Effect of Static Pressure on the Ultrasonic Activation of Chemical Reactions. Selective Oxidation at Benzylic Carbon in the Liquid Phase

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The effects of sonoactivation on kinetic rates and chemical yields of a model reaction, selective oxidation at the benzylic site of indane, was studied at subatmospheric static pressures ranging from 200 to 760 Torr. The reaction occurs at a rate up to five times higher when a suitable ultrasonic field activates the reagents in solution. By varying the pressure applied to the system, the total sonochemical yields were found to follow a non-monotonic trend, with a peak value related to the frequency of ultrasounds irradiated. According to the general theory of acoustic cavitation, the results obtained are accounted for in terms of distribution and dynamics of the cavitating bubbles, whose average radius of equilibrium reaches its resonant value when tuned to a definite value of pressure, so allowing the best coupling with the ultrasonic field; under these conditions, the sonocatalytic effects on reaction parameters are maximized.

The catalytic effects of ultrasonic waves on chemical reactions, in the liquid phase, have been long observed; only recently, however has their application to problems of organic synthesis attracted interest.[1] Remarkable results have been achieved in synthesizing compounds not easily available, mainly because of experimental difficulties often related to a rather slow rate of reaction.

The most generally accepted interpretation for the experimental results relates the catalytic behaviour of ultrasound mainly to cavitation phenomena involving gases, or vapours, present in the liquid phase. In this context, the ultrasonic waves couple to the chemical system, by means of cavitation, inducing the physical requirements for the occurrence of a chemical reaction. For the latter to take place under sonic activation, a more stringent condition is the sudden growth and collapse of gaseous microbubbles in the reaction medium, leading to the production of local high gradients of temperature and pressure.[2] In such a physical environment the chemical reactions can occur mainly *via* two concomitant or independent paths: (a) enhancement of the direct interactions between reagents; (b) formation of transient chemical species from which definite reactions may develop *in situ*.

There are only scant reports[3] attempting to rationalize the effects of parameters coinvolved in the interactions between chemical reactivity and sonic field, and therefore achieving optimum results.

In this paper, the basic parameters have been identified, which allow the optimization of the 'sonochemical interaction', taking into account present views on ultrasonic cavitation. It will be shown how the application of these parameters to a model chemical reaction activates the reagents in a 'transient cavitation field', and how such ideal conditions can be obtained by coupling under resonance the sonic waves to the 'bubbles' field' present in the reaction environment.

An Appendix covers the fundamentals of cavitation theory on which the present work is based; we refer to the basic reviews by Flynn[4] and Neppiras[5] for a more comprehensive treatment.

Experimental

A diagram of the apparatus used is shown in Figure 1. A three-necked round-bottomed static glass reactor, **6** (100 ml), was used, capable of withstanding pressure variations; two cylindrical liquid addition funnels, with a pressure-equalizing side tube, **7**, were inserted and separately filled with the reacting species. The internal reactor temperature was controlled by means of a precision Cr–Al thermocouple **3**. The reaction system was kept at a constant value of static subatmospheric pressure by means of a rotary pump, **15**, equipped with a vacuum flow controller, **14**, and automatically regulated through a variable constant-pressure monitoring device, **12**, driven by an electrovalve, **13**, and a calibrated pressure-drop mercury manometer, **10**. A mobile photoresistive microswitch, **11**, was applied to the latter, at a height corresponding to a given pressure; this device is linked to the electrovalve, **12**, by means of an on-off relay, whose actuation maintains the reacting system at constant pressure. An air inlet valve, **9**, completes the vacuum line. The vessel is immersed into a thermostatted bath, **1**, which prevents temperature variations induced by ultrasonic irradiation; an electronic thermoregulator, **2**, is used to monitor the temperature of the cooling liquid during each run. A magnetomechanical stirring unit, **4**, is placed below **1**, and is made to run at constant speed.

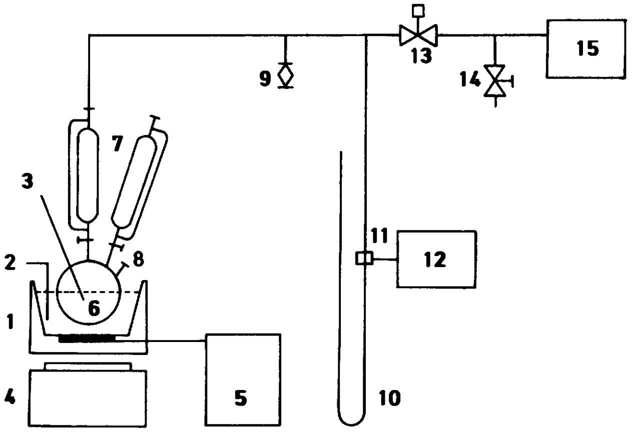

Figure 1. Schematic diagram of the apparatus: **1**, stainless steel thermostatted bath; **2**, thermoregulator; **3**, Cr–Al thermocouple; **4**, stirring unit; **5**, ultrasound generator; **6**, glass reactor; **7**, addition funnels; **8**, sampling valve; **9**, air inlet valve; **10**, pressure-drop mercury manometer; **11**, photoresistive microswitch; **12**, variable constant-pressure controller; **13**, electrovalve; **14**, vacuum flow controller; **15**, rotary vacuum pump

