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Ultrasound-enhanced reactivity of calcium in the reduction of aromatic hydrocarbons

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Abstract

Reductions of aromatic hydrocarbons by calcium in ethylenediamine–*n*-alkylamine mixture were investigated under ultrasonic conditions. Using an ultrasonic probe, with naphthalene as test molecule, it has been demonstrated that under ultrasonic action the reactions proceed faster (×10) and require a lower metal quantity (0.5) than the reactions conducted with an efficient mechanical stirrer. In addition, at ambient temperature and depending on the specific alcohol addition, selective naphthalene reduction can be performed using ultrasound. 1,2-Dihydronaphthalene (88% yield) results from the reaction in the presence of 2-propanol, and 1,4,5,8-tetrahydronaphthalene (88% yield) is obtained with *tert*-butanol. Investigation of the metal surface points out the characteristics of the calcium ultrasonic activation. The procedure was efficiently tested with several aromatic hydrocarbons.
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1. Introduction

Calcium in an ethylenediamine–*n*-alkylamine mixture substituting sodium or lithium in ammonia is an attractive and safe method to reduce organic compounds [1–5]. However, because of the low activity of calcium, this method suffers some drawbacks. The reaction requires a metal excess, and the calcium must be activated by efficient mechanical stirring (Hershberg stirrer), sometimes in combination with the use of sand to remove the coatings.

In many cases, the use of ultrasonic irradiation offers an advantageous solution to inactivation problems [6–9]. Related to the mechanical hardness of the reagent, the ultrasound activation has several types of consequence. It has been shown that small particles of Ni, Zn or Cu are activated by removal of the passivating oxide shell [10–12]. A lithium surface is fractured [13], and a soft metal like Na or K is finely dispersed in the solvent [14,15]. In a few studies it appears that the preparation of a physically very active reagent is not the only consequence of the ultrasonic irradiation that is also able to modify the course of a reaction [16–19].

In this experimental work we report the use of ultrasonic waves to improve the reduction of aromatics with calcium. We demonstrate that interactions between the substrate and reagent may be different according to whether the reaction is conducted under ultrasonic or stirring conditions.

2. Experimental

Naphthalene and 2-methylnaphthalene from Aldrich were used as-received. *n*-Butylamine, 2-propanol, and liquid aromatic compounds were distilled from sodium under an argon atmosphere immediately before use. Ethylenediamine was distilled under argon from the purple lithium solution. It was previously pretreated by refluxing for 1 day and then distilled on sodium hydroxide. Calcium shots came from Sigma.

Infrared spectra were recorded on a Perkin–Elmer 1640 FTIR spectrometer. Melting points (uncorrected) were determined with a Buchi Tottoli apparatus. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ solution on a Varian 200 MHz

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spectrometer. The chemical shifts were referenced to tetramethylsilane as internal standard. The electron impact mode was used in the mass spectra experiments recorded on a Finnigan MAT 311A mass spectrometer instrument.

Ultrasonic irradiation was performed in a previously described home-made reactor [20]. Calcium shots were maintained in a basket holder in the ultrasonic field at a distance of 5 mm from the tip of the probe. The system, dried and flushed with argon, was thermostatically controlled with a cooling jacket. The internal temperature was maintained at $20 \pm 2^{\circ}C$ and monitored with the help of an iron–constantan thermocouple. When the reduction is performed with *tert*-butanol, precipitation of the alkoxide occurs during the later stages of the reaction and the temperature increases to 27°C. The power used, 45 W, was estimated through the calorimetric method [21].

Stirred reactions with sand were performed in a three-necked round bottom flask equipped with a mechanical stirrer holding a Teflon blade (no advantage was found using a Hershberg stirrer). The rotation speed, maintained at 750 rpm, was monitored with the help of a stroboscope. The temperature was held constant at 20°C by the use of a thermostatically controlled water bath.

A typical reaction is performed in a 1:1 mixture of ethylenediamine–*n*-butylamine (36 ml) under an argon atmosphere. The reaction is particularly sensitive to the amount of alcohol, and does not start if the total amount is present at the beginning. Half of the required amount is added with the starting material; the other portion is added 5 min later if a polyaromatic compound is used, or 30 min later in the case of mononuclear benzenic ring. The reaction mixture becomes viscous as it progresses, and cannot be well stirred at the end. The quantity of calcium used has to be less than 0.83 M for a reaction without alcohol, 0.33 M for the reduction with *tert*-butanol and 0.41 M with 2-propanol. At the end of the reaction, the mixture was cautiously poured into ammonium chloride saturated solution at 0°C. The reaction products were extracted with pentane and dried with sodium sulfate. The purifications were effected by silica gel column chromatography (230–400 mesh) with pentane as eluent.

