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Efficient and Selective Oxidation of D-Glucose into Gluconic acid under Low-Frequency Ultrasonic Irradiation

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The production of gluconic acid from p-glucose represents an attractive target for industry. In this work, we propose an efficient, eco-friendly, and selective method to oxidize p-glucose with aqueous H_2O_2 in the presence of FeSO₄ as a catalyst. The reaction was improved significantly under ultrasonic (US) activation, which led to excellent yields in only a few minutes. In

addition, we determined that the reaction occurred through a sono-Fenton process by studying the production of hydroxyl radicals and optimizing the experimental conditions of the reaction. The energy consumption of the process was also investigated in this study.

Introduction

Biodegradable gluconic acid is used industrially as a watersoluble chelating and acidifying agent for cleaning applications and as an additive in food and pharmaceutical industries.^[1] In medicine, gluconic acid is also used as a dietary supplement to prevent cancer. Each year, approximately 100000 tons of gluconic acid are produced around the world^[2] essentially through biotechnological processes from D-glucose that involve Aspergillus niger fungi and Gluconobacter suboxidans bacteria.^[3] To solve the problems related to microbe separation, control of byproducts, and the disposal of waste water produced by the industrial fermentation process, interest in the oxidation of glucose by electrochemistry, $\ensuremath{^{[4]}}$ by photocatalysis, $\ensuremath{^{[5]}}$ and/or in the presence of solid catalysts^[6] has increased recently. In their review, Corma et al. highlighted the challenging catalytic oxidation of D-glucose, the most abundant monosaccharide in nature, and its conversion into D-gluconic acid, which remains an attractive target for industry.^[2]

The oxidation of p-glucose has been investigated widely in aqueous media with O₂ or air as oxidants in the presence of noble-metal catalysts. To be competitive with biotechnological processes, these catalysts require high activity and selectivity, and long term-stability. Researchers have investigated different catalytic systems based on Pd and Pt catalysts, but side-reactions and catalyst deactivation limited the production of gluconic acid.^[7,8] Doped with small amounts of Bi, the catalytic activity was improved, but the partial leaching observed from the catalyst surface into the reaction medium is not appropriate for food or pharmaceutical applications.^[9,10] Some traces of byproducts were also obtained.

Recently, Au-based catalysts were investigated to improve the selectivity of the aerobic oxidation of D-glucose.^[11-13] Au

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E-mail: gregory.chatel@univ-poitiers.fr nanoparticles dispersed on various supports or in colloidal form can enhance catalytic activity, selectivity, and stability.^[14, 15] Generally, the pH of the reaction medium had a direct impact on the reaction rate, and a pH around 9 was favored. For example, during recycling studies, analysis of fresh and used catalysts revealed significant leaching of metal at pH 7 (18%), whereas no leaching was observed at pH 9.5. Under uncontrolled pH conditions, 10% of the metal was lost in only two runs and approximately 70% was lost after six runs.^[14]

An aqueous solution of H_2O_2 was employed successfully for the oxidation of p-glucose.^[16-17] Indeed, the use of H_2O_2 has received much attention in recent years because of its reasonable price, safe storage, and low environmental impact as it generates water as the only theoretical byproduct.^[18] In addition, compared to O_2 or air, higher concentrations can be applied easily and external mass-transfer limitations are excluded because of the complete water solubility.

As a general method, the catalysis-based processes proposed in the literature for the oxidation of p-glucose into gluconic acid are often performed systematically in pH-controlled conditions to avoid the leaching of metal, require the preparation and characterization of expensive catalysts, need to be heated from 40–80 °C for several hours, and suffer from a lack of selectivity in many examples. To solve all these limitations, in this study we propose a simple method based on cheap iron(II) sulfate as a catalyst using low-frequency (20 kHz) ultrasound (US) at 25 °C as an activation method over short times (<1 h) to convert p-glucose selectively into gluconic acid with excellent yields (Scheme 1). Here, the oxidative $H_2O_2/FeSO_4$ system was clearly improved by sonication thanks to the enhanced production of hydroxyl radicals.

