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Selective Reduction of Biomass by Hydriodic Acid and Its In Situ Regeneration from Iodine by Metal/Hydrogen

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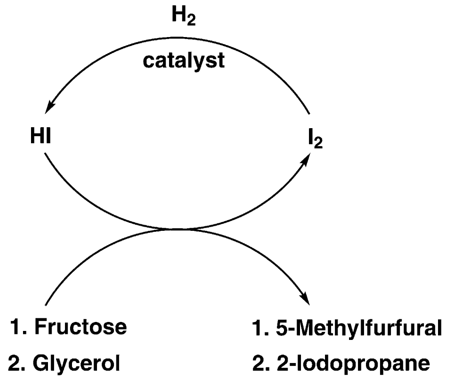
At present, most chemicals and polymer intermediates are derived either directly or indirectly from fossil fuels.[1] However, due to the increasing cost of fossil fuels and concerns about their environmental impact, the production of chemicals directly from renewable biomass has gained increased urgency.[2,3] Among other advantages, the use of biomass substantially reduces net carbon dioxide emissions because the latter is recycled during regeneration of the biomass. Compared to the fermentation methods, which use sensitive enzymes or microbes, chemical catalysis is fast, robust, and conditions are easily controlled.[4] Carbohydrates and their derivatives are the most common biomass-derived substrates and their conversion typically require a reduction step to remove the undesired hydroxyl groups. This step usually involves metal catalysts, which need to be fine-tuned for the specific transformation and need to be separated and recycled at the end of the reaction. Here, we report the use of HI for two selective transformations of biomass to important chemicals. Both processes involve the use of HI as the reducing agent, resulting in the formation of I_2 that we are able to reconvert, either in situ or in a separate step, back to HI by metal-catalyzed hydrogenation (Scheme 1).



Scheme 1. Iodine-catalyzed biomass conversion.

HI has been reported to be an effective reducing agent for a wide range of substrates.[5] The difficulty in reconverting the product I_2 back to HI has limited its use for this purpose. In the laboratory, elemental phosphorus is usually used for this purpose,[6] however, the reaction is slow and the process inconvenient. The alternative has been to use either phosphorous acid or hypophosphorous acid, but the accumulation of resulting phosphoric acid can affect the reaction, and it needs to be removed periodically.[7]

The industrial preparation of HI involves the reaction of I_2 with hydrazine.[8a] HI is also prepared by bubbling hydrogen sulfide through an aqueous solution of iodine, with elemental sulfur formed as byproduct. In principle, the best way to convert I_2 back to HI is by hydrogenation with H_2. This is usually achieved by passing H_2 gas and I_2 vapor over a heated platinum sponge at 500 °C. The method is employed to generate high-purity samples.[6a] HI production by the reaction of hydrogen and iodine at high temperature (300 °C) and pressure (1000 psi; $1\ \text{psi} = 6.895 \times 10^3$ Pa) has also been employed to reduce alcohols to alkanes.[8b]

Herein, we show that iodine can be quantitatively converted to hydroiodic acid by metal-catalyzed hydrogenation under mild reaction conditions (100–140 °C; 100–300 psi H_2) in the presence of water. Table 1 summarizes the results on the catalytic hydrogenation of I_2 to HI. The reaction proceeds in pure water with complete conversion to HI, as indicated by the solution turning colorless and by titration with a 0.05 M solution of NaOH. As expected, the conversion rate increases with increasing pressure (entry 1 versus 2) and reaction temperature (entry 2 versus 4). The presence of water is indispensible. For example, no conversion occurred when the reaction was carried out with I_2 dissolved in toluene (entry 3). However, the addition of water resulted in rapid and complete conversion. The purple color of I_2 dissolved in toluene was discharged and the

Table 1. Catalytic reaction of H_2 and I_2 to form HI.[a]

Entry	Iodine [mmol]	Catalyst	Amount [mmol]	P_{H_2} [psi]	T [°C]	t [h]	Conv.[b] [%]
1[c]	0.2	Pd/C	0.005	300	100	2	100
2[d]	0.2	Pd/C	0.005	100	100	4	100
3[e]	0.2	Pd/C	0.005	300	100	16	0
4	0.2	Pd/C	0.005	100	140	1	100
5	0.2	RhI_3	0.005	300	100	0.5	100
6	0.2	Rh/C	0.005	300	100	0.2	100
7	0.2	Ru/C	0.005	300	100	1	100

[a] Water (2 mL) was used as solvent in all entries, except entry 3. [b] The full conversion of the iodine was indicated by the formation of a colorless solution and by titration with a 0.05 M solution of NaOH. [c] The reaction was not complete in 1 h, as shown by the yellow color of the solution. [d] The reaction was not complete in 3 h, as shown by the yellow color of the solution. [e] Toluene (2 mL) was used as solvent, which was purple before and after the reaction. Then, after adding 2 mL of water, the conversion was complete in 2 h and the solution became colorless.

