On the Quantitative Measure of a Sonochemical Effect in Heterogeneous Sonochemistry

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The measurement of a sonochemical effect (SE) requires the definition of the reference conditions for the so-called "silent reaction". It is shown that it is impossible to define SE correctly in the case of heterogeneous reactions, due to the dramatic effect of the agitation on reaction rates. This is true not only from the quantitative point of view (effect of ultrasound on reaction rates) but also from the qualitative perspective (change of reaction pathway when ultrasound is applied). The first, and most dramatic, example of chemical switching described in the literature, and claimed to be due to ultrasound, is proven also to be observable under efficient agitation conditions.

Introduction

Sonochemistry, the chemistry occurring in an acoustically cavitating fluid, is a well-developed field.[1] The number of papers describing rate increases in various reactions under sonication conditions is significant, meetings about sonochemistry are regularly organized, and books and specialized journals are devoted to this field, often described as a new kind of chemistry. Classically, sonochemistry is divided into homogeneous and heterogeneous sonochemistry.[2] This paper is specifically devoted to heterogeneous sonochemistry, the study of the effects of ultrasound on the reactivity of heterogeneous systems (immiscible liquid phases or solid suspensions in liquids).

A survey of the literature shows that heterogeneous sonochemistry is a more active field of research than homogeneous sonochemistry. Heterogeneous sonochemistry is important, from a synthetic point of view, as an increase in a reaction rate by a factor of two, even if difficult or impossible to interpret, is potentially useful for organic chemists and, obviously, rate increases of many orders of magnitude, as sometimes observed,[3] are of prime importance in synthesis.

People interested in homogeneous sonochemistry are frequently physical chemists mostly concerned with the origin of the effects of ultrasound. The majority of measurements are performed in water, and the bases of the majority of papers dealing with homogeneous sonochemistry involve changes of the redox properties of the cavitating field, oxidation of ferrous cation and iodide anion by OH radicals or H_2O_2,[4,5] or reductive formation of metal colloids.[6,7]

While homogeneous sonochemistry is a product of the high temperature/high pressure conditions occurring in the gas phase of the collapsing cavitation bubbles,[8] heterogeneous sonochemistry is essentially independent of these so-called extreme conditions. Heterogeneous sonochemistry depends on various effects occurring at different scales. Acoustic streaming is the origin of large scale effects,[9] while microstreaming,[10] jetting, splashing.[11,12] and shock waves[13] associated with the bubble collapse are the origins of microscale agitation, erosion of solids,[14] shocks between solid particles,[15] and shearing effects.[16] Although homogeneous and heterogeneous sonochemistry both find their origin in the acoustic cavitation phenomenon, the two fields are very different in many ways. The main difference lies in the fact that heterogeneous reactions are very sensitive to the agitation conditions. To be more precise, whilst a magnetic stirrer may be fully sufficient to obtain conditions of perfect mixing in the case of a homogeneous solution (except in highly viscous media, a case not being considered here), this is definitely not the case in heterogeneous media. The relevance of quantification of an effect in heterogeneous sonochemistry by comparison of the rates of a reaction under magnetic stirring and under sonication conditions, is therefore questionable. In this paper, we demonstrate that such quantification is meaningless and that the majority of published heterogeneous sonochemical effects concerning heterogeneous reactions are therefore open to challenge.

Heterogeneous Mixture Agitation and the Delicate Measurement of Sonochemical Effects in Heterogeneous Sonochemistry

In the past, agitation was considered an important technique in organic synthesis. In his well-known "Practical Organic Chemistry",[17] published in 1949, Vogel described the various kinds of stirrers and agitation techniques over nine pages. In 1955, only two pages of Fieser's "Experiments in Organic Chemistry"[18] are still devoted to agitation techniques, while in two books published in 1969, which describe many experimental techniques of general use in organic chemistry in full detail, agitation is not mentioned at all.[19,20] Why is this? It is obviously impossible to give a

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definitive response to this question, but a partial answer can be found in the fact that, by the end of the 1960s, magnetic stirrers had already "invaded" all organic chemistry laboratories. Apparently, chemists of this time had nothing to say about these user-friendly instruments. This, of course, was the situation in research laboratories but not in industry. In industrial synthesis, agitation was and remains a challenge and an active research subject for chemical engineers.[21]

