JOURNAL OF CATALYSIS 147, 1–4 (1994)

The Influence of Sonication on the Palladium-Catalysed Dehydrogenation of Tetrahydronaphthalene

T. J. Mason,* J. P. Lorimer,* L. Paniwnyk,* P. W. Wright,† and A. R. Harris†

**School of Natural and Environmental Sciences, Coventry University, Coventry CV1 5FB, United Kingdom; †Fisons plc, Pharmaceutical Division, R&D Laboratories, Bakewell Road, Loughborough, Leicestershire LE11 0RH, United Kingdom*

Received October 1, 1993; revised December 17, 1993

The dehydrogenation of tetrahydronaphthalene to naphthalene using 3% Pd/C in diethylene glycol (digol) under the influence of sonication is reported. The conventional reaction in digol at 200°C reached 55% conversion in 6 h, whereas using sonication at 180°C, complete reaction could be achieved in the same time. Pulsed ultrasound (at 50% cycle) was as effective as continuous sonication. The activity of the catalyst in the absence of sonication fell as the reaction proceeded but could be revitalised by applying ultrasound. Sonication had a much smaller effect on the reaction performed in triethylene glycol dimethyl ether. © 1994 Academic Press, Inc.

INTRODUCTION

Saturated or partially saturated six-membered carbocyclic compounds can usually be dehydrogenated to the corresponding aromatic compounds (1, 2). The reaction can be carried out chemically using reagents such as sulphur, selenium, or 2,3-dichloro-5, 6-dicyano-*p*-benzoquinone (DDQ). Such reactions often give low yields and noxious by-products. A "cleaner" reaction can be achieved using catalytic dehydrogenation over palladium, or less frequently platinum, rhodium, or nickel catalysts (1), but harsh conditions involving high temperatures are usually required.

In general, the catalytic activity of metals is enhanced by ultrasonic irradiation (3) and this has been used to improve reactions such as catalytic hydrogenation (4, 5). In contrast, catalytic dehydrogenation under the influence of ultrasound does not appear to have received much attention, although Boudjouk and Han (6), in a paper concerned with catalytic transfer hydrogenation, have noted the disproportionation of cyclohexene to cyclohexane and benzene with a palladium catalyst under the influence of ultrasonic irradiation.

We hypothesized that the use of ultrasound might allow catalytic dehydrogenation reactions to be performed under less forcing, and hence under more synthetically useful conditions than those used conventionally. In order to test this hypothesis, we chose to use tetrahydronaphthalene (tetralin) as the model reactant using 3% Pd/C as the catalyst. Although a wide range of high-boiling solvents have been used for this type of reaction, we chose digol (diethylene glycol) and triglyme (triethylene glycol dimethyl ether), since solvents of this type offer the advantage, in syntheses, of ease of removal during workup by virtue of their miscibility with water.

EXPERIMENTAL

In a typical sonochemical reaction, 25 cm^3 digol (diethylene glycol) was added to a dimple cell (7), and this was placed into an electromantle and heated to a steady temperature of approximately 170°C under nitrogen. On reaching the required temperature, tetrahydronaphthalene (3 g, 0.023 mol) was added together with 3% palladium on activated charcoal catalyst (0.1 g). Sonication was introduced via a Sonics and Materials (VC500 sonicator system operating at 20 kHz, equipped with a tapered horn with tip diameter 0.3 cm operating at power setting 2. Sonication caused the temperature within the reaction vessel to rise to approximately 180°C, where it remained relatively stable. The reaction was sonicated for 6 h and aliquots were withdrawn hourly and filtered through silica to remove the solid catalyst. Samples were analyzed by glc on a 2 m × 0.5 cm 5% Carbowax column at 210°C using a Perkin–Elmer F33 instrument.

The corresponding "thermal" reactions were treated as above, but the solvent temperature was maintained entirely by the electromantle. The reaction vessel was a three-necked, round-bottomed flask fitted with a condenser, a thermometer, a nitrogen inlet, and an overhead mechanical stirrer. All reactions were studied with the same stirring speed.

RESULTS AND DISCUSSION

The Effect of Sonication

Conventional dehydrogenation of tetrahydronaphthalene using palladium on charcoal was carried out in

0021-9517/94 $6.00
Copyright © 1994 by Academic Press, Inc.
All rights of reproduction in any form reserved.