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Table 2. Metal-free synthesis of 5-methylfurfural from fructose.[a]

Entry	Reagents used	Amount	Solvent	T [°C]	t [h]	Gas	P [psi]	Yield [%]
1	HI	3 equiv	toluene/H_2O	120	1	N_2	300	47
2	HI NaI	1 equiv 2 equiv	C_6H_6/H_2O	105	12	He	300	38
3	HI NaI	1 equiv 2 equiv	C_6H_6/H_2O	105	24	He	300	51
4[b]	HI	3 equiv	toluene/H_2O	100	6	N_2	15	44
5[c]	Pd/C	20 mg	C_6H_6/H_2O	90	16	H_2	300	No reaction

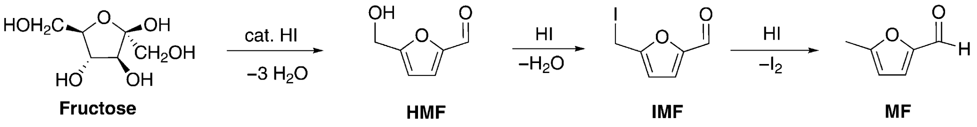
[a] Fructose (1 mmol), HI (57 wt% in water), water (1.6 mL), benzene or toluene (2 mL). [b] Reaction performed under reflux without an autoclave. [c] HI not added to the reaction mixture.

aqueous layer became highly acidic. A variety of metal catalysts are effective for the transformation. Of the catalysts tested, those based on rhodium appear to be the most active (compare entry 6 to entries 1 and 7). The catalysts were recycled several times without significant decrease in reactivity.

The reaction $I_2+H_2 \rightarrow 2\,HI$, is favorable from a thermodynamic standpoint, even in the gas phase [$K_{eq}(100\,^{\circ}C)=409$]. However, the presence of water provides significant added driving force because of the solvation of ions derived from HI. The free energy of hydration of gaseous HI is $-118\,kJ\,mol^{-1}$ at 100 °C [$K_{eq}(100\,^{\circ}C)=3.3\times10^{16}$].

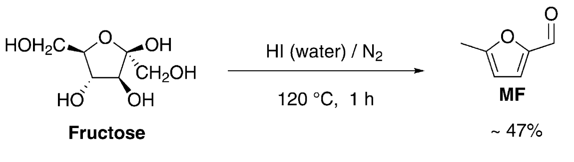
The fact that a) HI is a strong reducing agent, and b) I_2 can be readily reconverted back to HI in the presence of water has allowed us to efficiently convert a number of carbohydrate derivatives to useful chemicals *without involving a metal catalyst in the actual biomass reduction step* (Scheme 1). This is important because it avoids the search for an appropriate metal catalyst that is tolerant of the specific reaction conditions. We illustrate our approach with two important transformations: a) fructose to 5-methylfurfural, and b) glycerol to 2-iodopropane.

5-Methylfurfural (MF) is a useful intermediate for the production of pharmaceuticals, agricultural chemicals, perfumes, and other applications.[9] It is also a common flavoring component in the food industry,[10] and is even considered a potential antitumor agent.[11] Recently we have reported the conversion of fructose and other hexoses to 2,5-dimethyltetrahydrofuran (DMTHF) or MF in the presence of HI, H_2, and an active hydrogenation catalyst.[12] HI was essential for the reaction; other acids, such as HCl and H_2SO_4, were not effective. We now find that the actual conversion of fructose to MF does not need either H_2 or a metal catalyst: comparable yields of MF can be obtained with HI alone (Scheme 2). This is the first example of MF formation from fructose without the use of a metal catalyst.



Scheme 3. Proposed pathway for MF formation from fructose.