The rapid development of heterogeneous sonochemistry in the last 20 years must be considered in this general context. As far as the agitation of a heterogeneous mixture is concerned, an ultrasonic cleaning bath is as simple as a magnetic stirrer but much more efficient. It then naturally follows that its use results in systematic rate increases, compared to the rates observed under magnetic agitation conditions. In some ways, the great success of heterogeneous sonochemistry is the direct consequence of the generalized use of the friendly, but very inefficient, magnetic stirrer. As the obtaining of more product in less time is an important challenge in organic synthesis, the success of heterogeneous sonochemistry is fully justified. What is less justified is any comparison between sonochemical effects measured in different laboratories or between sonochemical effects measured for different reactions. It is not even possible to give any credence to the majority of quantitative measurements of sonochemical effects published in literature as soon as they concern heterogeneous reactions.

By definition, an effect is the ratio of two properties, P/P_0, where P_0 is the property measured under reference conditions and P is the property measured under conditions in which all the parameters but one are the same. If P and P_0 are different, it is considered an effect due only to the experimental parameter that has been changed.

To measure a photochemical effect, P_0 is measured in the dark and P under light irradiation conditions. To measure a sonochemical effect, P_0 is measured under so-called "silent conditions" and P under sonication conditions. A question we have clearly addressed in previous papers, but which still remains underestimated, is "what do we mean by silent conditions?".[22,23] If we examine the literature, it appears that "silent conditions", when they are defined (which is far from the general case), means "under magnetic stirring conditions" without any indications of the size of the magnet, the rotation rate, and the size and shape of the vessel. Such a situation has dramatic consequences. How can we be sure that a claimed effect is a fact and not an artifact? How can we be sure that the effect measured by an author is larger than the effect measured by another author? How can we be sure that, in order to obtain a spectacular effect, an author who does not give any indication about the silent conditions used has not performed the silent reaction in the absence of any agitation? Unfortunately, all these questions frequently remain unanswered.

Problems frequently encountered by chemists trying to repeat a sonochemical experiment described in the literature are related to the nature and the definitions of the reference or silent conditions, as we have already described in a short paper.[22]

Table 1 gives a summary of those published results in which sonication was systematically compared to efficient agitation and to magnetic stirring. It is hardly necessary to make additional comments to convince the reader that the silent conditions must be specified before a claim can be made that sonication has an effect on the rate of heterogeneous reactions.

Table 1. Comparison of the effect of ultrasound and of agitation on the alkaline hydrolysis of benzoate and on the cyclopropanation of cyclohexene by dichlorocarbene (synthesized in situ from chloroform and sodium hydroxide)

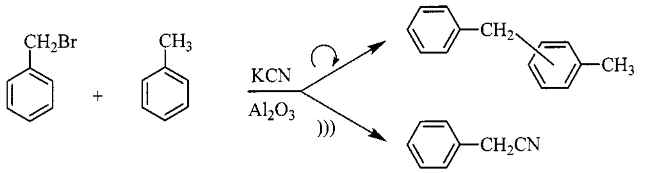
Reaction conditions	Yields (%) Sodium benzoate	Yields (%) 7,7-Dichloro-bicyclo[4.1.0]heptane
Magnetic agitation	0	0
Ultrasound	44 ± 2	20 ± 1
UltraTurax 8000 rpm	9 ± 1	23 ± 6
UT 16000 rpm	28 ± 2	53 ± 3
UT 24000 rpm	33 ± 3	70 ± 4

Sonochemical Switching: A Proof that Sonochemistry is a "New Kind of Chemistry"?