digol at 200°C. Below this temperature, there was no significant reaction (Table 1). At 200°C, however, the initial rate of the thermal reaction was relatively rapid, giving 36% conversion in 2 h, but thereafter the reaction slowed. This was a common characteristic of the conventional reaction and suggested that the catalyst was becoming deactivated, perhaps via the preferential adsorption of hydrogen and/or reaction product onto the surface, which might mask the active sites. It has been suggested that competition for active sites between the fully aromatic product and the partially saturated starting material and intermediates would favour the product as a consequence of the greater degree of π-bonding possible (1). It has also been reported that conventional thermal catalytic dehydrogenation of tetralin occurs only in a vigorously refluxing media (8, 9). This might suggest that removal of the hydrogen formed in the reaction from the solution is important in that it would favour desorption of gas from the catalyst surface and release the active sites for further reaction. As our reactions were carried out below the reflux temperature of the solvent, a buildup of hydrogen on the catalyst might explain the slowing of the reactions. Certainly in our reaction, the addition of portions of fresh catalyst during the reaction countered the poisoning effect. Thus, the dehydrogenation at 200°C was run for 5 h until the reactivity "tailed off," fresh catalyst was added, and this resulted in a temporary increase in the reaction rate. When the rate once again began to tail off, a further portion of catalyst was added. After 12 h, the conversion was only 72.9%, even with the aid of these two extra additions of catalyst.

Sonicated reactions, on the other hand, did not exhibit the falloff in reaction rate, which was fairly constant throughout (Table 1). In fact, the sonicated reaction at 160°C had a similar rate of dehydrogenation to that observed at 200°C for the thermal reaction, while the dehydrogenation under sonication was complete at 180°C after 7 h. The sonochemical activation can be attributed to the disruptive effect of cavitational collapse near the surface, which produces an asymmetrical inrush of fluid to fill the void and generates a liquid jet targeted at the surface. The jet can be sufficiently powerful to cause pitting of the surface (erosion) and/or fragmentation and individual particles can also be projected in the medium and collide violently with others, causing surface erosion. These processes serve to activate solid catalysts and increase mass transfer to the surface by disruption of the interfacial boundary layers. In addition to this, the well-known degassing effect of sonication (10) might result in removal of hydrogen from the system at temperatures well below the boiling point of the liquid.

If the root cause of the falloff in catalytic activity is some form of deactivation of the catalyst, then it should be possible to "rejuvenate" a thermal reaction which has run its course by reactivation of the catalyst through sonication. To test this hypothesis, a thermal reaction was stirred for a period of 5 h at 200°C, after which time the conversion was 48.5% and was no longer increasing rapidly. Sonication was applied and the reaction was "activated," producing 15% more product in the next hour, compared with only an additional 5% produced under conventional thermal conditions at 200°C in the same amount of time.

All of the studies above were carried out using sonication at the low power setting of 2, and so the effect of increasing the power was investigated (Table 2). Using the same ultrasonic horn system, the power was increased to setting 5 which, under continuous sonication (100% pulse), improved the conversion at 180°C from 93.3% to 100% in 6 h.

TABLE 1

Oxidation of Tetrahydronaphthalene (THN) at Different Temperatures under Conventional and Sonochemical Conditions[a]

	Thermal (°C)			Sonicated[b] (°C)	
Time (h)	160	180	200	160	180[c]
1	3.3	7.1	29.5	9.4	18.4
2	6.5	9.5	36.6	19.9	36.1
3	10.1	10.6	40.9	27.2	48.5
4	13.9	13.5	45.9	35.7	63.3
5	16.9	15.2	50.6	46.5	79.3
6	19.0	17.8	54.6	58.4	93.3

[a] THN 3 g, digol 25 cm^3, 0.1 g 3% Pd/C.

[b] 0.3 cm tip, power setting 2.

[c] 100% conversion after 7 h.

The Effect of Ultrasonic Dose

The question remains as to what dosage of ultrasound is sufficient to give this conversion; i.e., does the ultrasound need to be continuous? The instrumentation allows the irradiation to be applied in a pulse mode. The pulse is measured as a percentage, viz., percentage of time for which the ultrasound is switched on per S (100% = continuous, 0 = ultrasound off). A short high-powered burst (or pulse) of sonication should be enough to expose fresh active sites on the catalyst, although the rate would then be expected to fall during the off period. From the results obtained (Table 2), it can be seen that a 50% pulse cycle gave a similar rate of conversion to the continuously sonicated reaction. However, a 10% pulse cycle gave a slightly slower rate. In each case, the rates under sonication were much faster than the corresponding thermal reactions.

These results indicate that continuous sonication is not necessary to achieve significant rate enhancement and that the pulse mode would offer considerable energy savings, particularly on processes carried out on a large scale.

The Effect of Solvent

The nature of the solvent used for sonicated reactions is very important. The dehydrogenation of tetrahydronaphthalene was attempted in two solvents, digol and triglyme, and the conventional thermal and sonicated reactions were compared (Table 3).

For thermal reactions at 200°C, the more effective solvent was triglyme. In this solvent, after 5 h reaction, 81.3% conversion was achieved, compared with only 50.6% in digol under otherwise identical conditions. It would therefore appear that an ether-type solvent is more efficient for a thermal reaction.