Results and Discussion

First, we explored the impact of experimental parameters such as reaction time and temperature under silent conditions (i.e., traditional heating) on the oxidation of D-glucose in the

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Scheme 1. Oxidation of D-glucose into gluconic acid under ultrasonic conditions.

presence of the two selected salts, FeSO₄ and V₂O₅ (10 wt%), at 70 °C with an excess of H₂O₂ (12 equivalents relative to the substrate). Under these conditions, quantitative glucose conversion occurred after 5 and 30 min in the presence of FeSO₄ and V₂O₅, respectively (Figure 1). However, in the absence of catalyst, the reaction was very slow, and the glucose conversion reached only 4% after 60 min.

We compared the results obtained after 15 min under the same conditions and varied the temperature from room temperature to 70 °C (Figure 2). With a large excess of H_2O_2 (12 equivalents), the FeSO₄ catalyst allowed the quantitative



Figure 1. Oxidation of D-glucose as a function of reaction time and catalyst (Reaction conditions: 1 mmol glucose, 12 mmol H₂O₂, 10 wt% catalyst, 4 mL H₂O, 70 °C).



Figure 2. Oxidation of D-glucose as a function of temperature and catalyst (Reaction conditions: 1 mmol glucose, 12 mmol H₂O₂, 10 wt% catalyst, 4 mL H₂O, 15 min).

conversion of D-glucose at room temperature (>99% at 22 °C), whereas V₂O₅ showed a good conversion at a higher temperature (91% at 70 °C). Interestingly, under these oxidative conditions, the selectivity to gluconic acid was almost complete, and only some traces of fructose were observed (<5%) from the known isomerization of D-glucose in presence of some metals or according to the experimental conditions.^[19,20]

The amount of catalyst was also investigated under silent conditions. With 10 wt% catalyst (V_2O_5 or FeSO₄), the conversion into gluconic acid was quantitative or almost quantitative

in only 15 min. Interestingly, Sasaki et al. reported the oxidation of D-glucose with H_2O_2 in the absence of catalyst, which reached a conversion of over 80% after 1 h at 200°C with poor selectivity.^[17] In the latter

study, the best results were obtained at 160 $^\circ C$ for 15 min, which led to yields of 15% in gluconic acid and 10% in formic acid.

Then, we investigated the effect of the activation method on the oxidation reaction; in particular, cavitation (i.e., the formation, growth, and collapse of gaseous microbubbles in the liquid phase)^[21] using low-frequency ultrasound (20 kHz). It is known that the implosion of these bubbles creates local high pressures (up to 1000 bar) and temperatures (up to 5000 K) that can lead to high-energy radical mechanisms and some interesting physical effects.^[22] In the 2000s, some sonochemical oxidations of carbohydrate compounds were reported by promoting the physical and chemical effects provided by ultrasound.^[23] However, the efficient but not eco-friendly NaOCl/ 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)/NaBr system was used for the oxidation of glucosides.^[24]

A comparison of silent conditions (at 70 °C) and US conditions (at 22.5 °C) is shown in Figure 3. In the absence of catalyst, the glucose conversions were slightly higher (1.5 times)



Figure 3. Oxidation of D-glucose as a function of catalyst amount and activation conditions (Reaction conditions: 1 mmol glucose, 12 mmol H₂O₂, 4 mL H₂O, 70 °C, 15 min).

under ultrasonic irradiation. However, it was not possible to increase this conversion significantly under ultrasonic irradiation, even with the portionwise addition of H_2O_2 or by increasing the reaction time. For different amounts of V and Fe salts, the effects of ultrasound were not highlighted compared to silent conditions because of the high conversion in the large excess of oxidant (Figure 3). However, the same conversions were obtained in silent and ultrasonic conditions in spite of the great difference of reaction temperature (70 °C in silent conditions vs. only 22.5 °C under ultrasound), which shows an interesting advantage of the ultrasonic activation.