For the comparative studies between stirring and ultrasonic conditions with 2-propanol and *tert*-butanol, the reaction was done with calcium, naphthalene and alcohol (12 mM, 4.5 mmol, and 24 mmol respectively). Progress was followed by periodic withdrawals of aliquots. After hydrolysis with saturated aqueous ammonium chloride solution, the organic compounds were extracted with pentane and the solution dried with sodium sulfate. The samples were analyzed by gas chromatography (GC) on a carbowax 10% column. The areas were recorded on a Shimatsu integrator.

2.1. Sample preparation for scanning electron micrography

Under an inert atmosphere, with the help of forceps, calcium is removed from the reaction mixture and washed with tetrahydrofurane (THF) in an Erlenmeyer flask. To remove the sticky salts, the shots are then transferred to another flask with fresh THF and submitted to ultrasonic irradiation in an ultrasonic bath cleaner for 5 min. Observations were made using a Hitachi S-800 microscope in the case of naphthalene reduction with calcium, using *tert*-butanol as hydrogen donor.

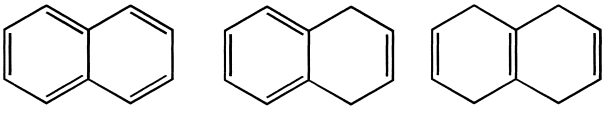
3. Results, discussion

3.1. Reduction of aromatics with calcium in ethylenediamine–n-butylamine mixture

Table 1 displays the results obtained with several compounds. It has to be noted that experiments conducted in a cleaning bath did not give any reaction. The reaction was studied with a classical sonicator equipped with a titanium immersion tip, with a vessel that permits the retention of calcium in the ultrasonic field. A comparison with the few available data demonstrates the advantage of the ultrasonic procedure in terms of time, quantity of metal and yield. This process leads to fast reaction rates, lower amounts of calcium, and enhances the selectivity. Interestingly, with a stoichiometric amount of calcium it is possible to reduce only one ring of naphthalene.

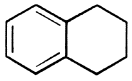
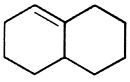
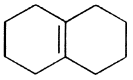
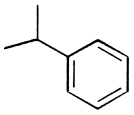
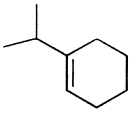
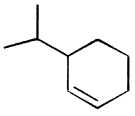
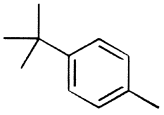
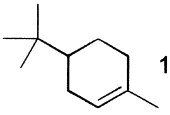
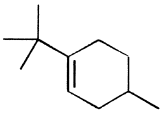
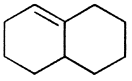
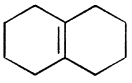
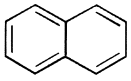
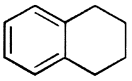
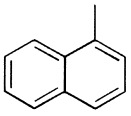
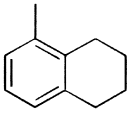
3.2. Reduction of aromatics with calcium in ethylenediamine–n-butylamine mixture with alcohol as proton source

At ambient temperature, calcium reduction of aromatics in *n*-butylamine–ethylenediamine solvent mixture with an alcohol as proton source [1] leads to products that are generally obtained at low temperature in the Birch reaction with lithium or sodium in liquid ammonia [22–25]. An efficient stirring system is required in order to clean the metal surface from the oxide, and to avoid the repassivation by reaction products. This reduction can only be obtained using a high-speed mechanical stirrer in conjunction with the addition of sea sand as an abrasive [1,26,27]. This method is compared with ultrasonic activation with naphthalene **1** as the substrate and *tert*-butyl alcohol the proton source in Fig. 1.



1 **2** **3**

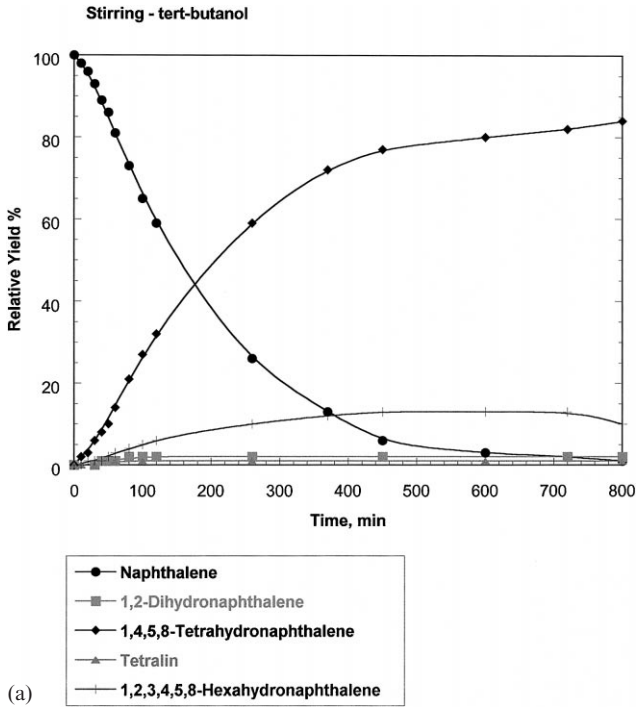
Table 1
Calcium reduction of aromatic compounds in *n*-butylamine–ethylenediamine mixture under ultrasonic conditions[a]

