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Research Note

The effect of cavitating ultrasound on the heterogeneous aqueous hydrogenation of 3-buten-2-ol on Pd-black

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Abstract

The effect of ultrasound at 20 kHz on the heterogeneous aqueous hydrogenation of 3-buten-2-ol employing a Pd-black catalyst has been studied isothermally at 295 K, forming 2-butanone and 2-butanol products. Our work here shows that adding 1-pentanol as an inert dopant had the effect of inducing cavitation in the ultrasound-treated reaction where it otherwise would not occur. The selectivity showed a 700% increase toward 2-butanol formation and the activity enhanced a factor of 10.8 compared to the noncavitating high-power ultrasound experiment. This study demonstrates that "inert dopants" may have use as synthetic tools in sonocatalysis.

Keywords: Inert dopant; Sonocatalysis; Hydrogenation; Cavitation

1. Introduction

Using ultrasound to enhance activity, and to a lesser extent to alter selectivity, in heterogeneous condensed-phase reactions is well known [1–7], with the first paper on sonocatalysis having been published over 30 years ago [8]. In principle, there exists two separate domains for sonochemistry, these are noncavitating and cavitating ultrasound regimes. For commercially available instruments, bath systems by virtue of their lower acoustic intensity are usually non cavitating whereas probe systems can be either noncavitating or cavitating. One objective of the present study is to contrast differences in a heterogeneous catalysis reaction for noncavitating and cavitating ultrasound compared to a control (stirred and silent) system. Only through "doping" our solution were we able to initiate the fast onset of cavitation during ultrasound treatment, and to enable the chemical effects arising from cavitating conditions to be studied. To our knowledge, this cavitation-enabling doping procedure is the first such study of its kind.

The aqueous phase hydrogenation of 3-buten-2-ol was the subject of a prior investigation by us [9] and is an excellent choice for probing the chemical effects of ultrasound as it undergoes competing reaction pathways yielding two products. The full reaction process is summarized in Scheme 1. For example, in one pathway H-atom elimination reactions generate the intermediate 3-buten-2-one, which eventually becomes hydrogenated to 2-butanone. In a second competing reaction pathway, H-atom addition results in direct hydrogenation to the saturated alcohol 2-butanol. Most notable in our earlier study [9] was the observation of a constant 2-butanone-to-2-butanol ratio throughout the course of the reaction for the control (e.g., silent) experiment. Conversely, for the ultrasound-assisted reaction, a pronounced increase in 2-butanol concentration during the latter half of the reaction occurred. Concomitant with the rise in 2-butanol concentration was a decrease in ultrasound power delivered to solution. Empirical observations we have made suggest that short-chain alcohols encourage cavitation; thus, the formation of product 2-butanol initiates onset from high-power noncavitating to cavitating sonocatalysis. The effects of which are a change in selectivity and enhanced activity. In this Research Note we propose, using "inert dopants,"

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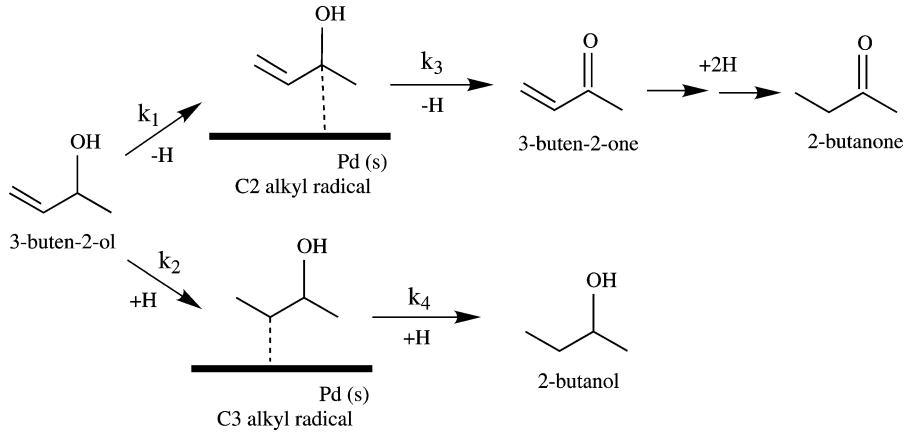

Scheme 1. The reduction of 3-buten-2-ol is shown. Reaction pathway 1 leads to a Pd surface-bound C2 alkyl radical, followed by 3-buten-2-one formation, and eventually 2-butanone generation. Pathway 2 is proposed to form a C3 alkyl radical and eventually the saturated alcohol (2-butanol).

a novel way of controlling cavitation with applications in catalysis.