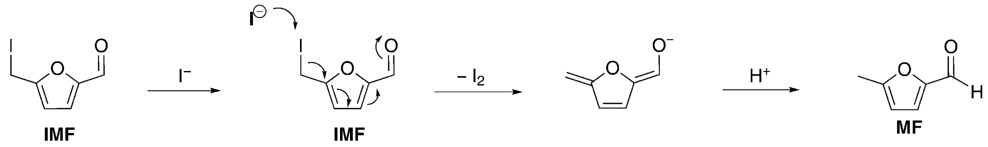
Our results are summarized in Table 2. The reaction was typically carried out in a glass-lined stainless steel autoclave (although this is not necessary, as shown in entry 4). A biphasic reaction system with water and an organic extracting solvent (benzene or toluene) was employed. Fructose and HI were first dissolved in the aqueous phase before the reaction. Then the autoclave was flushed with nitrogen or helium and heated in an oil bath. After the reaction, the organic layer was purple, with some humin formed at the bottom of the liner. For entry 1, GC analysis of the organic layer gave a 47% yield of MF, and ^1H NMR analysis of the aqueous layer indicated 68% fructose conversion. Longer reaction times led to decreased yields of MF, due to its instability. The purple color in the organic layer was determined to be due to I_2 formation, as confirmed by a titration experiment with starch solution.



Scheme 2. Metal-free conversion of fructose to MF.

The overall reaction is shown in Scheme 3. The first step in the reaction is the well-studied acid-catalyzed dehydration of fructose to 5-hydroxymethyl-2-furaldehyde (HMF),[4,13,14] which subsequently converts to 5-iodomethylfurfural (IMF) with HI present. As shown in Table 2, longer reaction times are required if the amount of acid is reduced by substituting part of the HI by NaI (entries 1 and 4 versus entries 2 and 3). The formation of chloro- and bromomethylfurfural by the reaction of carbohydrates with HCl and HBr, respectively, is also known.[15,16] IMF has never been isolated in pure form.[17] The intermediate 5-iodomethylfurfural (IMF) was found to be easily reduced to MF with the concomitant formation of iodine as a byproduct under the given reaction conditions, due to the weak C–I bond (the analogous aromatic compound benzylic iodide has a bond strength of $180\,kJ\,mol^{-1}$[18]).

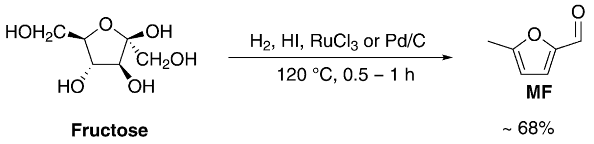
The reaction shown in Table 2, entry 1 was repeated using HMF as the starting material leading to a 47% yield of MF, the same yield obtained with fructose. In both instances, dark solid (humin) was observed to have precipitated out of solution. HMF, due to its reactive hydroxyl and carbonyl groups, is highly susceptible to the formation of humin under aqueous acidic conditions. In the reduction of HMF with HI, the IMF intermediate was observed by GC and ^1H NMR spectroscopy (see



Scheme 4. Mechanism for MF formation from IMF.

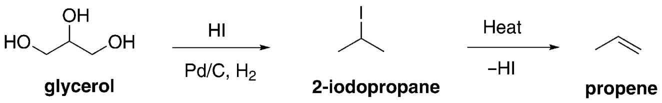
Supporting Information). The reaction of HMF with one equivalent of HI resulted in a mixture of MF, IMF, and unreacted HMF (Scheme 4).

As has been reported,[12b] when a metal catalyst and hydrogen are also present in the reaction, no iodine is formed during the conversion of fructose to MF. As shown in Scheme 5, 68 % of MF can be obtained at 120 °C (oil bath temperature) in 0.5 h with Pd/C (20 mg), 300 psi H_2, and 3 equiv of HI. In the previous paper, the catalyst (metal complex and HI in aqueous solution) was recycled twice and no deactivation of the catalyst was observed. Here, the Pd/C catalyst was recycled four times, and the yield decreased only slightly from 68 to 61 %. Thus, the hydrogen serves to convert iodine back to HI in situ, while HI functions as dehydration and reducing reagent to convert fructose to MF continuously. As a control experiment, a reaction involving fructose with only metal catalyst (Pd/C)/H_2 and no HI was performed under the same reaction conditions (Table 2, entry 5). No fructose conversion was observed, which confirmed that HI is the actual dehydration and reducing reagent in the fructose conversion process.



Scheme 5. Direct fructose conversion to MF with metal/HI/H_2 catalyst.