In their well-documented chapter published in 1997, Mason and Luche addressed the problem discussed in this paper.[24] They pointed out that "critics of the technique regarded sonochemistry merely as a kind of super-agitation" and as an argument against these critics, and as the first proof of what they called "the specific nature" of sonochemistry, they gave the case of sonochemical switching, first discussed by Ando.[25,26] By "sonochemical switching", they meant a change in a reaction pathway under sonication conditions, a reaction giving products that differ depending on whether the reaction is performed under sonication conditions or if it is performed whilst stirring. The conclusion of these authors is very clear. The chemical switching phenomenon "shows that sonication is definitively not just another method of providing agitation of a medium". This statement contradicts results that we presented previously[22] and deserves attention. The reaction studied by Ando was, therefore, performed under efficient agitation conditions and compared with the results obtained under magnetic agitation conditions.

As shown in Scheme 1, this so-called "sonochemical switching"[26] takes place during a reaction that can be described as a competitive nucleophilic substitution on a benzylic carbon atom, the leaving group being a bromide ion. The two nucleophiles in competition are a cyanide ion on the one hand, and a neutral toluene molecule on the other. Of course, it is also possible to describe the competition, and therefore the switching, in a more dramatic way by speaking about a competition between an electrophilic Friedel−Crafts reaction and a nucleophilic substitution.

Thus in terms of competition of two nucleophiles, a charged one and a neutral one, for the same substrate, the reaction with agitation by a vibration device, after 3 h at 50 °C, gives 83% of substitution by the neutral aromatic derivative and 0% of benzyl cyanide.[26] At the same temperature, but after 24 h of sonication, benzyl cyanide is obtained in a yield of 76% and substitution by toluene is not observed.[26] It is important to note that one of the reactants (toluene) is also the solvent and that the reaction is performed in the presence of alumina.



Scheme 1. Heterogeneous sonochemical switching (⌒: mechanically agitated reaction;))): sonochemical reaction)

We performed the same reaction at the same temperature under sonication conditions, but also under efficient agitation conditions with an UltraTurax system, providing adjustable stirring rates between 8000 and 24000 rpm. From analysis of the products (Table 2), it clearly appears that the switching is not solely sonochemical in nature; it is also observed on comparison of the reaction performed under magnetic stirring conditions to the reaction performed under efficient stirring conditions. Furthermore, when ultrasound is used, the results obtained in the presence of 2,2-diphenyl-1-picrylhydrazyl (DPPH), a radical scavenger, are similar to the results of the "normal" sonochemical reaction (Table 2). This is in contradiction with the hypothesis that the specificity of ultrasound might be related to the production of radicals in the sonicated medium.[27] These results clearly indicate that ultrasound does not have a specific effect; it is just another kind of agitation. It is unnecessary to call it "super", it is the reference magnetic stirring that is "sub"! This observation fully confirms what has been stated in the previous paragraphs in the case of other heterogeneous reactions: the mechanical effects of sonication are quantitatively and, in the last case, qualitatively very similar to those produced by an efficient stirrer. Interestingly, a rough linear relationship exists between the benzyl cyanide yield and the rotation rate of the stirrer. Under our experimental conditions, sonication was equivalent to stirring at 14000 rpm and definitively less efficient than stirring at higher rates.

Table 2. The heterogeneous sonochemical switching; yields of reaction products obtained under magnetic agitation, ultrasound, and efficient agitation (UltraTurax) conditions; $T = 50$ °C, reaction time = 3 h

Reaction conditions	Yields (%)	
	$PhCH_2CN$	Friedel−Crafts product
Magnetic agitation	0	82 ± 6
Ultrasound	16 ± 2	0
Ultrasound + DPPH	13 ± 3	0
UT 8000 rpm	7 ± 1	traces (0.5%)
UT 13500 rpm	15 ± 1	traces (0.5%)
UT 20500 rpm	21 ± 4	0
UT 24000 rpm	28 ± 4	0

It is interesting to search for the origin of the switching, a question already addressed by Ando himself in 1984.[28] When a pre-treated KCN/alumina mixture is used, the only reaction product is benzyl cyanide. As can be seen in Table 3, if 3 h pre-treatment of a suspension of KCN and alumina in toluene is performed under efficient agitation conditions, the reaction yield is exactly the same whether magnetic stirring or sonication are used. If the pre-treatment is 3 h sonication, a higher yield is obtained if the reaction with benzyl bromide is performed under sonication conditions than if performed under magnetic stirring conditions (see Table 3). This result confirms that the switching is associated with a change in the KCN/alumina solid phase produced by mechanical effects and that, under our experimental conditions, this modification is more important under efficient stirring conditions than under sonication conditions. It is important to insist on the fact that efficient stirring and, to a lesser degree, sonication not only favor the formation of benzyl cyanide but also inhibit bromide substitution by toluene. This can easily be seen in Tables 2 and 3, taking into account that the reaction times are identical for all experiments.