2. Experimental

2.1. Materials and apparatus

The 3-buten-2-ol reagent was supplied by Aldrich Chemical Company (97% purity). A commercial Pd-black catalyst (Aldrich, 99.9% purity metals basis) with a N_2 BET surface area of 42 m^2/g was used in this study. Deionized water (18 MΩ-cm) was used as the solvent. Hydrogenations were performed with hydrogen gas (A&L specialty gas, 99.99% purity) at a pressure of 6.5 atm (80 psig). All components used for the reaction apparatus are commercially available and have been described in detail previously [9,10]. Experiments were conducted isothermally with a temperature uncertainty of ±2.5 K. Analyses of samples collected during an experiment were analyzed on a Hewlett–Packard GC/MS (5890 GC and 5972 MSD). Authentic standards were employed in the calibration of mass area counts. The column selected for separation was a 30-m, 0.5-μm DB-5MS column.

2.2. Experimental procedure

For all experiments, 50 mL of water and catalyst (3.0 ± 0.2 mg Pd-black) were added to the reaction cell. For ultrasound-assisted, as well as stirred (blank) experiments, the catalyst was reduced with hydrogen (80 psig) in water using noncavitating ultrasound at an average power of 360 W (electrical; 90% amplitude) for 4 min prior to reaction. The concentration of the reagent employed was 100 mM (33 M/g-catalyst based on initial concentrations). The first sample for each experiment was taken for time equal to zero minutes and filtered through a 0.45-μm hydrophilic Millipore filter to remove catalyst powder into a capped vial for subsequent GC/MS analyses.

For stirred (control/silent) experiments, the cell was connected to the probe assembly and pressurized with hydrogen. Stirring was commenced and after the system reacted a (filtered) sample was collected. Further samples were taken for subsequent time intervals using the same method of pressurizing and stirring.

For ultrasound-treated experiments, the cell was connected, vented, and pressurized with hydrogen as just described. The solution in the cell was irradiated with ultrasound and samples were collected. During noncavitating sonication, an amplitude of 90% was employed, resulting in 360 ± 15 W delivered from the power supply. For cavitating ultrasound 50 mM 1-pentanol dopant in solution caused cavitation within 7 s of turning on the sonifier resulting in 190 ± 12 W delivered to the convertor, again at 90% sonifier amplitude.

3. Results and discussion

3.1. Noncavitating versus cavitating ultrasound processing

For us to contrast noncavitating and cavitating ultrasound conditions requires that we have clear criteria identified by which we can identify the onset of cavitation in an ultrasonically treated system. Three events occurred that made the onset of cavitation unambiguous in our experiments. Our criteria are based on both beaker experiments, as well as sealed-cell reactor experiments, employing simple (terminal) alcohols of methanol through 1-heptanol. First, for our 90% probe amplitude and 6.5 atm of static reactor pressure, the applied sonifier power decreased from ∼ 350 to ∼ 200 W when the solution changed from noncavitating to cavitating. (The power drop may, in part, be rationalized by the increased acoustic impedance mismatch between the titanium horn and solution by incorporating gas (air or hydrogen) into the liquid.) Second, the solution volume doubled upon cavitation, and in so doing the solution went from clear to white, which is reasonable for a system that possesses

a volume equivalent of dissolved gases. For the sealed-cell that we cannot see inside of during ultrasound treatment, upon venting we observed a spray of foam emitted from the vessel, consistent with a volume doubling. Third, upon cavitation the usually loud audible sound became silent aside from the 20 kHz carrier frequency. The alcohols methanol, ethanol, and 1-heptanol, at 50 mM aqueous concentration, did not demonstrate the above signs of dramatic cavitation onset, either in the sealed reactor cell (nitrogen atmosphere) at 6.5 atm or in a beaker at ambient pressure. We observed 1-pentanol to cavitate in the shortest period of time (~ 7 s) of all the simple alcohols studied. Since all of the simple alcohols tested in our experiments have comparable surface tensions, with only a gradual trend of increasing surface tension with increasing chain length, it remains unclear as to why 1-pentanol cavitation is most rapid.