Substrate	Ca/ga	time/hour	Products	Isolated yields %
	2.5 (5)	2 (26)	 24% (19%)  76% (81%)	96% (92%)
	2.5 (6)	2.5 (22)	 97% (78%)  3% (14%)	88% (82%)
	3.3	6	 12%  73%	94%
	5 (10)	2 (23)	 24% (23%)  76% (77%)	96% (92%)
	2.1	1		84%
	2.1	0.5		90%

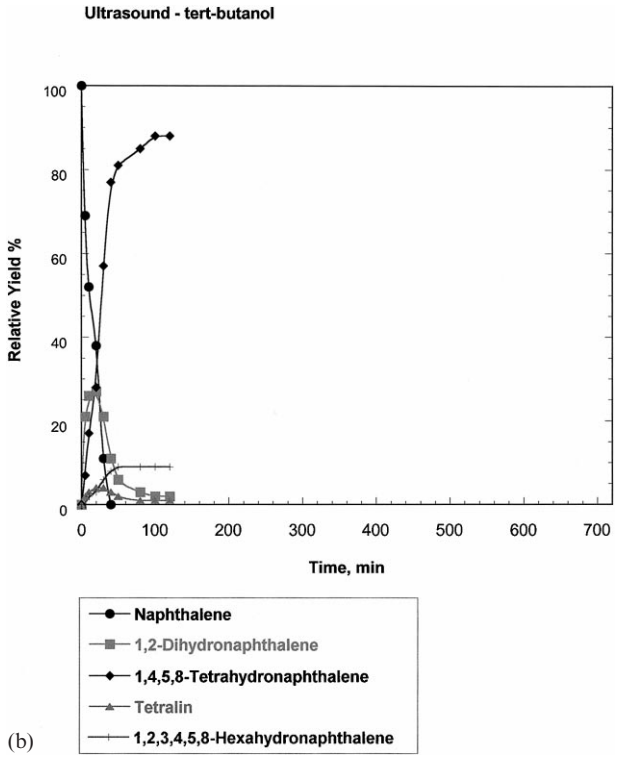
[a] Values in parentheses refer to Ref. [2] under stirring conditions.

The Birch reduction product 1,4,5,8-tetrahydronaphthalene **3** is obtained in high yield in both cases. The reaction rate is higher without an induction period in the ultrasonically activated reaction. On the other hand, in this case, the transitory formation of 1,2-dihydronaphthalene **2** is observed. Substituting *tert*-butanol for 2-propanol (a better proton donor) favored this tendency. **2** is the major product formed in the first step of the reaction performed with ultrasound. The transformation **2** to **3** occurs when all of **1** is consumed (Fig. 2). In the stirring experiment, **2** is no longer a major product during the course of the reaction. In both cases (with 2-propanol or *tert*-butanol) it was impossible to start a reaction without the help of sea sand or with simple magnetic stirring. Thus it appears clearly that ultrasound and a vigorous abrasive effect are drastic procedures required for calcium activation, but the comparison shows clearly the difference in the products distribution.

To understand the phenomenon leading to these results, the surface of the calcium was examined with the help of electron microscope (Fig. 3). In both cases the surface was bright, but the micrographs show characteristic differences in morphologies. Calcium shots from the stirred experiment show scratches and punctures on the smooth area, and it is remarkable that the place of an accident is not the center for initiation of a particular corrosive effect consecutive to the reaction. In the ultrasound experiment, calcium exhibits patterns of deep conical holes. This typical effect of ultrasound was previously observed on the chemical attack of a lithium surface [13]. However, an important difference must be noted when the two metals are submitted to ultrasound in the absence of a substrate. When submitted to ultra-

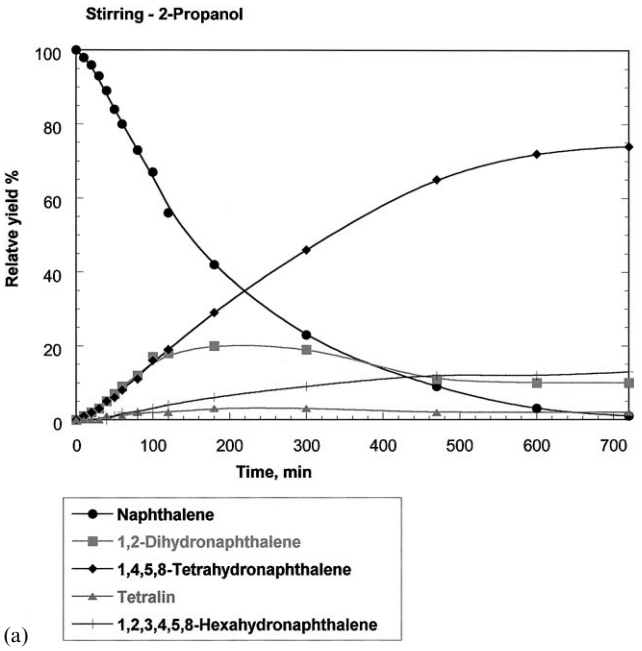


(a)