The second example involves the conversion of the abundant biomass-derived glycerol to propene. The propene market is driven by the strong demand for polypropylene, which is one of the most important thermoplastic resins. The global polypropylene demand was 26.6 million tonnes in the year 2000, and it is expected to reach 59.6 million tonnes in the year 2020.[19] Thus, the direct conversion of glycerol to propene is a very useful and attractive process. However, reports of selective propene production from glycerol are limited.[20] For example, Sousa Fadigas has reported the conversion of glycerol to propene using a multi-metallic catalyst composed of molybdenum oxide and iron nitrate.[20a] Our procedure for the highly selective conversion of glycerol to propene is shown in Scheme 6. Under optimal conditions, near complete conversion of glycerol to propene was observed.



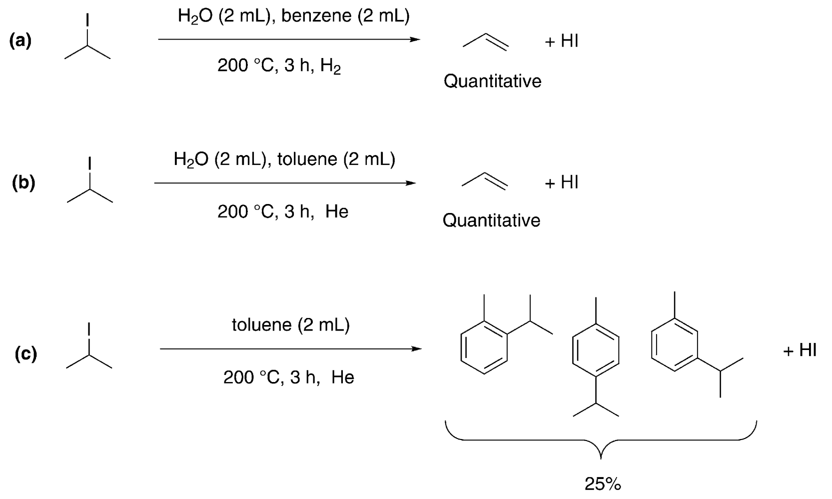
Scheme 6. HI-mediated conversion of glycerol to propene.

The stoichiometric conversion of glycerol to 2-iodopropane (2-IP) using excess HI has been reported and is represented by Equation (1) (see Table 3, entry 1).[21] Iodine formation was indicated by the dark purple solution formed. We were able to reduce the iodine byproduct back to HI in situ by using a metal catalyst and hydrogen in the presence of water (Scheme 6, step 1). Using 3 equivalents of HI and $RhCl_3$ (0.3 %), 80 % yield of 2-IP was obtained after 6 h under the biphasic reaction conditions, with some small amounts of propane and propene formed as the side products (Table 3, entry 2). Around 10 % of glycerol remained in the water phase. After taking the organic layer out, more glycerol (5 mmol, 460 mg) was added to the aqueous layer together with fresh benzene (4 mL). Since 1 equivalent of HI relative to glycerol is consumed in the iodopropane formation, the reaction rate was slower in the second cycle due to lower HI to substrate ratio. After 16 h at 120 °C, 94 % of 2-iodopropane was obtained, and around 15 % of glycerol was left in the aqueous phase (for both cycles). After separating the organic layer, more glycerol was added to the aqueous phase for the third cycle. At this time, only around 1 equivalent of HI was left, and the reaction rate was even slower. After reacting for 16 h at 120 °C, 72 % of 2-IP was obtained, and around 43 % of glycerol was left (accumulated from 3 cycles). No deactivation of the homogeneous $RhCl_3$ catalyst

Table 3. Conversion of glycerol to 2-iodopropane.

Entry	Metal catalyst	Amount [mmol]	Amount of HI [mmol]	V_{H_2O} [mL]	T [°C]	t [h]	Yield [%]
1[a]	None	–	15	0.2	100	16	100
2[b]	$RhCl_3$	0.0015	15	0.2	120	6	80
3[c]	From entry 2		From entry 2	From entry 2	120	16	94
4[d]	From entry 3		From entry 3	From entry 3	120	16	74
5[e]	Pd/C	0.005	15	0.2	120	6	100
6	Pd/C	0.005	none	0.2	120	16	No reaction
7	Pd/C	0.005	HCl (18)	0.5	140	16	10 % conversion[f]

[a] Glycerol (1 mmol), HI (57 wt % in water, 2 mL), benzene (2 mL), N_2 (300 psi). [b] Glycerol (5 mmol), $RhCl_3$ (1.5 μmol, 4 mg), HI (57 wt % in water, 15 mmol, 2 mL), benzene (4 mL), H_2 (300 psi). [c] The aqueous phase from entry 2 was recycled for entry 3. [d] the aqueous phase from entry 3 was recycled for entry 4. [e] Glycerol (1 mmol), Pd/C (5 wt %, 0.005 mmol, 20 mg), HI (57 wt % in water, 15 mmol, 2 mL), benzene (2 mL), H_2 (300 psi). [f] Chloropropane was the principal product.