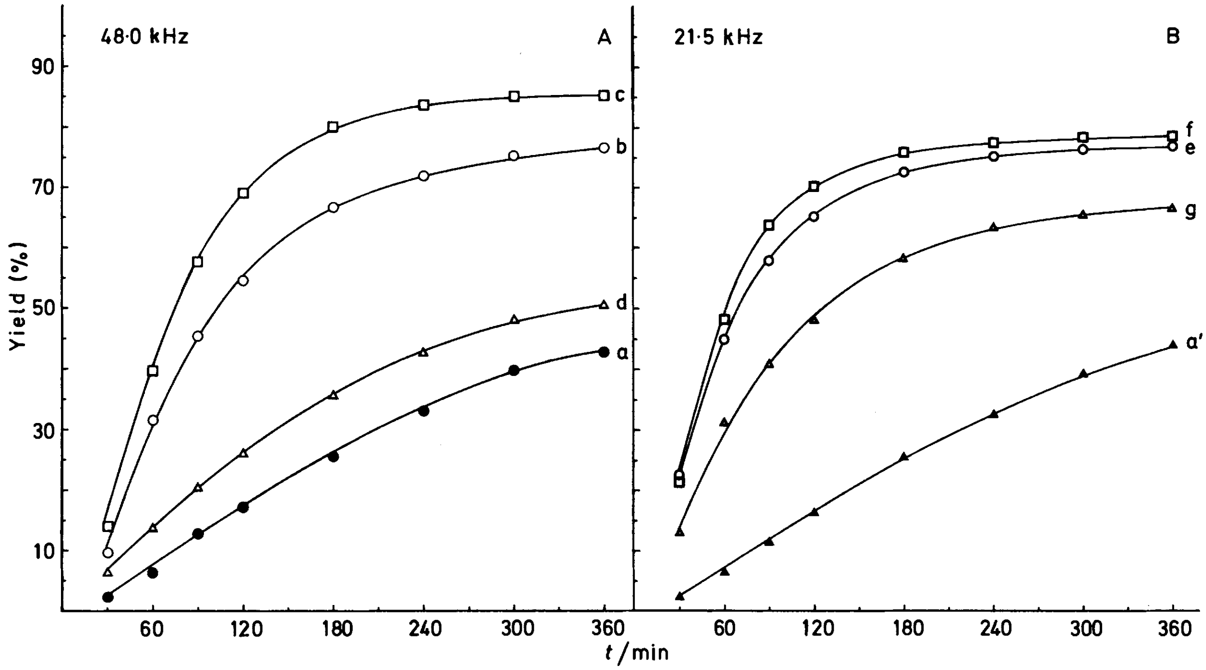

Figure 2. Reaction profiles for the $KMnO_4$–H_2SO_4 oxidation of indane to indan-1-one, at 298 K and at some representative values of static pressure, without (curve a, 760 Torr; curve a', 200 Torr) and with ultrasonic irradiation; A, at 48.0 kHz (curve b, 760 Torr; curve c, 450 Torr; curve d, 250 Torr) and B, at 21.5 kHz (curve e, 760 Torr; curve f, 300 Torr; curve g, 200 Torr)

Two commercial transducers, **5**, were used alternatively: (i) a Bransonic model B12, operating at a frequency of 48.0 kHz and driven by a 55 W power supply, and (ii) an AGE Electronics model CP400/VL4, operating at 21.5 kHz (90 W electrical power output).

The positioning of the glass reactor was monitored in order to ensure constant incidence of the maximum ultrasonic power on the reacting mixture.

In a typical experiment, the oxidaton of indane to indan-1-one took place under stirring (500 r.p.m.), at 298 K, in the glass reactor, **6**, filled with potassium permanganate (12 mmol) in distilled water (20 ml); a solution of sulphuric acid (12 mmol) in distilled water (10 ml) was added from, **7**, followed by an indane (3 mmol) solution in pure benzene (20 ml). All reagents and solvents were of analytical grade quality and were used after recrystallization or distillation if required.

The relative static pressure had been previously settled at the established value, and kept constant for the duration of the experiment. Single values of pressure were corrected, if necessary, taking into account the variations of external atmospheric pressure, whenever they occured.

The progress of the reaction was monitored by vapour phase chromatography, on discrete microsamples (*ca.* 0.2 ml) withdrawn at definite intervals from the reaction mixture, through the silicone septum of the sampling valve, **8**, fitted to the reaction vessel, by means of a vacuum-tight syringe; the latter was designed to prevent any leakage of the inner static pressure towards external atmosphere. The samples were immediately quenched by adding a little sodium metabisulphite.

A C. Erba Fractovap model 2150 gas chromatograph was used, equipped with a flame ionization detector and employing a 3 mm i.d. × 2 m stainless steel column packed with 3% SE 30 on 80—100 mesh silanized Chromosorb G. The injector and oven temperatures were 573 and 433 K, respectively. Nitrogen was the carrier gas (gauge pressure 112 kPa; 30 ml min^{-1} flow rate). Signals were processed by a Perkin-Elmer model. Sigma 10/8 integrator for direct normalization of chemical species to percentage values. No by-product of reaction was detected.

The results of indane oxidation rate, as obtained with and without ultrasonic irradiation, are shown in Figure 2, at selected values of the applied static pressure, in the range 200—760 Torr. The dependence of the product yields from static pressure, at 48.0 and 21.5 kHz respectively, is shown in Figure 3; curves at different reaction time intervals were considered. Each point represents the average value of at least three separate experimental runs, as reported in Tables 1—3. The rate constants, $k_{obs.}$, were obtained, either from the slopes of the plots of $-\ln(Y_\infty - Y_t)$ against time, where Y_t and Y_∞ are the percentage yields of indan-1-one (measured by g.c.) at time t and at the end of the reaction, respectively, *or*, when Y_∞ could not be measured, from a best non-linear least-squares fit of the experimental Y–t data to the expression: $Y_t = Y_\infty + (Y_0 - Y_\infty)\exp(-k_{obs.}t)$, with Y_0 (the yield at $t = 0$), Y_∞, and $k_{obs.}$ as parameters to be optimized.

Results and Discussion

The need for a better understanding of the influence of the different parameters (*i.e.*, frequency, intensity, *etc.*) involved in the catalytic activation of a chemical system by ultrasound, prompted us to investigate their effects on the factors characterizing a reaction, that is, its rate, selectivity, and yield.