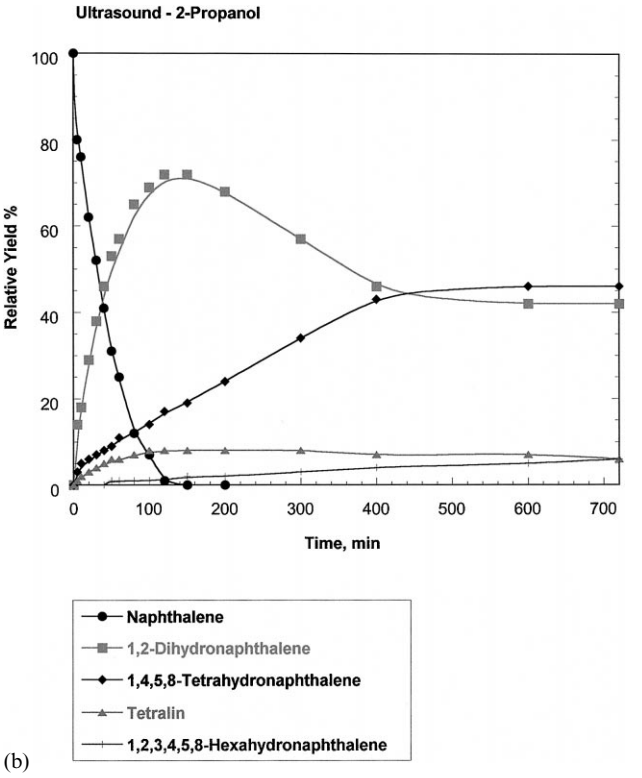


(b)

Fig. 1. Naphthalene reduction with calcium in ethylenediamine–*n*-butylamine mixture with *tert*-butanol as proton source.



(a)



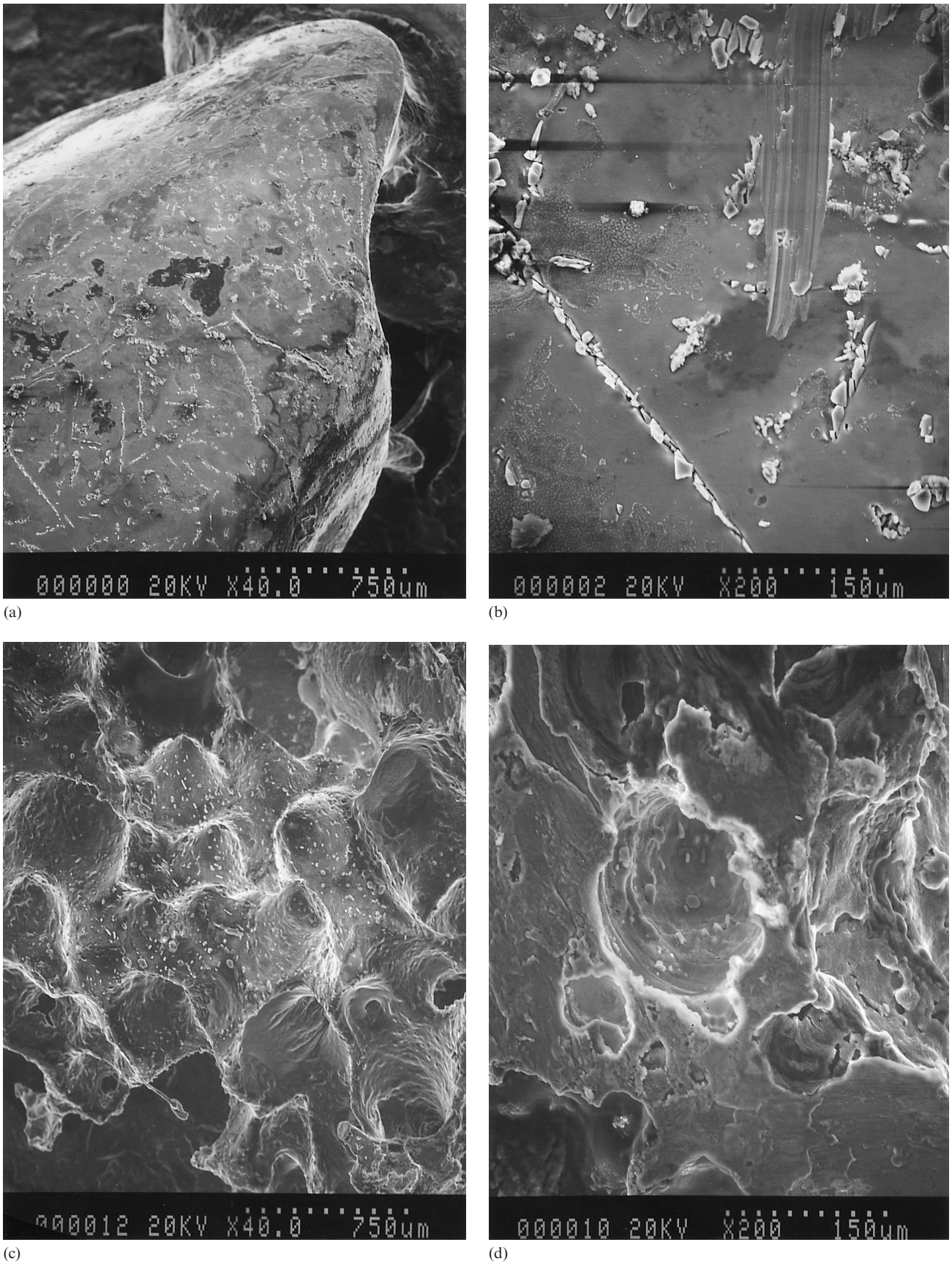
(b)