Table 3. The heterogeneous sonochemical switching; yields of substitution and Friedel−Crafts products with pre-sonicated alumina (lines 1−2) and pre-agitated by UltraTurax alumina (lines 3−4); $T = 50$ °C, reaction time = 3 h

Reaction conditions	Yields (%)	
	$PhCH_2CN$	Friedel−Crafts product
Pre-sonicated alumina		
Magnetic agitation	12	Traces (0.5%)
Ultrasound	43	Traces (0.5%)
Pre-agitated by UT alumina		
Magnetic stirrer	55	0
Ultrasound	55	0

At this stage, we confirm what has already been suggested in previous literature: the sonochemical switching (which, incidentally, could be also described as an "efficient stirring switching") depends on the change in the KCN/alumina solid phase. It may be due in part to a deactivation of the acidic sites of alumina, as suggested by Suslick,[29] but at the same time, it is associated with an activation of the nucleophilicity of the cyanide anion. In order better to understand this activation, a systematic study of the alumina and alumina/KCN solid system was performed.

Efficient Agitation and the Associated Changes in the Alumina/KCN System

All of our experiments were performed with γ-alumina, a highly porous solid with a specific area that can reach 200 $m^2 \cdot g^{-1}$. It is common knowledge that the catalytic properties of alumina are dependent on its degree of hydration.[30,31] In the absence of water molecules, acidic sites (Al^{3+}) and basic sites (O^{2-}) are exposed on the surface. If water molecules are present, the surface is covered by OH groups; following the heterolytic cleavage of H_2O, a proton is fixed on the negative oxygen atom and an OH anion is fixed on the aluminium cation.[32]

For the reaction under study, adsorption of KCN onto the alumina surface is certainly very efficient, due to the presence of negative and positive charges on this surface. Of course, competition could exist between water molecules, K^+, and CN^-. A nonhydrated alumina of Brockmann activity equal to I was therefore used.[33,34] In view of the great complexity of the system under study, we decided to perform an ensemble of physico-chemical measurements in order to characterize the alumina/KCN.

We first measured the powder particle size distribution by laser granulometry. Figure 1 shows the volume distribution of the alumina/KCN powder as a function of the average particle diameter. Magnetic agitation does not change the distribution compared to the untreated powder, while sonication and efficient agitation both produce significant particle size reduction. It was tempting to imagine that the reduction in the particle size was associated with an increase in the accessible reactive or catalytic surface of the solid. Measurements of the specific area of alumina (Table 4), determined by the BET nitrogen adsorption method[35], before any treatment give a value of 218 $m^2 \cdot g^{-1}$, while this is only 198 or 176 $m^2 \cdot g^{-1}$ for alumina treated by ultrasound or efficiently agitated. Moreover, the specific area is reduced to about 60 $m^2 \cdot g^{-1}$ when the alumina/KCN system is sonicated or efficiently agitated. Clearly, simple correlation in the macroscopic surface/volume ratio is not relevant in the case of a highly porous solid like alumina. Strong agitation or sonication seems to reduce the pore accessibility to dinitrogen molecules slightly, probably through a change in the superficial structure of the powder grains. The KCN treatment results in a dramatic decrease in the pore accessibility due to pore clogging, which is clearly observable in images obtained by scanning electronic microscopy (see Figure 2).