From the theory of acoustic cavitation (Appendix), equation (6) was derived to verify how the behaviour of a chemical system is affected by variables, such as density ρ, viscosity μ, and surface tension σ; in fact, these are peculiar properties of the liquid phase in which the ultrasound operates, while the bubbles' average radius R_0 is a physical quantity which couples the reacting system to the field of the ultasonic waves [see equation (2)]. Moreover, equation (6) shows how the R_0 value can be modified, by varying the external static pressure, at constant temperature.

Almost all previous investigations on the effects of ultrasound on chemical reactions have been carried out at atmospheric pressure; only a few results have been reported which relate the

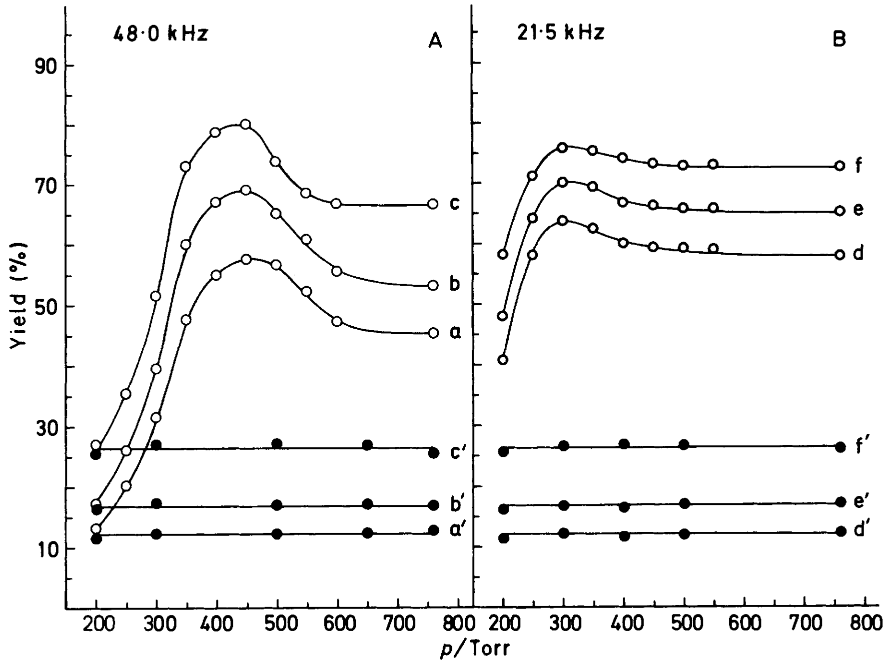

Figure 3. Effect of subatmospheric static pressure on the sonochemical yields of the $KMnO_4$–H_2SO_4 oxidation of indane to indan-1-one, at 298 K, with ultrasonic irradiation at: A, 48.0 kHz and B, 21.5 kHz (curves a and d, after 90 min; curves b and e, after 120 min; curves c and f, after 180 min), and without ultrasonic irradiation (curves a' and d', after 90 min; curves b' and e', after 120 min; curves c' and f', after 180 min)

variation of static pressure to the rate and product yield of sonoactivated chemical reactions.

The study of Neppiras and Hughes[6] attempted to establish the influence of high pressure on the disintegration of yeast cells during ultrasonic irradiation at high frequency; they found that, as the pressure was increased beyond the atmospheric value, the percentage of yeast cells destroyed increased and decreased following an alternating pattern.

Chendke and Fogler[7] determined sonochemical yields and sonoluminescence intensity from aqueous solutions saturated with carbon tetrachloride and sonoirradiated at 20 kHz, as well as the variations of these parameters in the static pressure range from 1 to 20 atm. In a subsequent report,[8] the same authors studied the luminescence intensity of nitrogen-saturated water, at static pressures ranging from 1 to 14.6 atm. They found a linear relationship between sonochemical yield and sonoluminescence over the entire range of applied pressures, and assigned the non-linear increment of the latter effect to 'an increase in the number of cavitation events at higher static pressure rather than an increase in the intensity of events'.

The reaction most appropriate for our investigations is the liquid-phase oxidation at the benzylic site of an aralkyl hydrocarbon, for which a marked effect of ultrasonic irradiation was observed, at atmospheric pressure;[9] as a typical example, the conversion of indane into indan-1-one, by means of aqueous acidic potassium permanganate, was selected. These oxidation reactions of hydrocarbons have a very high synthetic value, although they often suffer from low yields and/or require significantly greater than stoicheiometric amounts of the oxometal active species, such as MnO_4^- or $Cr_2O_7^{2-}$, owing to the insolubility of the organic substrates in water and to the difficulties of finding a proper solvent not attacked by the oxidant. Therefore, since reactants are usually distributed in a biphasic aquo–organic system, reaction rates are usually slow, and the effectiveness of the powerful oxidizing agent, *e.g.* potassium permanganate, is severely reduced.[10] In recent years, techniques such as interfacial,[11] micellar,[12] and phase-transfer catalysis[13] have been developed, to affect the solubility of these oxidants in relatively non-polar solvents, such as methylene dichloride, toluene, *etc.*, but some complications have been necessarily introduced.

Effects of Sonoactivation on Reaction Rates and Chemical Yields.—In the experimental conditions selected and in the absence of ultrasonic irradiation, the reaction investigated proceeds as shown in Figure 2A (a), *i.e.* in the mode typical of such an oxidation; the regiospecific conversion of one benzylic methylene group into the corresponding carbonyl function is achieved. The pseudo-first-order rate constant $k_{obs.}$ at 760 Torr is $(5.12 \pm 0.04) \times 10^{-5}\ s^{-1}$, and the final yield of indan-1-one is $\leqslant 27\%$ after 3 h. It reaches its maximum value (45%) after 6 h. A similar pattern is obtained in Figure 2B.