Fig. 2. Naphthalene reduction with calcium in ethylenediamine–*n*-butylamine mixture with 2-propanol as proton source.

sound effects lithium shows a dislocated surface, but no alteration was observed for calcium.

The advantage of the differences in selectivity observed in the ultrasound method was used to obtain a stepwise reduction of several aromatic compounds. Compared with previously described stirring reactions [1,26,27], the reaction times are shorter and substituted phenyl and naphthalene derivatives can be reduced (Table 2).

Addition of a proton source in the reaction mixture avoids the formation of calcium amide. Hence, non-conjugated products are obtained instead of the

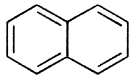
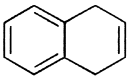
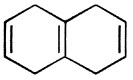
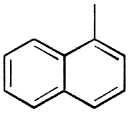
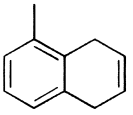
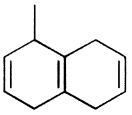
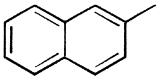
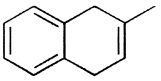
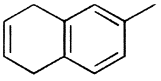
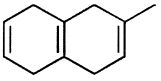
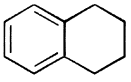
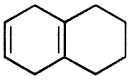
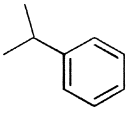
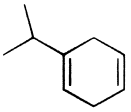
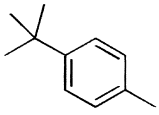
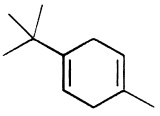


(a) (b)

(c) (d)

Fig. 3. Calcium surface activated by abrasion with sand in the stirred experiment (a), (b). In ultrasonic conditions (c), (d).

Table 2
Calcium reduction of aromatic compounds in *n*-butylamine–ethylenediamine mixture under ultrasonic conditions

substrate	Calcium (equivalents)	Alcohol mmol	Time min	products	Isolated Yields %
	1.66	2-propanol (5)	120		88
	2.66	tert-butanol (5.3)	120		88
	1.66	2-propanol (4.3)	60		74
	2.66	tert-butanol (5.3)	180		35 (a)
	1.66	2-propanol (4)	150	 (61%)  (39%)	89
	2.66	tert-butanol (5.3)	60		81
	1.5	tert-butanol (3)	120		84
	1.5	tert-butanol (3)	120		75
	1.5	tert-butanol (3)	240		34

1,3-conjugated one that can be easily reduced to olefin. It was claimed that results are similar regardless the alcohol. We found that if it is valid with stirring, the ultrasonic procedure leads to different products according to the alcohol used:

- with *tert*-butyl alcohol, each aromatic was reduced to 1,4-cyclohexadiene;
- it was difficult to reduce a trisubstituted ring or a disubstituted one bearing a *tert*-butyl group, even so the quantity of calcium was higher. With 2-propanol, it is impossible to start the reaction with the simple substituted benzene rings shown in Table 2 and calcium remains unchanged. It was then feasible to reduce partially naphthalene and substituted naphthalenes.