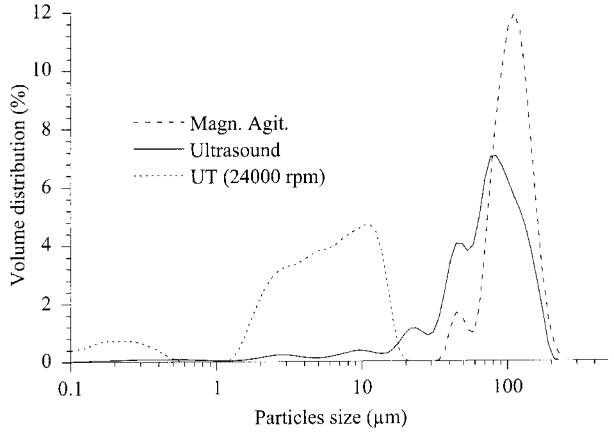


Figure 1. Size distribution of the powders after treatment under different conditions

Table 4. Specific surfaces determined by the multi-point method of different powders prepared under different conditions; UltraTurax used at 24000 rpm

Analyzed solid	Preparation condition	Specific surface (m^2/g)
Alumina alone	Mag. agit.	218
	Ultrasound	198
	UltraTurax	176
Alumina + KCN	Ultrasound	67
	UltraTurax	53

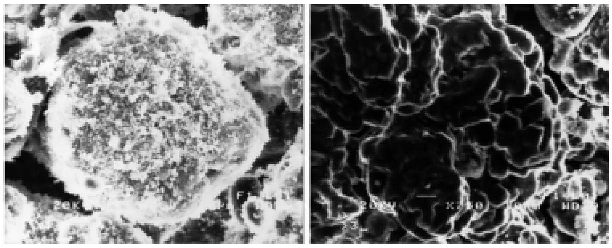


Figure 2. The KCN treatment produced a dramatic decrease in the pore accessibility due to pore clogging, clearly observable in images obtained by scanning electronic microscopy

With the chemical switching thus not correlated in any direct way with the powder-specific area, it became necessary to test other possible explanations. Competition reactions with alumina of different hydration levels were performed (Table 5). The presence of water strongly favored substitution by CN^-, while it was only with alumina I that substitution by toluene (Friedel−Crafts product) was observed in an 82% yield under magnetic stirring conditions, but not under sonication or efficient stirring conditions. The role of water in the competition between the two nucleophilic substitutions had already been observed by Ando in 1984,[28] but strangely enough, this observation remained disconnected from the so-called sonochemical switching phenomenon. As KCN is a hygroscopic solid, we performed the competition reactions using a KCN sample previously heated in a vacuum at 100 °C for 4 h. As shown in Table 6, under such conditions and even with sonication or efficient agitation, substitution by toluene takes place together with substitution by the cyanide ion.

Table 5. The heterogeneous sonochemical switching; yields of substitution product obtained with alumina of different activity; T = 20 °C, reaction time = 3 h

Alumina activity	Water content (%)	Yields of $PhCH_2CN$ (%)		
		Magn. agit.	Ultrasound	UT (24000 rpm)
I	0	0[a]	16 ± 1	28 ± 4
II	3	2	33 ± 2	−
III	6	9 ± 1	54 ± 1	50 ± 8
IV	10	20 ± 1	39 ± 3	−

[a] In the case of alumina of activity I, 82 % of the Friedel−Crafts product is formed under silent conditions.

From all these results, we conclude that the presence of water favors substitution by the cyanide ion and inhibits

Table 6. The heterogeneous sonochemical switching; yields of reaction products obtained under ultrasound and UltraTurax conditions with nondesiccated and desiccated reagents and solvents; T = 50 °C, reaction time = 3 h

Reaction conditions	Yields (%)	
	$PhCH_2CN$	Friedel−Crafts product
Non-desiccated reagents		
Ultrasound	16	0
UT (24000 rpm)	28	0
Desiccated reagents		
Ultrasound	9	11
UT (24000 rpm)	18	3

substitution by toluene, probably through a reduction in the number of Lewis acid sites on the alumina surface. Strong agitation or sonication results in much better hydration of alumina than achieved by magnetic stirring, the source of water being the KCN hydration water or air humidity.

In the context of this work, the most important conclusion of this study of the so-called sonochemical switching lies in the fact that sonication again appears to be "just" an efficient agitation procedure.

