cong 12$ at $C_{\mathrm{AcNa}} = 0$ mol/L).

In Figure 6 the ratio k/k^*, as a function of the radiated power, shows that a saturation effect limits the increases of the kinetic constant as the radiated power increases. This highlights the fact that, unless other effects appear (that is, thermal effects), even very low microwave power is sufficient to enhance the rate of reaction 1.

Note

The table with experimental ΔD vs. t data can be obtained by writing to the corresponding author either as a PDF file or as an EXEL file.

Notation

a = extinction coefficient
b = intercept in the linear Eq. 2
C_{P} = concentration of phenol, mol L^{-1}
C_{PA} = concentration of phenyl acetate, mol L^{-1}
C^0_{PA} = concentration of phenyl acetate at $t = 0$, mol L^{-1}
D_{x} = optical density at X, nm
k = kinetic constant in radiated environment
k^* = kinetic constant in nonradiated environment
k_0 = kinetic constant without catalytic acetate ions
k_{AcNa} = catalytic coefficient for sodium acetate
R_{PA} = generation velocity of phenyl acetate, mol L^{-1} h^{-1}
t = time, h or min
ΔD = difference of two optical densities read at two different wavelengths

Literature Cited

Adamek, F., and M. Haijek, "Microwave-assisted Catalytic Addition of Halocompounds to Alkenes," *Tetrahedron Lett.*, **33**, 2039 (1992).

Baghurst, D. R., and D. M. P. Mingos, *Microwave Enhanced Chemistry*, H. M. Kingston and S. Hawell, eds., American Chemical Society, Washington, DC (1997).

Buchachenko A. L., and E. L Frankevich, *Chemical Generation and Reception of Radio and Microwaves*, VCH, New York (1994).

Carta, R., and S. Dernini, "Kinetic Study of the Acetate-Catalysed Hydrolysis of Phenyl Acetate," *Chem. Eng. J.*, **81**, 271 (2001).

Carta, R., and L. Loddo, "Catalytic Effect of Microwave Radiation on the Acetate-Catalysed Hydrolysis of Phenyl Acetate at 25°C," *Ind. Eng. Chem. Res.*, **41**, 5912 (2002).

Chemat, F., and E. Esveld, "Microwave Super-heated Boiling of Organic Liquids: Origin, Effects and Application," *Chem. Eng. Technol.*, **24**, 735 (2001).

Gabriel, S., E. H. Gabriel, E. H. Grant, B. S. J. Halstead, and D. M. P. Mingos, "Dielectric Parameters Relevant to Microwave Electric Heating," *Chem. Soc. Rev.*, **27**, 213 (1998).

Gattavecchia, E., and I. Giovanardi, "Kinetic Effects of Microwave on the Hydrolysis of Indomethacin," *Proc. Conf. on Microwaves and High Frequency Heating 1997*, Fermo, Italy, Sep. 9–13, 1997, p. 161.

Gedye, R. N., F. E. Smith, and K. C. Wasteway, "The Rapid Synthesis of Organic Compounds in Microwave Ovens," *Can. J. Chem.*, **66**, 17 (1988).

Lewis, D. A., J. S. Summers, T. C. Ward, and J. E. McGrath, "Accelerated Imidization Reactions Using Microwave Radiation," *J. Polym. Sci. Part A: Polym Chem.*, **30**, 1647 (1992).

Metaxas, A. C., and R. J. Meredith, *Industrial Microwave Heating*, Peter Peregrinus, London (1993).

Pagnotta, M., C. L. F. Pooley, B. Gurland, and M. Choi, "Microwave Activaton of Mutarotation of a D-Glucose: An Example of an Intrinsic Microwave Effect," *J. Phys. Org. Chem.*, **6**, 407 (1993).

Santagada, V., F. Fiorino, E. Perissutti, B. Severino, V. De Filippis, B. Vivenzio, and G. Caliendo, "Microwave-Enhanced Solution Coupling of the alpha, alpha-Dialkyl Amino Acid, Aib," *Tetrahedron Lett.*, **42**, 5171 (2001).

Sun, W. C., P. M. Guy, J. H. Jahngen, E. F. Rossomando, and E. G. E. Jahngen, "Microwave-Induced Hydolysis of Phospho Anhydride Bonds in Nucleotide Triphosphates," *J. Org. Chem.*, **53**, 4414 (1988).

Villa, C., M. T. Genta, A. Bergogne, E. Mariani, A. Louppy, "Microwave Actived and Solvent-free Phase Transfer Catalysis for the Synthesis of New Benzylidene Cinole Derivatives as Potential UV Sunscreens," *Green Chemistry*, **3**, 196 (2001).

von Hippel, A. R., *Dielectric Materials and Applications*, MIT Press, Cambridge, MA (1954).

Whittaker, A. G., and D. M. P. Mingos, "The Application of Microwave Heating to Chemical Synthesis," *J. Microw. Power Electromagn. Energy*, **29**, 195 (1994).

Manuscript received Oct. 21, 2002, and revision received Sep. 22, 2003.