The average value of all rate constants, $k_{obs.}$ $(5.11 \pm 0.15) \times 10^{-5}\ s^{-1}$, calculated from experimental measurements in the absence of ultrasonic irradiation at different values of static pressure, is in agreement with that at 760 Torr, reported above.

On the other hand, oxidation of indane takes place at a rate from four to five times higher when a suitable ultrasonic radiation field activates the reacting chemical system. No significant variations occur in the rate, when different frequencies of ultrasound are used, as shown by the values of the related kinetic constants at 760 Torr; $k_{48.0\ kHz}$ $(1.99 \pm 0.01) \times 10^{-4}\ s^{-1}$; $k_{21.5\ kHz}$ $(2.96 \pm 0.02) \times 10^{-4}\ s^{-1}$.* Accordingly, in the same conditions of temperature and pressure as above, *i.e.*, 298 K and 760 Torr, the corresponding value for the yield of indan-1-one reaches 67% after 3 h, at 48.0 kHz (Figure 2A b); at 21.5 kHz, a slightly higher yield (73%) is obtained, under identical experimental conditions (Figure 2B e). Product

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* The values of rate constants at 48.0 and 21.5 kHz are affected to some extent by the different power outputs of the sources used to sonoirradiate the reacting system at the two frequencies.

Table 1. Reaction data for the $KMnO_4$–H_2SO_4 oxidation of indane to indan-1-one, under 48.0 kHz ultrasonic irradiation, at different values of static pressure and at 298 K

	p 200 Torr					*p* 250 Torr					*p* 300 Torr					*p* 350 Torr					*p* 400 Torr				
	Yields (%)					Yields (%)					Yields (%)					Yields (%)					Yields (%)				
Time (min)	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD
30	1.9	2.3	2.9	2.4	0.5	5.7	6.2	6.9	6.3	0.6	7.7	8.4	8.9	8.3	0.6	10.6	11.1	11.8	11.2	0.6	12.6	13.2	14.3	13.4	0.9
60	4.8	5.2	6.1	5.4	0.7	12.6	13.6	14.1	13.4	0.8	19.4	20.2	21.6	20.4	1.1	30.8	32.6	32.9	32.1	1.1	37.4	38.4	39.2	38.3	0.9
90	12.1	13.4	13.9	13.1	0.9	19.5	20.1	21.3	20.3	0.9	30.4	31.2	32.4	31.3	1.0	46.8	47.6	48.4	47.6	0.8	54.3	54.9	55.7	55.0	0.7
120	16.3	17.4	17.8	17.2	0.8	25.6	26.1	26.9	26.2	0.7	38.6	39.2	40.6	39.5	1.0	59.1	60.3	60.9	60.1	0.9	66.3	67.4	68.0	67.2	0.9
180	26.4	27.3	27.6	27.1	0.6	34.9	35.4	36.5	35.6	0.8	50.8	51.4	53.1	51.8	1.2	71.9	73.2	73.8	73.0	1.0	76.7	78.4	79.9	78.3	1.6
240	34.6	34.9	36.7	35.4	0.8	42.4	43.3	44.2	43.3	0.9	57.1	57.9	59.2	58.1	1.1	77.8	78.1	79.5	78.5	0.9	78.1	80.2	80.8	79.7	1.4
300	39.5	40.2	41.1	40.3	0.7	47.8	49.2	49.9	49.0	1.1	61.5	62.5	63.0	62.3	0.8	79.6	80.2	81.5	80.4	1.0	79.6	80.4	81.5	80.5	1.0
360	44.0	44.4	45.3	44.6	0.7	49.6	50.6	51.8	50.7	1.1	64.4	65.2	66.5	65.4	1.1	80.2	81.7	82.1	81.3	1.0	80.3	81.4	81.9	81.2	0.8

	p 450 Torr					*p* 500 Torr					*p* 550 Torr					*p* 600 Torr					*p* 760 Torr				
	Yields (%)					Yields (%)					Yields (%)					Yields (%)					Yields (%)				
Time (min)	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD
30	12.9	13.1	13.0	13.0	0.1	11.6	12.4	13.1	12.4	0.8	11.0	11.4	12.3	11.6	0.7	10.5	11.3	11.9	11.2	0.7	8.8	9.4	9.9	9.4	0.6
60	39.3	40.1	40.9	40.1	0.8	37.1	38.3	39.3	38.2	1.1	35.6	36.2	37.3	36.4	0.9	30.2	31.7	32.4	31.4	1.1	29.8	30.2	30.6	30.2	0.4
90	58.1	57.8	59.0	58.3	0.6	56.4	57.1	57.6	57.0	0.6	51.6	52.4	53.4	52.5	0.9	46.6	47.8	48.3	47.6	0.9	45.2	45.4	45.9	45.5	0.4
120	69.3	70.2	71.4	70.3	1.1	64.8	65.4	66.9	65.7	1.1	60.7	60.9	61.9	61.2	0.6	54.9	56.2	56.8	56.0	1.0	52.5	53.3	53.9	53.2	0.7
180	80.3	80.7	81.5	80.8	0.6	73.3	73.6	74.4	73.8	0.6	68.3	68.6	69.7	68.9	0.7	66.2	67.3	67.9	67.1	0.9	65.9	67.6	68.4	67.3	1.3
240	84.1	84.2	84.7	84.3	0.3	76.9	77.5	78.3	77.6	0.7	70.9	71.5	72.7	71.7	0.9	70.9	72.2	72.8	72.0	1.0	71.5	71.8	72.9	72.1	0.7
300	85.3	85.4	86.7	85.8	0.8	78.4	79.4	79.7	79.2	0.7	72.5	73.4	74.8	73.6	1.2	73.7	74.6	75.2	74.5	0.8	74.6	75.4	76.0	75.3	0.7
360	85.8	86.0	87.1	86.3	0.7	78.7	79.6	79.8	79.4	0.6	74.4	75.2	76.1	75.2	0.9	74.9	75.4	76.4	75.6	0.8	75.9	76.7	77.1	76.6	0.6

AV = Average value; SD = standard deviation.