Acoustic Cavitation versus Hydrodynamic Cavitation

An efficient stirrer such as the UltraTurax system creates cavitation. This cavitation, known as hydrodynamic cavitation or vortex cavitation, is not qualitatively different from acoustic cavitation.[36] It can be concluded that what is important, in the case of heterogeneous reactions, is to induce cavitation in the medium. Cavitation itself is behind the previously enumerated agitation phenomena at the microscopic level. For physicists, cavitation is a unique phenomenon divided into sub-classes such as "travelling bubble cavitation", "attached cavitation", "vortex cavitation", or "acoustic cavitation".[36] Sonochemistry would be better called cavitation chemistry, as it is clearly the choice made by Shah, Pandit, and Moholkar;[37] these authors include some examples of heterogeneous sonochemical reactions in their book on cavitation reaction engineering. The question that remains open concerns the advantages or disadvantages of acoustic cavitation with respect to hydrodynamic cavitation. It is doubtful that it is possible to give an unequivocal response to this question. Indeed, cavitation depends not only on the mechanical energy source but also on the shape and size of the vessel in which the reaction is performed.[38,39] If what is important is to obtain the highest yield in the shortest time, it is definitely not necessary also to perform the reaction under magnetic agitation conditions.

Cavitation Chemistry versus Mechanochemistry

As pointed out in 1984 by Heinicke,[40] cavitation chemistry is part of mechanochemistry. In 1993, Luche also underlined possible links between sonochemistry and mechanochemistry.[41] Today we must conclude, without any doubt, that sonochemistry, being part of cavitation chemistry, is also part of mechanochemistry. For people using sonication to accelerate a heterogeneous reaction, the awareness that they are actually doing mechanochemistry might be of great help. Over the years, mechanochemists have accumulated a huge amount of experimental results and have elaborated models to explain what they have observed in the case of solid-state mechanochemistry and tribochemistry. In many ways, it is simpler to study what is happening at the molecular level in a mechanochemical experiment than in a sonochemical reaction; the system is simpler, the mechanical effects are better characterized, and the presence of a liquid phase is not necessary.

In science, it is always a advantageous when artificial barriers can be suppressed. The recognition that mechanochemistry, cavitation chemistry, and heterogeneous sonochemistry are a unique scientific discipline must have positive consequences in the various domains.

Conclusion

Nobody would publish a paper describing the change of the rate of a heterogeneous reaction as a function of the rotation rate of the stirrer. It is also doubtful that such a paper, if submitted, would ever be accepted. Nevertheless, each year, many papers describing the so-called rate increase of various heterogeneous reactions under sonication conditions are still published, without any serious discussion about the reasons why agitation through acoustic cavitation is preferable to the "old-fashioned" stirring system. By "old-fashioned", we mean the use of efficient agitation and not, of course, the use of inefficient systems such as manual stirring with a glass rod or magnetic stirring.

The aim of this paper is certainly not to try to convince the reader that heterogeneous sonochemistry is of no interest at all. Cavitation as a nonlinear phenomenon in fluid mechanics is an extremely complex problem. It remains an active research area for engineers, who are essentially interested in reducing the negative effects of cavitation, such as noise and erosion. Cavitation could also be studied by chemists or engineers interested in its positive effects on the reaction rates of heterogeneous reactions. In the context of organic synthesis, for example, the optimization of acoustic cavitation and the optimization of hydrodynamic cavitation remain important challenges. Strangely enough, it is not always considered as such by chemists working at the laboratory scale level. It would be much more interesting and useful to pay attention to these optimization problems than to measure so-called sonochemical effects, which, as we have seen, cannot have any significance when the reference (the silent reaction) is performed under the worst possible conditions. Acoustic cavitation, and hence heterogeneous sonochemistry, is of true interest only when it gives better results than any other agitation procedure. "Better" can mean "less expensive", "easier to handle", or any other convincing criterion.

In this paper, we mean to be clear that the described results and all the conclusions concern heterogeneous reactions. Homogeneous sonochemistry is obviously also a kind of cavitation chemistry but not a kind of mechanochemistry; it is basically high temperature chemistry even if the high temperatures reached inside the bubbles at the end of the collapse obviously have a mechanical origin, adiabatic compression in a very short period of time.