Ultrasound supplies mechanical energy that is partially absorbed and transformed to heat. As the absorption is relative to the viscosity of the medium, it is essential to control the temperature with an efficient cooling system when the composition of the mixture

changes during the course of a reaction. This is especially significant in our case, where the concentration of calcium is limited by the solubility in the medium of by-products, calcium amide, calcium *tert*-butoxide or isopropoxide. The quantity of calcium used has to be less than 0.83 M for a reaction without alcohol, 0.33 M for the reduction with *tert*-butanol, and 0.41 M with 2-propanol.

These experimental data suggest some hypotheses in the field of the ultrasonic activation of a metal and on the mechanism of the reduction with calcium in amine mixture.

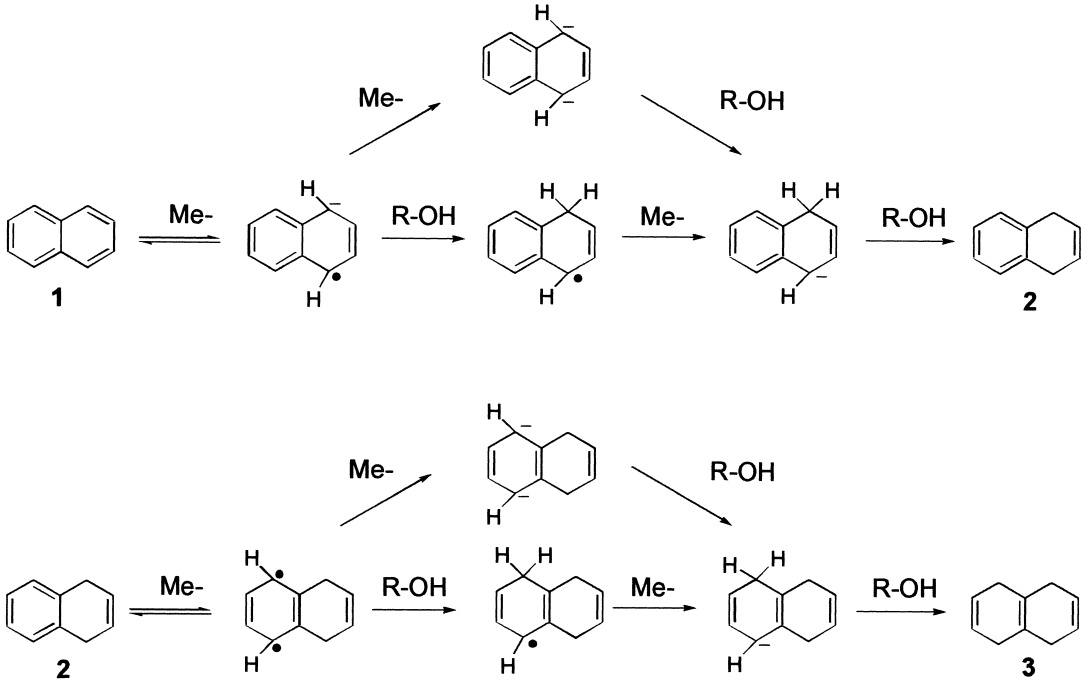
Activation of a metallic surface in the ultrasonic field is the result of cavitation, that is the phenomenon including the formation and behavior of bubbles in a liquid submitted to variations of pressure [28–30]. The lifetime and properties of a bubble are directed by the coupling between its size and the parameters of the ultrasonic wave in the medium (amplitude, wavelength). Close to or on a boundary the bubble may pulse during several cycles (stable cavitation), the diameter increases by rectified diffusion, and for specific values the cavity collapses (transient cavitation). It is generally assumed that this latter event is able to activate the metal by removing small particles of the solid because the unsymmetrical collapse generates a high velocity jet of liquid towards the surface [31–34]. Nyborg and coworkers have demonstrated that a pulsating bubble generates high velocity microstreaming in its vicinity that is also able to remove a film from a surface [35,36]. We believe, too, that such a phenomenon must be important for surface activation because this is a rather long phenomenon compared with the stress induced by a cavity collapsing in 10^{-5} s. This could be an explanation for the typical craters observed on a metal during a reaction.

The reaction pathway proposed for the Birch reaction can be accepted for the reduction of an aromatic nucleus with calcium in the mixture ethylenediamine–*n*-butylamine; even so, it clearly appears that electrons added to the substrate come from the metal surface rather than from a dissolved 'ion pair' (M^+, e^-). The reaction **1→3** can be constituted by the two successive transformations **1→2** and **2→3**, the kinetics of both reactions being controlled by the first electron transfer and the protonation rate. **1** Has a higher electron affinity than **2**; consequently, it would be preferentially reduced [37–39], but the access to the reactive surface for one or another species depends on diffusion processes through the surrounding liquid film [40].

Thus, in spite of the concentration difference, **2** can be reduced faster than **1**. This is the situation observed in the stirred diffusion-controlled experiments. When the calcium surface is submitted to ultrasound, the stable and the transient cavitations induce eddies that suppress the kinetic control of the reaction by mass transport. As a consequence, close to the solid surface the concentration of **2** cannot increase relative to **1**, and the latter, with a higher electron affinity, is preferentially reduced.