Table 2. Reaction data for the $KMnO_4$–H_2SO_4 oxidation of indane to indan-1-one, under 21.5 kHz ultrasonic irradiation, at different values of static pressure and at 298 K

	p 200 Torr					*p* 250 Torr					*p* 300 Torr					*p* 350 Torr					*p* 400 Torr				
	Yields (%)					Yields (%)					Yields (%)					Yields (%)					Yields (%)				
Time (min)	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD
30	12.6	13.1	13.4	13.0	0.4	16.9	17.4	17.6	17.3	0.4	21.2	21.6	22.0	21.6	0.4	18.9	19.7	20.1	19.6	0.6	19.1	19.6	19.9	19.5	0.4
60	30.4	32.3	32.7	31.8	1.2	43.7	44.8	45.2	44.6	0.8	46.9	47.5	48.1	47.5	0.6	46.4	47.1	47.6	47.0	0.6	45.1	45.8	46.7	45.9	0.8
90	39.7	41.2	41.8	40.9	1.1	56.9	57.9	58.4	57.7	0.8	63.3	63.4	63.7	63.5	0.2	61.8	62.3	63.0	62.4	0.6	59.1	60.1	60.9	60.0	0.9
120	46.6	48.1	48.5	47.7	1.0	63.6	64.3	64.7	64.2	0.6	69.7	70.2	70.2	70.0	0.3	68.5	69.6	69.9	69.3	0.7	66.5	67.3	67.9	67.2	0.7
180	57.5	58.3	58.7	58.2	0.6	70.6	71.7	71.9	71.4	0.7	75.0	75.5	76.2	75.6	0.6	74.7	76.1	76.6	75.8	1.0	73.6	74.2	75.2	74.3	0.8
240	62.5	63.4	63.8	63.2	0.7	72.9	73.8	74.4	73.7	0.8	77.1	77.7	77.9	77.6	0.4	77.9	78.7	79.3	78.6	0.7	76.3	77.3	77.8	77.1	0.8
300	65.0	66.0	66.3	65.8	0.7	74.8	76.1	76.3	75.7	0.8	77.6	78.2	78.4	78.1	0.4	78.9	79.3	80.0	79.4	0.6	77.1	78.3	78.6	78.0	0.8
360	65.9	67.2	67.4	66.8	0.8	75.2	76.2	76.3	75.9	0.6	77.9	78.4	78.7	78.3	0.4	79.2	79.9	80.1	79.7	0.5	77.6	78.5	78.7	78.3	0.6

	p 450 Torr					*p* 500 Torr					*p* 550 Torr					*p* 760 Torr				
	Yields (%)					Yields (%)					Yields (%)					Yields (%)				
Time (min)	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD
30	19.5	19.9	20.5	20.0	0.5	19.0	19.6	20.2	19.6	0.6	19.2	19.4	19.8	19.5	0.3	20.6	22.0	23.3	22.0	1.4
60	44.7	44.9	46.2	45.3	0.8	44.6	45.3	45.8	45.2	0.6	44.5	45.1	46.1	45.2	0.8	43.8	44.8	44.9	44.5	0.6
90	58.6	59.4	60.0	59.3	0.7	59.0	59.1	59.6	59.2	0.3	58.1	59.3	60.0	59.1	1.0	57.4	58.3	58.7	58.1	0.7
120	66.0	66.7	67.6	66.8	0.8	65.7	65.9	67.0	66.2	0.7	65.0	65.9	67.0	66.0	1.0	65.2	65.5	66.0	65.6	0.4
180	72.4	73.2	74.4	73.3	1.0	72.8	73.1	74.2	73.4	0.7	72.3	72.8	74.1	73.1	0.9	72.4	72.5	73.3	72.7	0.5
240	75.7	76.4	77.8	76.6	1.1	75.7	76.4	77.3	76.5	0.8	75.3	76.5	77.3	76.4	1.0	74.8	75.0	75.6	75.1	0.4
300	77.5	78.0	78.5	78.0	0.5	77.2	77.7	78.5	77.8	0.7	76.5	78.0	78.4	77.6	1.0	76.1	76.6	76.6	76.4	0.3
360	78.0	78.1	78.4	78.2	0.2	77.6	77.8	78.7	78.0	0.6	77.7	78.1	78.6	78.1	0.5	76.6	76.9	77.0	76.8	0.2

AV = Average value; SD = Standard deviation.

Table 3. Reaction data for the $KMnO_4$–H_2SO_4 oxidation of indane to indan-1-one, without ultrasonic irradiation, at different values of static pressure and at 298 K

	p 200 Torr					*p* 300 Torr					*p* 400 Torr				
	Yields (%)					Yields (%)					Yields (%)				
Time (min)	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD
30	1.9	2.0	2.3	2.1	0.2	2.0	2.1	2.4	2.2	0.2	1.9	2.0	2.3	2.1	0.2
60	5.6	6.0	6.2	5.9	0.3	5.9	6.3	6.9	6.4	0.5	5.8	6.4	6.8	6.3	0.5
90	11.5	12.1	12.2	11.9	0.4	12.2	12.4	12.8	12.5	0.3	12.0	12.2	12.7	12.3	0.4
120	16.4	16.9	17.2	16.8	0.4	17.1	17.4	18.2	17.6	0.6	16.8	17.2	18.0	17.3	0.6
180	26.2	26.6	27.3	26.7	0.6	26.9	27.4	27.7	27.3	0.4	26.3	27.0	27.5	26.9	0.6
240	32.7	33.2	33.5	33.1	0.4	33.6	34.1	34.8	34.2	0.6	33.3	34.1	34.4	33.9	0.6
300	39.2	39.7	40.4	39.8	0.6	39.7	40.6	40.9	40.4	0.6	39.4	40.4	40.5	40.1	0.6
360	43.5	43.7	44.4	43.9	0.5	44.1	44.6	45.3	44.7	0.6	43.3	43.8	44.5	43.9	0.6