Scheme 7. Thermal conversion of 2-iodopropane to propene and HI.

was observed in this process. A quantitative yield of 2-IP was obtained with a large excess of HI (15 equiv) in 6 h, as revealed by the GC analysis of the organic layer (Table 3, entry 5). No I_2 formation was observed in all the cases (the solution was colorless). While 2-iodopropane was quantitatively converted to propane with Pd/C and hydrogen at 120 °C, this did not occur in the presence of excess HI. It appears that HI poisons the ability of Pd/C catalyst to hydrogenate iodoalkanes.

$$\mathrm{HOCH_2CH(OH)CH_2OH + 5\,HI \rightarrow CH_3CH(I)CH_3 + 3\,H_2O + 2\,I_2} \tag{1}$$

In a control reaction, no glycerol conversion was observed with only metal catalyst and no HI present under similar reaction conditions, which confirms that HI is the actual dehydration and reduction reagent (Table 3, entry 6,). When HCl was used, the reaction rate was slow, and only 10% of the glycerol was converted at 140 °C in 16 h; chloropropane was the major product.

Unlike starting glycerol, the 2-IP formed is soluble in the organic layer and automatically partitions out of the aqueous reaction mixture. This organic solution with 2-IP can be directly used in the second step involving thermal conversion to propene and HI. As shown in Scheme 7, in the presence of water, quantitative conversion to propene was observed at 200 °C (reactions a and b). No other products were detected. Again, we believe that water provides significant added driving force by the solvation of HI. The aqueous HI formed can be recycled in the conversion of glycerol to 2-IP. In the absence of water, a large amount of 2-IP remained unconverted (75%) and the remainder formed Friedel–Crafts products with the aromatic solvent with around 25% yield (catalyzed by HI) (reaction c). The products were determined and quantified by GC–MS.

In conclusion, the common currently used methods to convert I_2 to HI employ either expensive or toxic reagents, and typically form side products that need to be removed from the system. The method described here is clean and quantitative, and the only reagent consumed is hydrogen. The metal catalyst used is easily separated and recycled. The mild conditions employed make HI an attractive and recyclable reducing agent.

To demonstrate the utility of the above procedure, we have described a metal-free process to produce MF directly from fructose. HI is the only reagent needed and functions as both a dehydrating reagent and a reductant. The iodine formed can be hydrogenated back to HI either in situ or subsequently with metal catalysts. Another example described is a two-step continuous conversion of glycerol to propene with very high yield and selectivity. Again, HI functions as the reducing agent and the product iodine can be readily hydrogenated back to HI. Given the simplicity and versatility of HI as a reducing agent, our procedure opens up the possibility of employing HI in a variety of reductive transformations and obviates the need for tailoring expensive metal catalysts for specific substrates and reaction conditions.

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Keywords: biomass · halogens · homogeneous catalysis · polymers · reduction

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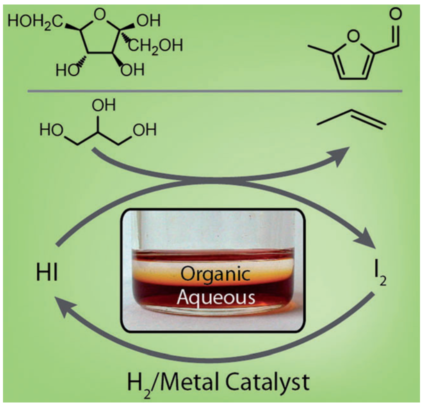

HI returns: Hydroiodic acid is a highly selective reducing reagent for a wide variety of substrates. Its application is limited by the formation of iodine and the difficulty in reconverting that iodione back to HI in situ. We report the facile conversion of I_2 to HI by metal-catalyzed hydrogenation in the presence of water, and demonstrate the utility of this process in the conversion of fructose to 5-methyfurfural and glycerol to 2-iodopropane.