4. Conclusion

These results point out some specific effects of ultrasound in heterogeneous systems. Suppression of the



kinetic control of a reaction by mass transfer is underlined. This phenomenon is especially important for any kind of catalysis on a surface (e.g. electrochemistry, heterogeneous photochemistry). The use of ultrasound is not limited to surface activation, but can be used to modulate a selectivity. Concerning the promotion of a heterogeneous reaction, it seems that a violent collapse of a bubble is not the only event of the cavitation that can be involved in the typical surface *cleaning* by ultrasound. Microstreaming induced by a pulsating bubble could also create activated pits in the metal.

5. Sample characteristics

1,4-Dihydronaphthalene [41], colorless oil, IR: 3062, 3030, 2981, 2866, 2821, 1666, 1580, 1497, 1456, 1426, 1183, 1041, 998, 920, 745, 659 cm^{-1}. NMR: $CDCl_3$, ^1H; 7.48 (m, 4H), 6.32 (m, 2H), 3.78 ppm (s, 4H). ^{13}C; 133.9, 128.2, 125.7, 124.5, 29.6 ppm. MS: 131, 130, 129, 128, 127, 102, 77, 64, 63, 51, 43, 39.

1,4,5,8-Tetrahydronaphthalene [42], white crystals, mp = 54°C, IR: 3029, 2877, 2845, 2816, 1661, 1430, 1397, 1261, 1216, 1099, 987, 979, 972, 758, 669 cm^{-1}. NMR: $CDCl_3$, ^1H; 5,71 (s, 4H), 2.53 ppm (s, 8H). ^{13}C; 124.3, 123.1, 30.7 ppm.

1,2,3,4,5,8-Hexahydronaphthalene [43], colorless oil, IR: 2924, 2829, 1440, 1322, 1277, 1162, 906, 830, 817, 801 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.71 (s, 2H), 3.52 (s, 4H), 1.87 (m, 4H), 1.63 ppm (m, 4H). ^{13}C; 125.5, 124.5, 31.6, 29.9, 23.3 ppm.

1,2,3,4,5,6,7,8-Octahydronaphthalene [2], colorless oil, IR: 2924, 2855, 2829, 1440, 1322, 1277, 1162, 987, 906, 830, 817, 801 cm^{-1}. NMR: $CDCl_3$, ^1H; 1.83 (m, 8H), 1.57 ppm (m, 8H). ^{13}C; 127.9, 30.4, 23.2 ppm. MS: 136, 121, 107, 95, 91, 79, 67, 53, 41. The minor isomer appears to be 1,2,3,4,5,6,7,10-octahydronaphthalene. It was characterized from the mixture of isomers. In the ^1H NMR experiment the characteristic chemical shift of the vinyl proton was found at 5.35 ppm. ^{13}C chemical shifts: 119.5, 37.5, 35.7, 31.2, 28.0, 26.5, 25.6, 11.47 ppm. The two isomers were separated and identified by GC mass spectroscopy experiment and show identical fragmentations.

1,2,3,4-Tetrahydro-5-methylnaphthalene, colorless oil, IR: 3018, 2928, 2857, 2835, 1587, 1463, 1449, 1434, 795, 764, 706, 665 cm^{-1}. NMR: $CDCl_3$, ^1H; 6.95 (m, 3H), 2.77 (tr, 2H), 2.59 (tr, 2H), 2.20 (s, 3H), 1.81 ppm (m, 4H). ^{13}C; 137.0, 136.5, 135.4, 127.1,127.0, 125.2, 30.2, 26.8, 23.6, 23.1, 19.5 ppm. MS: 147, 146, 132, 131, 129, 128, 118, 117, 115, 91, 77, 51, 39.

1,4-Dihydro-5-methylnaphthalene, [44], colorless oil, IR: 3070, 3029, 2968, 2861, 2821, 1672, 1466, 1438, 1424, 767, 704, 660 cm^{-1}. NMR: $CDCl_3$, ^1H; 7.01 (m, 3H), 5.87 (s, 2H), 3.37 (tr, 2H), 3.21 (tr, 2H), 2.21 ppm (s, 3H). ^{13}C; 135.9, 133.7, 132.6, 127.2, 126.1, 125.6, 124.4, 124.2, 29.9, 27.4, 19.3 ppm. MS: 145, 144, 143, 142, 141, 130, 129, 128, 127, 115, 77, 71, 65, 63, 51, 38, 31.