Experimental Section

A typical experiment was conducted according to this procedure: Merck type 90 neutral aluminium oxide (63−210 mesh), of activity I according to Brockmann (3.2 g, 31 mmol), and Merck potassium cyanide (2 g, 30 mmol) were suspended in 10 mL of toluene (Aldrich, purity 99.5%) containing benzyl bromide (Aldrich, purity 98%, 0.8 mL, 7 mmol). Magnetic stirring (1100 rpm), ultrasound (270 W), or UltraTurax (185 W at 24000 rpm) were switched on just after the mixing of reactants. The UltraTurax was a CAT X-620 equipped with a TN 10 axis-impeller. The ultrasound source was a home-made immersion horn with a CHEMSONIC ultrasound generator with a frequency of 20 kHz, working at about $20\ \mathrm{W{\cdot}cm^{-2}}$. The reaction time was 3 h, the temperature 50 °C, the reaction cell was thermostated with a NESLAB RTE-101 apparatus. After the reaction time, the medium was filtered. The filtrate was analyzed by gas chromatography (Delsi DI 200 apparatus equipped with an FID detector and an integrator ENICA 31; a glass column, 3 m long and 2 mm in diameter, filled with Carbowax 20M 10% on Chromosorb P or with OV-1 3% on Chromosorb W), with naphthalene as internal reference. − In the reactions performed in the presence of 2,2-diphenyl-1-picrylhydrazyl (DPPH), the concentration of radical scavenger was about $5 \cdot 10^{-6}$ mol/L. Aluminium oxides of activities higher than I were prepared by addition of the defined quantity of water to the solid, shaking vigorously, and letting it stand overnight. − The powders were analyzed with a JEOL JSM-820 scanning electron microscope (SEM). − The size distribution of the powders was measured with a COULTER LS 130 granulometer. − Specific surface measurements (multipoint method) were carried out with a MICROMERITICS ASAP 2010 apparatus. For these measurements, the adsorbed gas was nitrogen mixed with helium in order to vary its partial pressure.

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[1] K. S. Suslick, Y. T. Didenko, M. M. Fang, T. Hyeon, K. J. Kolbeck, W. B. McNamara III, M. M. Mdleleni, M. Wong, *Phil. Trans. R. Soc. Lond. A* **1999**, *357*, 335−353.

[2] K. S. Suslick, *Ultrasound, Its Chemical, Physical, and Biological Effects*, VCH Publishers, Inc., New York, **1988**.

[3] K. S. Suslick, D. J. Casadonte, *J. Am. Chem. Soc.* **1987**, *109*, 3459−3461.

[4] K. Makino, M. M. Mossoba, P. Riesz, *J. Am. Chem. Soc.* **1982**, *104*, 3537−3539.

[5] C. von Sonntag, G. Mark, A. Tauber, H.-P. Schuchmann, *Adv. Sonochem.* **1999**, *5*, 109−145.

[6] F. Grieser, R. A. Caruso-Hobson, J. Z. Sostaric, P. Mulvaney, *Ultrason. Sonochem.* **1996**, *34*, 547−550.

[7] K. Okitsu, Y. Mizukoshi, H. Bandow, Y. Maeda, T. Yamamoto, Y. Nagata, *Ultrason. Sonochem.* **1996**, *3*, S249−S251.

[8] K. S. Suslick, D. A. Hammerton, R. E. Cline, *J. Am. Chem. Soc.* **1986**, *108*, 5641−5642.

[9] O. Dahlem, J. Reisse, V. Halloin, *Chem. Eng. Sci.* **1999**, *54*, 2829−2838.

[10] S. A. Elder, *J. Acoust. Soc. Am.* **1958**, *31*, 54−64.

[11] A. Philipp, W. Lauterborn, *J. Fluid Mech.* **1998**, *361*, 75−116.

[12] R. P. Tong, W. P. Schiffers, S. J. Shaw, J. R. Blake, D. C. Emmony, *J. Fluid Mech.* **1999**, *380*, 339−361.

[13] G. E. Reisman, Y. C. Wang, C. E. Brennen, *J. Fluid Mech.* **1998**, *355*, 255−283.