3.2. Kinetics for control (stirred) experiments

The 2-butanone to 2-butanol product ratio and observed first-order loss of reagent 3-buten-2-ol was measured for the control experiments and enabled k_1 and k_2 of Scheme 1 to be determined, assuming that the initial H-atom elimination and addition reactions are rate-limiting. There is precedence for this assumption based on both a model put forth by Horuiti and Polanyi [11], and support by experiments examining chemistry in hydrogen-deuterium mixtures [12]. Additional support, although less compelling, arises from our observation of the only stable intermediate 3-buten-2-ol occurring at small concentrations (not exceeding 5 mol%). The temperature dependence of k_1 and k_2 has been determined from stirred and silent experiments performed at 280, 295, 310, 325, and 340 K. The Arrhenius rate parameters for the fits are: $\ln(A_1) = 22.59 \pm 1.73$ and $E_1 = 53.7 \pm 4.4$ kJ/mol; and $\ln(A_2) = 9.70 \pm 1.97$ and $E_2 = 20.8 \pm 5.0$ kJ/mol. These rates are given as a per site (turnover) frequency. The turnover frequencies were computed from the pseudo-first-order k_1 and k_2 rate coefficients, the BET surface area (42 m^2/g), and the index-averaged Pd-atom surface density of 1.27×10^{19} sites/m^2. The experimental error is such that temperature uncertainty, as determined from the k_1/k_2 ratio or equivalently from the 2-butanone-to-2-butanol ratio, is ± 4.7 K. These temperature dependencies will enable us to assign effective temperatures arising from ultrasound treatment.

3.3. Ultrasound versus control selectivities

Arguably the most important parameter that ultrasound may have an effect on is selectivity, even more so than activity that can often be increased by enhancing mass transport in multiphase reacting systems. Table 1 compares two ultrasound experiments, each to their respective control experiment, by examining the product ratio of ketone-to-saturated alcohol for solution temperatures of 295 K. The product ratios listed in Table 1 were measured at similar extents of reaction of $\xi = 0.94$–1.00 for all experiments. Also worth noting was the observation that for the cavitating experiment, the power change from 360 → 190 W occurred within 7 s. The second data column of Table 1 lists the equivalent "bulk thermal" temperature necessary to generate the same observed product ratio, as determined from the Arrhenius plot of Fig. 1. The final data column simply lists the ultrasound power applied to solution during reaction (if applicable).

Table 1
Comparing 2-butanone/2-butanol ratio at 295 K for stirred, noncavitating ultrasound, and cavitating ultrasound experiments

Experiment	2-Butanone/2-butanol ratio (molar)	Effective temperature (K)	Ultrasound power (W)
Stirred	0.74	299 ± 5	N/A
Noncavitating ultrasound	0.56	294 ± 5	360
Stirred (with 1-pentanol)	0.50	292 ± 5	N/A
Cavitating ultrasound (with 1-pentanol)	0.080	256 ± 5	190

Three primary conclusions can be put forth regarding the data of Table 1. First, although a small difference in selectivity (product ratio) is seen for the noncavitating ultrasound compared to control experiment, the equivalent bulk solution temperatures agree within experimental error. Second, a much more pronounced difference is seen comparing the doped cavitating ultrasound compared to stirred solution (factor of 6.2 smaller ketone-to-saturated alcohol ratio), resulting in a 36 K bulk-equivalent temperature difference. Third, the measured powers for the noncavitating ultrasound and cavitating ultrasound show the characteristic decrease upon, or for, cavitation. It is tempting to try to assign a physical effect to the bulk-equivalent temperature. Contrary to intuition is the observed reduction in equivalent bulk temperature for the cavitation experiment. The only reasonable scenario is that the product ratio is caused by the preferential increase in the H-atom addition (delivery) pathway.