1,4,5,8-Tetrahydro-1-methylnaphthalene, colorless oil, IR: 3025, 2966, 2927, 2874, 2846, 2815, 1663, 1455, 1429, 1055, 982, 964, 908, 734, 682, 661 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.73 (m, 2H), 5.66 (m, 2H), 2.77 (m, H), 2.51 (m, 6H), 1.07 ppm (d, 3H, $J = 7$ Hz). ^{13}C; 131.4, 127.8, 124.7, 123.9, 123.1, 122.7, 34.3, 31.1, 31.07, 28.46, 20.4 ppm. MS: 39, 51, 77, 83, 91, 92, 105, 115, 128,129, 131, 146.

1,4-Dihydro-2-methylnaphthalene, **1,4-dihydro-6-methylnaphthalene**. The two isomers were separated and identified in a GC mass spectroscopy experiment. The spectra are in agreement with those of literature data [44]. In addition, ^1H and ^{13}C NMR spectra of each compound could be deduced from a sample contaminated with 20% of the other isomer.

1,4-Dihydro-2-methylnaphthalene. NMR: $CDCl_3$, ^1H; 7.11 (m, 5H), 5.58 (m, H), 3.32 (m, 4H), 1.79 ppm (s, 3H). ^{13}C; 131.8, 128.1, 125.7, 118.8, 34.5, 30.4, 23.1 ppm. MS: 144, 143, 142, 141, 130, 129, 128, 127, 115, 102, 89, 77, 71, 63, 51, 39.

1,4-Dihydro-6-methylnaphthalene. NMR: $CDCl_3$, ^1H; 6.94 (m, 3H), 5.88 (m, 2H), 3.27 (m, 4H), 2.28 ppm (s, 3H). ^{13}C; 128.9, 126.7, 125.6, 29.6, 29.3, 23.1 ppm. MS: 144, 143, 142, 141, 143, 141, 130, 129, 128, 127, 115, 102, 89, 77, 71, 63, 51, 39.

1,4,5,8-Tetrahydro-2-methylnaphthalene, colorless oil, IR: 3026, 2964, 2873, 2840, 2811, 1659, 1431, 1375, 968, 781, 658 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.72 (m, 2H), 5.42 (m, H), 2.54 (m, 6H), 1.68 ppm (s, 3H). ^{13}C; 131.3, 124.4, 124.3, 123.1, 118.6, 35.7, 31.8, 30.7, 30.5, 22.9 ppm. MS: 146, 131, 129, 128, 117, 116, 115, 105, 92, 91, 77, 68, 65, 51,39.

1-Isopropyl-1-cyclohexene [45], colorless oil, IR: 2959, 2927, 2872, 2858, 2837, 1664, 1458, 1438, 1381, 1288, 1140, 1033, 918, 801, 770, 655 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.38 (m, H), 2.12 (qui, H), 1.96 (m, 4H), 1.57 (m, 4H), 0.97 ppm (d, 6H, $J = 6.8$ Hz). ^{13}C; 143.4, 118.3, 35.35, 25.99, 25.26, 23.23, 22.89, 21.35 ppm. MS: 124, 109, 95, 81, 67, 55, 51, 41, 38.

1-Isopropyl-1,4-cyclohexadiene [46], colorless oil, IR: 2960; 2874; 2822; 1687; 1648; 1464; 1429; 1396; 1380; 1361; 1033; 959; 908; 735; 698; 665 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.70 (m, 2H), 5.43 (m, H), 2.64 (m, 4H), 2.17 (m, H), 1.10 ppm (d, 6H, $J = 6.8$ Hz). ^{13}C; 140.5, 124.4, 124.2, 115.9, 34.86, 26.73, 26.52, 21.05 ppm. MS: 39, 41, 51, 77, 78, 79, 80, 84, 91, 105, 107, 122.

4-Methyl-1-*tert*-butyl-1,4-cyclohexadiene, colorless oil, IR: 3022, 2964, 2906, 2871, 2818, 1657, 1478, 1463, 1446, 1360, 1163, 949, 782 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.50 (m, 1H), 5.44 (m, 1H), 2.63 (m, 4H), 1.66 (s, 3H), 1.04 ppm (s, 9H). ^{13}C; 142.5, 130.7, 119.2, 115.3, 34.8,

31.9, 29.0, 25.9, 22.8 ppm. MS: 39, 41, 43, 57, 77, 79, 80, 93, 94, 107, 135, 150.

4-Methyl-1-*tert*-butyl-1-cyclohexene [47], colorless oil, IR: 3051, 2953, 2871, 1478, 1462, 1363, 1257, 798 cm^{-1}. NMR: $CDCl_3$, ^1H; 5.44 (m, 1H), 2.10 (m, 4H), 1.64 (m, 3H), 1.03 (s, 9H), 0.95 ppm (d, 3H, $J=$ 6.3 Hz). ^{13}C; 121.4, 117.1, 34.3, 31.9, 29.2, 28.5, 27.3, 24.6, 22.0 ppm. MS: 41, 57, 67, 77, 81, 95, 109, 137, 152.

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