[14] A. Karimi, J. L. Martin, *Int. Met. Rev.* **1986**, *31*, 1−26.

[15] S. J. Doktycz, K. S. Suslick, *Science* **1990**, *247*, 1067−1069.

[16] A. B. Pandit, J. B. Joshi, *Chem. Eng. Sci.* **1993**, *48*, 3440−3442.

[17] A. Vogel, *Practical Organic Chemistry*, Longmans, Green and Co., London, **1948**.

[18] L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., D. C. Heat and Co., Boston, **1955**.

[19] R. M. Roberts, J. C. Gilbert, L. B. Rodewald, A. S. Wingrove, *An Introduction to Modern Experimental Organic Chemistry*, Holt, Rinehart and Winston, USA, **1969**.

[20] J. S. Swinehart, *Organic Chemistry: An Experimental Approach*, Meredith Corporation, USA, **1969**.

[21] J. Y. Oldshue, D. B. Todd, in *Encyclopedia of chemical technology* (Ed.: Kirk-Othmer), John Wiley and Sons, Inc., New York, **1981**, pp. 604−637.

[22] Y. Kegelaers, J.-L. Delplancke, J. Reisse, *Chimia* **2000**, *54*, 48−50.

[23] J. Reisse, T. Caulier, C. Dekerckheer, Y. Kegelaers, N. Segebarth, K. Bartik, in *Sonochemistry and sonomuminescence* (Eds.: L. A. Crum, K. S. Suslick, J. Reisse, T. J. Mason), NATO ASI series, Amsterdam, **1999**, pp. 205−224.

[24] T. J. Mason, J.-L. Luche, in *Chemistry under extreme or non-classical conditions* (Eds.: R. van Eldik, C. D. Hubbard), John Wiley & Sons, Inc., Spectrum Akademischer Verlag, New York, Heidelberg, **1997**, pp. 317−380.

[25] T. Ando, T. Kawate, J. Yamawaki, T. Hanafusa, *Chem. Lett.* **1982**, 935−938.

[26] T. Ando, S. Sumi, T. Kawate, J. Ichihara, T. Hanafusa, *J. Chem. Soc., Chem. Commun.* **1984**, 439−440.

[27] J. L. Luche, *Ultrasonics* **1992**, *30*, 156−162.

[28] T. Ando, T. Kawate, J. Ichihara, T. Hanafusa, *Chem. Lett.* **1984**, 725−728.

[29] K. S. Suslick, in *Modern Synthetic methods*, vol. 4 (Ed.: R. Scheffold), Springer-Verlag, Berlin, Heidelberg, **1986**, pp. 1−60.

[30] B. C. Gates, in *Catalytic chemistry*, John Wiley & Sons, New York, **1992**, pp. 310−429.

[31] J. W. Hightower, W. K. Hall, *J. Chem. Soc., Faraday Trans.* **1970**, *66*, 477−489.

[32] J. M. Wittbrodt, W. L. Hase, H. B. Schlegel, *J. Phys. Chem. B* **1998**, *102*, 6539−6548.

[33] H. Brockmann, *Angew. Chem.* **1947**, *59*, 199−205.

[34] H. Brockmann, H. Schodder, *Ber. Dtsch. Chem. Ges.* **1941**, *74*, 73−78.

[35] S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309−319.

[36] C. E. Brennen, *Cavitation and bubble dynamics*, Oxford University Press, New York, **1995**.

[37] Y. T. Shah, A. B. Pandit, V. S. Moholkar, *Cavitation reaction engineering*, Kluwer Academic/Plenum Publishers, New York, **1999**.

[38] S. Dähnke, F. J. Keil, *Ind. Eng. Chem. Res.* **1998**, *37*, 848−864.

[39] A. Weissler, H. W. Cooper, S. Snyder, *J. Am. Chem. Soc.* **1950**, *72*, 1769−1775.

[40] G. Heinicke, *Tribochemistry*, Carl Hanser Verlag, München, **1984**.

[41] J.-L. Luche, in *Advances in sonochemistry*, vol. 3 (Ed.: T. J. Mason), JAI Press, London, **1993**, pp. 85−124.

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