	p 500 Torr					*p* 650 Torr					*p* 760 Torr				
	Yields (%)					Yields (%)					Yields (%)				
Time (min)	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD	run 1	run 2	run 3	AV	SD
30	1.8	2.2	2.4	2.1	0.3	1.8	2.1	2.5	2.1	0.4	1.6	2.1	2.4	2.0	0.4
60	5.9	6.4	6.6	6.3	0.4	5.8	6.4	6.7	6.3	0.5	5.9	6.0	6.3	6.1	0.2
90	11.9	12.6	12.9	12.5	0.5	11.7	12.1	12.5	12.1	0.4	12.0	12.3	12.8	12.4	0.4
120	16.6	17.2	17.9	17.2	0.7	17.0	17.2	17.6	17.3	0.3	17.1	17.4	17.9	17.5	0.4
180	27.1	27.5	28.1	27.6	0.5	26.9	27.2	27.7	27.3	0.4	26.2	26.5	27.3	26.7	0.6
240	34.3	35.2	35.8	35.1	0.8	34.5	35.1	36.0	35.2	0.8	33.7	34.2	34.6	34.2	0.5
300	39.8	40.3	40.6	40.2	0.4	39.2	40.3	40.8	40.1	0.8	39.9	40.2	40.8	40.3	0.5
360	44.7	45.3	45.6	45.2	0.5	44.2	44.5	45.3	44.7	0.6	43.7	44.1	44.9	44.2	0.6

AV = Average value; SD = standard deviation.

yields are always very high if compared with those obtained when the same reaction takes place without ultrasonic activation.

Dependence of Sonochemical Yields on Applied Static Pressure.—Following the theoretical considerations (Appendix), we investigated the possibility of rationalizing and improving the already satisfactory results obtained by sonoactivation of the model reaction; this can be achieved by taking into account the parameters involved in the ultrasonic irradiation, as represented in equations (2) and (6).

If all other experimental requirements are constant, we reckoned the external pressure to be one of the most important factors for our purpose. In fact, when the chemical parameters involved in the model reaction, *i.e.*, rate, concentration, and yield, were measured during several runs by varying in each case the static pressure applied above the free surface of the liquid phase, it was found that the kinetic rate and especially the maximum product yield are dependent on the established pressure value. The dependence of reaction rate and total product yield on pressure is shown in Figures 3A and B, which summarize the experimental results obtained when the oxidation reaction was run by stepwise variation of the static pressure applied over the solution in the range 200—760 Torr, with (curves a—f) or without (curves a′—f′) ultrasonic activation. Each yield–pressure curve has been obtained at a definite reaction time.

As can be seen in Figure 3A c, the yield reaches values as high as 80% in the optimum conditions. After 3 h irradiation at 48.0 kHz, at 450 Torr, the rate constant is $k_{48.0\ \text{kHz}}$ $(2.68 \pm 0.04) \times 10^{-4}\ s^{-1}$. It has to be recalled that the maximum yield attained is 85% after 6 h. Finally, curves a′—c′ of Figure 3A are flat and parallel to the abscissae axis: as expected, yields are low and do not change by varying the applied pressure, if no ultrasound is used.

The most significant aspect of the results from ultrasonic activation is the non-linear trend of the yield–pressure pattern, which shows the maximum yield (80% after 3 h) at 450 Torr.

The non-monotonic slope of the sonochemical yield, as a function of static pressure, suggests that it does not account only for the number of cavitation bubbles, as proposed by Chendke and Fogler,[7] but it rather indicates the predominant influence of the distribution and dynamics of the bubbles. As expected from the aforesaid observations and from the Appendix, the series of curves a—c in Figure 3A show a maximum that can correspond to the pressure at which the radius of equilibrium R_0 of the cavitating bubbles reaches its resonant value, so allowing the best coupling with the ultrasonic field.

As shown in the Appendix [equation (4)], knowledge of such physical parameters as density, viscosity, and surface tension, other than the distribution law of the bubbles' radii, would make it possible to calculate roughly the frequency at which the air bubble field will resonate, producing transient cavitation effects; in a single liquid phase an accurate calculation would be possible if all the damping terms are known.[5] Such numerical values are not available for our system, but an approximate calculation based on tabulated values of ρ, μ, and σ for water, benzene, and sulphuric acid[14] indicates a resonant radius R_0 *ca.* 54 μm, when the maximum yield occurs at 450 Torr and 48.0 kHz. Clearly this result cannot be taken as the exact value for R_0 in our system, but it can be considered to be reasonable as an order of magnitude for the bubbles at this pressure. Besides, when the maximum yield occurs at 300 Torr and 21.5 kHz, the resulting resonant radius R_0 is *ca.* 98 μm; its order of magnitude again seems to be reasonable in that even at such relatively low pressures, a small fraction of this type of bubble can exist.

Accordingly, the whole distribution of the bubbles' radii is shifted, in agreement with equation (6) (Appendix), while the whole population, *i.e.*, the total amount of air bubbles dissolved in the liquid system, must be accounted for in terms of Henry's law.

All curves taken at different time intervals follow a parallel alignment, each one showing two different non-symmetric slopes at the left (lower pressures) and right (higher pressures) sides of the maximum, respectively. In detail, the left side of all curves decreases more quickly towards low yields.