3.4. Ultrasound versus control kinetics

A knowledge of the first-order loss of reagent and product ratio enables us to compute, via the formula $\tau_{\text{loss}}^{-1} = \tau_1^{-1} + \tau_2^{-1}$, the lifetimes representing the H-atom elimination and addition pathways. Table 2 presents the results of this analysis. Typically three or more data points were used in determining lifetimes. Several important points can be made regarding these data. First, the 1-pentanol doping is seen to slow the control rates by a factor of ~ 2, the mechanism of which such as reaction site blocking, or alternatively inhibiting surface diffusion, remaining unclear. Second, the overall rates for cavitating ultrasound to noncavitating ultrasound to stirred (without dopant) are 52.9:4.9:1.0. This demonstrates

Table 2
Results of kinetics for stirred, noncavitating ultrasound, and cavitating ultrasound experiments

Experiment	τ_1 (min)		τ_{total} (min)
	To 2-butanone	To 2-butanol	
Stirred	82.0	60.7	34.9
Noncavitating ultrasound	19.8	11.1	7.1
Stirred (with 1-pentanol)	125.2	125.2	62.6
Cavitating ultrasound (with 1-pentanol)	8.9	0.71	0.66

that cavitation significantly enhances activity. It is also worth noting that the 4.9-fold enhancement in reaction rate for the noncavitating ultrasound compared to stirred is significantly greater than the 37% increase in surface area as determined by a H_2–O_2 titration method. Thus catalyst dispersion alone cannot account for the observed rate enhancement. Third cavitation compared to stirred yields a 14-fold enhancement in ketone formation rate, but a 176-fold alcohol formation rate increase.

4. Conclusions

The investigation here has shown that a relatively simple water-soluble olefin, 3-buten-2-ol, undergoes H-atom elimination and addition reactions on Pd-black to yield 2-butanone and 2-butanol, respectively. Cavitating ultrasound is seen to result in a selectivity change of 700%, and an activity change of 53-fold, compared to the noncavitating experiment. The novel approach of using an inert dopant species (1-pentanol) at low concentration to create a cavitating solution from what otherwise would remain noncavitating during the first half of the reaction may have practical application. A question that remains is: Can different dopants, at tuned concentrations, be chosen to effect selectivity in a predictable way? Work to pursue such questions is needed.

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References

[1] J.L. Luche (Ed.), Synthetic Organic Sonochemistry, Plenum, New York, 1998.
[2] T.J. Mason, Sonochemistry, Oxford Univ. Press, Oxford, 2000.
[3] K.S. Suslick, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 3, Wiley–VCH, Weinheim, Germany, 1997.
[4] T.J. Mason, Ultrasonics Sonochem. 10 (2003) 175.
[5] B. Torok, K. Balazsik, M. Torok, Gy. Szollosi, M. Bartok, Ultrasonics Sonochem. 7 (2000) 151.
[6] M.M. Mdleleni, T. Hyeon, K.S. Suslick, J. Am. Chem. Soc. 120 (1998) 6189.
[7] R.S. Disselkamp, T.R. Hart, A.M. Williams, J.F. White, C.H.F. Peden, Ultrasound-Assisted Hydrogenation of Cinnamaldehyde, Ultrasonics Sonochem. 2004, in press.
[8] J.W. Chen, J.A. Chang, G.V. Smith, Chem. Eng. Progress, Symp. Ser. 67 (1971) 18.
[9] R.S. Disselkamp, C.H.F. Peden, The Effect of Ultrasound on the Isomerization versus Reduction Reaction Pathways in the Hydrogenation of 3-Buten-2-ol and 1,4-Pentadien-3-ol on Pd-Black, Proceedings of the Organic Reactions Catalysis Society, Hilton Head, SC, 2004, in press.
[10] R.S. Disselkamp, K.M. Judd, T.R. Hart, C.H.F. Peden, G.J. Posakony, L.J. Bond, J. Catal. 221 (2004) 347.
[11] J. Horuiti, M. Polanyi, Trans. Faraday Soc. 30 (1934) 1164.
[12] J.E. Douglas, B.S. Rabinovitch, J. Am. Chem. Soc. 74 (1952) 2486.