To optimize the experimental conditions, we studied the effect of the excess of oxidant. We focused our study on the best salt tested, $FeSO_4$. A systematic comparison of the silent conditions at room temperature at 70 °C and ultrasonic condi-

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Figure 4. Oxidation of D-glucose as a function of glucose/ H_2O_2 molar ratio and activation conditions (Reaction conditions: 1 mmol glucose, H_2O_2 , 4 mL H_2O , 15 min).

tions at 22.5 °C is shown in (Figure 4). The smaller the excess of oxidant, the greater the effect of ultrasound compared to silent conditions at the same temperature. For example, for an equimolar ratio of glucose/ H_2O_2 , the glucose conversion reached 20% under silent conditions at 22°C, whereas 48% was obtained under US conditions at 22.5 °C.

Interestingly, if we decreased the excess of oxidant from 1:12 to 1:1 at 70 °C, the selectivity to gluconic acid decreased and the yield of fructose increased from 5 to 14% (Table 1). The best conditions (1:3 molar ratio under ultrasonic irradiation) led to a quantitative conversion of glucose in only 15 min with a gluconic acid yield of 97% at only 22.5 °C

(Table 1, entry 9). Globally, the reaction was very selective and no other byproduct was observed. Onda et al. reported the quantitative conversion of glucose with 45 and 43% yields of gluconic acid and lactic acid, respectively, using a Pt/C catalyst under flowing air for 2 h. However, they also identified the presence of glycolic acid (2.9%), formic acid (2.9%), acetic acid (0.8%), and other byproducts.^[8] In other work based on a PdBi/C catalyst, some traces of 2-ketogluconate, 5-ketogluconate, glucarate, and fructose were also obtained.^[9] Silicasupported nanogold catalysts suspended in 30% H₂O₂ with 5 min ultrasonic irradiation (ultrasonic bath, 35 kHz) led to 100% conversion and 80% selectivity after 15 min with magnetic stirring at room temperature with a 1:6 ratio of glucose/ H₂O₂.^[16] In this study, ultrasonic treatment was used for the activation of nanogold to catalyze the glucose oxidation, which led to a high reproducibility. Ti-containing zeolite catalysts were also used for the H_2O_2 oxidation of glucose at 70 °C, but the conversion was lower than 40%, and the maximum selectivity to gluconic acid was 27%.^[7b] In addition, some byproducts were observed such as glucuronic, tartaric, glycetic, and glycolic acids. Here, our method presents an additional advantage to work in practical uncontrolled pH conditions, and the pH at the end of the reaction was 1-2.

Contrary to preconceived ideas, sonochemistry is not an "intensive energy-consuming" technology, and if ultrasoundbased processes are optimized, they generally minimize the energy consumption in numerous chemical transformations.^[25] We report the measured energy consumed for the 15 min oxidative process, under silent conditions and under ultrasonic irradiation, in Table 2. Globally, the ultrasonic process needs 1.3 times more energy than that under conventional heating and stirring at 70 °C. However, the real electrical energy converted into acoustic energy corresponds to only 32 kJ, which is 4.5 times less than traditional heating. Indeed, 24 kJ is consumed intrinsically by the generator (standby internal power), and the major part of the energy costs are attributed to the cooling system. In our experimental assembly, the

Table 2. Energy consumption of the process measured under silent and US conditions.				
Silent co 22°C (stirring)	onditions 70°C (heating)	Generator in standby position	US conditions Generator in operating position	Cooling system maintained at 22.5 °C
7 kJ 144	137 kJ i kJ	24 kJ	32 kJ 191 kJ	135 kJ

Table 1. Selectivity in the oxidation of D-glucose as a function of glucose/H₂O₂ molar ratio and activation conditions.

Entry	Catalyst ^[a]	Activation ^[b]	Molar ratio (glucose/H ₂ O ₂)	Glucose conversion [%]	Fructose yield [%]	Gluconic acid yield [%]
1	V ₂ O ₅	−, 22 °C	1:12	8	<1	7
2		–, 70 °C	1:12	91	6	86
3		US, 22.5 °C	1:12	97	4	94
4	FeSO ₄	−, 22 °C	1:1	20	5	15
5		–, 70 °C	1:1	54	14	40
6		US, 22.5 °C	1:1	48	6	42
7	FeSO₄	−, 22 °C	1:3	76	4	72
8		–, 70 °C	1:3	91	7	84
9		US, 22.5 °C	1:3	99	2	97
10	FeSO ₄	−, 22 °C	1:12	98	5	93
11		–, 70 °C	1:12	99	5	93
12		US, 22.5 °C	1:12	99	3	95
[a] 10 wt%. [b] Reaction time: 15 min.						