Such a trend could be formally described by comparison with the general behaviour of a forced oscillator in the presence of damping; in effect, the quantity p is a measure of the resonance frequency of the cavitating system, *via* the bubbles' equilibrium radius R_0.

In addition, a reasonable explanation can be also put forward, which takes into account that (i) the conditions for resonance are no longer operative at pressures <450 Torr and (ii) the system contains large bubbles, their number however being small, in agreement with Henry's law. Accordingly, if 48.0 kHz is used, the sonoactivation becomes ineffective at 200 Torr, and the product yield approaches the same value obtained when ultrasound is not operating.

On the other hand, when pressure becomes >450 Torr, the cavitation bubbles do not resonate; their number is high, thus justifying a greater probability of occurrence of cavitation events which in turn induce higher product yields, if compared with the situation when the lowest pressure range is considered.

Dependence of Sonochemical Yields on Ultrasounds Frequency.—The use of ultrasound irradiated at different frequencies seemed to us to be an essential test to verify if the results previously obtained on our model reaction cope with the theory of acoustic cavitation. In order to confirm the results of the experiments at 48.0 kHz, a further set of data was obtained at a lower frequency; accordingly, when an ultrasonic frequency of 21.5 kHz was used, the same general behaviour was confirmed for the reacting system under investigation, although some significant differences arose. In fact, looking at Figure 3B it is noteworthy that (i) the yield–pressure curves d—f follow a pattern analogous to that of the corresponding ones a—c in Figure 3A; (ii) the relative maximum values of kinetic rate [$k_{21.5\ \text{kHz}}$ $(3.57 \pm 0.01) \times 10^{-4}\ \text{s}^{-1}$, at 300 Torr] and product yield (76%) are shifted towards lower pressures (300 Torr), because ultrasound of lower frequency needs larger bubbles to couple with, as expected from the theory of cavitation (see Appendix); (iii) the relative maximum values of yield are less pronounced than those at 48.0 kHz; (iv) the overall yields are always rather high, especially when the downfield pressure range is considered; the average values are however slightly lower than those measured in the corresponding curves at 48.0 kHz.

To explain these features, the different power output of the two ultrasound sources used must be taken into account, the one at 21.5 kHz being greater than that at 48.0 kHz (see Experimental section). As Figures 3B d—f clearly show, in the former case the effects of static pressure on the bubbles' resonance requirements are recognizable, although smoothed because of the masking effect due to the overall influence of the pressure of the ultrasound, and its power effect, as produced by the transducers and transferred to the reacting system.

The experimental results are well accounted for by the general theory of acoustic cavitation.[4] For our purpose, it seems appropriate to recall that if p_k is taken as a critical value for the acoustic pressure, p_A, associated with the sonic waves travelling in a liquid, the condition $p_A \geqslant p_k$ will allow the ultrasound to increase the size of the cavitating bubbles to radius values $>2R_0$, with an expansion rate of the bubbles approaching the velocity of ultrasound in the liquid phase; as a consequence the bubbles collapse in a transient cavitation mode, independent of resonance effects. It follows that, when p_A exceeds a definite threshold value, the sonocatalytic effect on the chemical reaction rate is not exclusively dependent on the resonance frequency, ω_r, but is mainly associated with the intensity of the sonic pressure (and power) supplied to the medium.

So far as our results are concerned, these circumstances occur in the experimental conditions selected to sonoirradiate the chemical system at 21.5 kHz, when the transducers are driven to operate at a relatively high sonic power output.

If attention is paid to an extensive definition of yield, namely to the ratio product of reaction: energy employed, a chemical reaction, such as the benzylic oxidation we have investigated, is better performed under ultrasonic irradiation at the resonant conditions, preferably for other conditions in which the acoustic pressure only drives the reaction activation. In this way, considerable success will be achieved in promoting the selective oxidation of an organic substrate, under optimum conditions and without high dissipation of energy.

Finally, the approach used leads to better understanding of some of the essential factors which influence sonoactivation, as well as to the solution of many synthetic problems in organic chemistry.

Conclusions.—The results show how the catalytic effect of ultrasound on a chemical reaction is explained by the theory of acoustic cavitation; its implications have been used to optimize some of the parameters, through the coupling of ultrasonic irradiation with chemical reactants in solution. First, the oxidation reaction investigated undergoes a marked catalytic effect by sonoactivation, as clearly shown by a three to five times enhancement of its reaction rate, compared with the corresponding value obtained without ultrasonic irradiation. Moreover, the related high sonochemical yields are obtained under mild experimental conditions, and compete favourably with alternative reaction procedures where polar organic solvents or phase transfer agents are used. Thus, most of the drawbacks so far encountered, such as low solubility of organic products and poor selectivities due to the very active oxidizing agent of choice, are eliminated.

The reaction rates and sonochemical yields obtained were found to be dependent, although non-linearly related, on the applied static pressure, over the entire range measured, 200—760 Torr; according to the frequency of ultrasonic irradiation (21.5 or 48.0 kHz), the aforesaid reaction parameters reach a maximum at 300 or 450 Torr respectively, and decrease gradually as the static pressure is raised to the atmospheric value.

This non-monotonic trend of sonochemical yields with pressure, and the observed shift of the corresponding maximum at different values of the ultrasonic frequency used, are consistent with the assumption that the variation of the average radius R_0 of a bubble, in the cavitation field, is the essential requisite to drive the system in the resonance conditions; this can be obtained when R_0 is suitably tuned by means of the corresponding variation of the static pressure applied to the reacting system.

Likewise, the influence of ultrasound power supplied to the medium, on kinetic rates and overall product yields, is accounted for in terms of a threshold value of the sonic pressure, which renders sonocatalytic effects on the chemical reaction not exclusively dependent on the resonance frequency.