Sonication of the reaction in triglyme at 180°C gave a rate similar to that of the conventional reaction at 200°C. This shows the beneficial effect of ultrasound in achieving the same conversion of ca. 85% in 6 h as a thermal reaction but at a lower reaction temperature. In contrast, using digol as the solvent, the thermal reaction at 200°C, which gives only 55% conversion in this amount of time, is enhanced markedly by sonication to give 100% conversion at 180°C.

The efficiency of a sonochemical reaction depends to some extent on the energy of cavitational collapse. This, in turn, depends on the vapour pressure of the solvent in that more violent collapse is achieved at lower vapour pressures (10). Under the reaction conditions employed, digol (b.p. = 245°C) will have a considerably lower vapour pressure than triglyme (b.p. = 216°C), which is in agreement with the larger sonochemical effect found in the former solvent.

TABLE 2

Oxidation of Tetrahydronaphthalene (THN) at Different Ultrasound Pulse Cycles[a]

	Sonic pulse (%)[b]			
Time (h)	100	50	10[c]	Thermal (for comparison)
1	24.7	27.3	10.6	7.1
2	42.5	48.9	21.1	9.5
3	56.6	55.0	31.7	10.6
4	72.7	70.2	52.7	13.5
5	90.2	88.9	77.3	15.2
6	100	100	83.1	17.8

[a] THN 3 g, digol 25 cm^3, 0.1 g 3% Pd/C, 180°C.
[b] 0.3 cm tip, power setting 5.
[c] 100% conversion after 7 h.

TABLE 3

Oxidation of Tetrahydronaphthalene (THN) in Different Solvents, Showing the Effect of Ultrasound[a]

	Solvent			
	Digol		Triglyme	
Time (h)	Thermal[a]	Sonicated[c]	Thermal[b]	Sonicated[c]
0.5	—	16.2	15.3	10.2
1	29.5	24.7	29.9	20.2
1.5	—	33.1	39.2	33.5
2	36.6	42.5	48.1	40.2
3	40.9	56.6	61.5	55.9
4	45.9	72.7	73.0	78.6
5	50.6	90.2	81.3	80.6
6	54.6	100	88.9[d]	84.4[d]

[a] THN 3 g, digol 25 cm^3, 0.1 g 3% Pd/C.
[b] 200°C.
[c] 0.3 cm tip, power setting 5, 180°C.
[d] Conversion after 10 h, thermal = 100%, sonicated = 93%.

In view of the difference in efficiency of these solvents under thermal conditions, it seems likely that the structure of the solvent has some bearing on reactivity. Hydrogen bonding present in digol will be absent from triglyme, and this may well reduce its efficiency as a conventional dehydrogenation solvent. Sonication disrupts hydrogen bonding, and this may contribute to the improved performance of the reaction in digol in an ultrasonic field.

In summary, it would appear that high-boiling ethereal solvents, such as triglyme, are the most efficient solvents for catalytic dehydrogenation. A preferred solvent for a sonicated reaction is the higher boiling hydroxyl-containing solvent digol. Efficient sonochemically assisted dehydrogenation was shown to occur at 20°C below the temperature required for the corresponding thermal reaction in digol. Continuous sonication was not necessary in this reaction, since a 50% pulsed cycle achieved a similar conversion.

ACKNOWLEDGMENT

We thank Fisons plc for supporting this work.

REFERENCES

1. Fu, P. P., and Harvey, R. G., *Chem. Rev.* **78,** 317 (1978).
2. Oxidations in Organic Chemistry, Hudlicky, M., *ACS Monogr.* **186,** 47 (1980).
3. Lindley, J., *in* "Critical Reports on Applied Chemistry" (T. J. Mason, Ed.), Vol. 28, Chap. 2, p 27. Elsevier, Amsterdam, 1990.
4. Suslick, K. S., Casadonte, D. J., and Doktycz, S. J., *Solid State Ionics* **32/33,** 444 (1989).
5. Cains, P. W., McCausland, L. J. Bates, D. M., and Mason, T. J., *Ultrasonics Sonochem.* **1,** 47 (1994).

6. Boudjouk, P., and Han, B. H., *J. Catal.* **79,** 489 (1983).
7. Mason, T. J., "Practical Sonochemistry," p. 82. Ellis Horwood, Chichester, U.K., 1991.
8. Linstead, R. P., and Michaelis, K. O. A., *J. Chem. Soc.*, 1134 (1940).
9. Malz, R. E., and Greenfield, H., *in* "Catalysis of Organic Reactions" (P. N. Rylander, H. Greenfield, and R. L. Augustine, Eds.), p. 262. Dekker, New York, 1988.
10. Mason, T. J., and Lorimer, J. P., "Sonochemistry," Chap. 2, p. 17. Ellis Horwood, Chichester, U.K., 1988.