use of a Minichiller cooling system is not adapted for the small volumes treated under ultrasound in this study, which explains the overconsumption of energy. A less sophisticated system would be possible by circulating water from a tap in this case, and the cooling parameters can be optimized for a larger-scale process. In conclusion, our process under ultrasound consumed less energy than traditional heating and led to a very high conversion and selectivity in only 15 min.

However, we tested the reaction under optimized conditions with ultrasonic irradiation without control of the reaction temperature. After 1 min, the medium reached 38 °C with an associated glucose conversion of 42% (93:7 glucose/fructose selectivity). After 2, 4, and 6 min, the conversion was capped at 57–58%

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 $(T=51, 61, and 69^{\circ}C, respectively)$, but the selectivity to gluconic acid decreased to 90% after 6 min. The best compromise is the use of ultrasound at room temperature to limit the production of fructose.

To understand clearly why the sonochemical oxidation of Dglucose was more efficient than traditional heating, we studied the mechanism of the reaction. In the presence of H_2O_2 and ferrous ions at acidic pH, it is known that we can produce hydroxyl radicals directly by a Fenton process according to the following reactions [Eqs. (1)–(3)].^[26]

 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet}$ (1)

 $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+$ (2)

$$Fe^{3+} + HO_2 \rightarrow Fe^{2+} + O_2 + H^+$$
(3)

Here, we suspected an improvement of the glucose oxidation through a sono-Fenton process.^[27,28] Chakma and Moholkar showed that the role of ultrasound in the sono-Fenton process was simply physical and caused intense mixing in the medium to give a volumetrically more uniform production of HO radicals in the solution.^[27] To confirm the role of HO radicals in our oxidation of D-glucose, we first studied the effect of the addition of *tert*-butyl alcohol, a known HO radical scavenger, to the solution [Eq. (4)].^[29,30]

$$(CH_3)_3COH + HO^{\bullet} \rightarrow (CH_3)_2 \cdot CH_2COH + H_2O$$
(4)

Thus, in the presence of *tert*-butyl alcohol under the optimized conditions (glucose/H₂O₂ 1:3, ultrasonic conditions, 10 wt% FeSO₄, 15 min, 22.5 °C), the glucose conversion and yield of gluconic acid were less than 1%, which shows that the presence of HO⁻ radicals is essential in this reaction.

In addition, we quantified the production of HO⁻ radicals through a KI dosimetry method, monitored easily by UV/Vis spectrophotometry, based on the reaction in Equation (5).^[31]

$$2 \text{ HO}^{-} + 3 \text{ I}^{-} \rightarrow 2 \text{ HO}^{-} + \text{ I}_{3}^{-}$$
 (5)

The formation rates of I₃⁻ under ultrasonic irradiation in the presence and absence of FeSO₄ and H₂O₂ are reported in Table 3. Interestingly, the production of radicals was slightly more important in water in the presence of FeSO₄ (Table 3, entries 1 and 2). We performed glucose oxidation in the absence of H₂O₂ (glucose, H₂O, 10 wt % FeSO₄, 15 min US, 22.5 °C) but the yield of gluconic acid reached only 6%. If H₂O₂ was introduced, the formation rates of I_3^- under ultrasound increased by a factor of 100 (Table 3, entries 3 and 4) and 1000 (Table 3, entries 5 and 6) in the absence and in the presence of $FeSO_4$, respectively, compared to water solution. This result confirms the importance of radical production in the oxidation of glucose. If we compare Tables 1 and 3, we can see that the slight improvement of radical production between one and three equivalents of H₂O₂ relative to glucose (Table 3, entries 5 and 6) led to an increased conversion from 48 to 99% (Table 1, entries 6 and 9). Here, through the use of a HO⁻ radical scavenger in the reaction and the measurement of radical production, we