Appendix

Effect of Static Pressure on the Resonant Ultrasonic Cavitation.—It is well known that insufficient data are available for a rigorous treatment of non-ideal gas–liquid solution

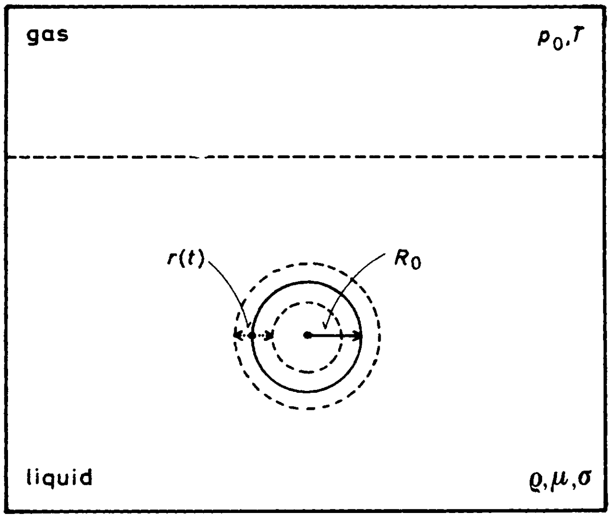

Figure 4. Dynamics of a gaseous bubble interacting with a sonic radiation field, in the liquid phase (see Appendix for symbols used)

behaviour. The absorption phenomena of ultrasound are still not completely defined. It is reasonable however to assume that, when a gas of external pressure p_0 and temperature T is partially absorbed through the free surface of a liquid following Henry's law, the gaseous molecules inside the solution will aggregate into spherical 'bubbles', whose sizes are distributed around an average equilibrium radius R_0. So far, neither formal models can be found to obtain the R_0 value of the bubbles, nor their distribution law values in a gas–liquid solution.

In these conditions, the effects of a sonic wave interacting with a bubble have been extensively studied.[2,4] The pressure of one such bubble, in a liquid of density ρ, viscosity μ, and surface tension σ (Figure 4) will be $p = p_0 + 2\sigma/R_0$.

For our investigation, if $r(t)$ is the displacement from the equilibrium value R_0 of a bubble radius excited by a wave of sonic pressure $p_A \sin\omega t$, its spherical wall will pulsate according to the motion equation (1)[5] in which the resonance frequency,

$$\frac{d^2r}{dt^2} + \omega_r^2 r = \frac{p_A}{\rho R_0}\sin\omega t \qquad (1)$$

ω_r, is defined by equation (2) where γ is the adiabatic term.

$$\rho\omega_r^2 R_0^2 = 3\gamma\left(P_0 + \frac{2\sigma}{R_0}\right) - \frac{2\sigma}{R_0} \qquad (2)$$

For ultrasonic frequencies $\omega \neq \omega_r$, equation (1) establishes that the bubble wall will pulsate steadily with radius $R = R_0 + r(t)$, where equation (3) is the solution of the differential

$$r(t) = \frac{p_A}{\rho R_0(\omega_r^2 - \omega^2)}\left[\sin\omega t - \left(\frac{\omega}{\omega_r}\right)\sin\omega_r t\right] \qquad (3)$$

equation (1). This kind of motion is usually referred to as 'stable cavitation'.

For ω approaching ω_r, or *vice versa*, the cavitation regime is no longer 'stable'; in the absence of damping forces, the bubble radius R tends to infinity within a few cycles of the sonic pressure and the cavitation field becomes of the 'transient type'. The latter cavitational regime is important to induce the so-called 'sonocatalytic effect', because under these conditions the bubbles' implosion produces, locally, high values of pressure and temperature such as to increase the kinetic rate of a hitherto slow chemical reaction.[2]

Furthermore, the viscosity of the liquid introduces a damping term in equation (1), thus shifting the resonance frequency towards lower values, according to equation (4).[5] Equations (2)

$$(\omega_r')^2 = \omega_r{}^2 - (2\mu/\rho R_0^2)^2 \qquad (4)$$

and (4) show how ω_r depends from R_0 as well as from the strongly temperature-dependent parameters ρ, μ, and σ; in turn, the parameter R_0 is also related to the external pressure, p_0, exerted on the solution, taken as the reaction medium. At constant temperature, the structure of equations (2) and (4) makes it possible to change the resonance frequency ω_r', changing R_0 *via* p_0.

Such a possibility finds very useful application, because ultrasound generators are usually tuned to the resonance frequency of the transducers, so that to a slight variation of the driving frequency corresponds to a severe decrease in the ultrasonic field power. Therefore, the control of R_0 by means of p_0 allows the distribution of the bubbles' radii to be driven over a range of values where the resonant coupling to the incoming ultrasound can be operative, so as to reach maximum efficiency for a given process.

Moreover, R_0 can be made to change over a rather wide range. In fact, if it is assumed that the behaviour of the gas corresponds to that of an ideal system, inside each bubble, as generated at equilibrium conditions by stabilization under normal pressure p_0^*, an isothermal expansion can take place, according to the Boyle's law (5) where the asterisk refers to normal conditions. It follows that equation (6) holds. In

$$\left(p_0^* + \frac{2\sigma}{R_0^*}\right)V_0^* = \left(p_0 + \frac{2\sigma}{R_0}\right)V_0 \qquad (5)$$

$$R_0^2(R_0 p_0 + 2\sigma) = R_0^{*2}(R_0^* p_0^* + 2\sigma) \qquad (6)$$

equation (6) the variation of the external static pressure, p_0, makes it possible to change each value of the bubbles' average radii, R_0', in the bubble field, so shifting the whole distribution in the range of interest.

It would be interesting to know the distribution law of the bubbles' radii in a liquid system: apart from a better appreciation of the resonant cavitation phenomena under investigation, this law would allow control of the bubbles' field. To our knowledge, the rationale of such a type of distribution is not yet available and its understanding is largely conjecture.

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