Table 3. Formation rate of I_3^- measured under US as a function of the presence of FeSO ₄ and the amount of H ₂ O ₂ .				
Entry	Conditions ^[a]	Formation rate of I_3^- under US [mol s ⁻¹]		
1	H ₂ O	3.1×10 ⁻¹¹		
2	H₂O, FeSO₄	3.8×10 ⁻¹¹		
3	H_2O , H_2O_2 (1 equiv.)	4.7×10^{-9}		
4	H_2O , H_2O_2 (3 equiv.)	9.1×10 ⁻⁹		
5	H ₂ O, FeSO ₄ , H ₂ O ₂ (1 equiv.)	6.5×10^{-8}		
6	H ₂ O, FeSO ₄ , H ₂ O ₂ (3 equiv.)	8.3×10 ⁻⁸		
[a] 10 mL water, 22.5 °C, US irradiation. Same proportion of FeSO ₄ and H_2O_2 as in the optimized experimental conditions (Table 1). For example, 1 and 3 equiv. correspond to the amount of H_2O_2 in the medium related to the qlucose in the oxidation process.				

demonstrated that the role of radicals in the oxidation of Dglucose into gluconic acid was improved under ultrasound by a sono-Fenton process. Further experiments are underway to better characterize the radical production by different methods and to explain the mechanism of this reaction in more detail.

Conclusions

We disclose an efficient method to oxidize D-glucose selectively into gluconic acid in the presence of a cheap and available catalyst (FeSO₄) and an eco-friendly oxidant (35 % H₂O₂ aqueous solution) under uncontrolled pH conditions by a sono-Fenton process. Indeed, low-frequency ultrasound activation was investigated and improved the selectivity of the reaction and the yield of gluconic acid with a decrease of the reaction temperature from 70 °C under silent conditions to 22.5 °C under ultrasound, which consumed 4.5 times less energy. The selectivity to gluconic acid was also increased if the glucose/ H₂O₂ molar ratio was greater than 1:3.

The role of hydroxyl radicals produced in the sono-Fenton process (FeSO₄/H₂O₂/ultrasound) was demonstrated in the oxidation of D-glucose. The application of this method is underway in our laboratory for the oxidation of other sugars and biomass-based chemicals. The use of high-frequency ultrasound is also under investigation to remove the catalyst in the reaction by controlling the production of radicals.

Experimental Section

Chemicals

All the chemicals were obtained and used without further purification. D-(+)-Glucose (>99.5%), V₂O₅ (>99.6%), and *tert*-butyl alcohol (>99%) were purchased from Sigma–Aldrich. FeSO₄·7H₂O (99%) and NaNO₃ were purchased from Prolabo, sodium gluconate was from Roquette, and H₂O₂ (35 wt% aqueous solution) was from Acros Organics.

Oxidation of D-glucose under silent conditions

p-Glucose (1 mmol, 180 mg) and FeSO₄ (10 wt % in optimal conditions, 18 mg) were dissolved in a 35% H₂O₂ aqueous solution (3 mmol in optimal conditions, 0.25 mL), and deionized water was

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added to obtain a total volume of 5 mL. After a desired time under 500 rpm stirring at 70 °C, the sample was diluted and analyzed by HPLC. The product was also identified by FTIR and ¹H NMR spectroscopy.

Ultrasound-assisted oxidation of D-glucose

Ultrasound was generated by using a Digital Sonifier S-250D from Branson (standby power $P_0 = 27.0$ W, nominal electric power of the generator $P_{elec} = 8.2$ W). A 3.2 mm diameter tapered microtip probe that operated at a frequency of 19.95 kHz was used, and its acoustic power in water ($P_{acous.vol} = 0.249$ WmL⁻¹) was determined by calorimetry using a procedure described in the literature.^[32] Energy consumption was measured by using a wattmeter (Perel). The reaction medium (p-glucose, catalyst, H_2O_2 , and water) was put in a glass cylindrical reactor (17 mm in interior diameter, 102 mm in height), thermostatted at 22.5 °C by using a Minichiller cooler (Huber). The ultrasonic probe was immersed directly in the reaction medium. After the desired time, the sample was diluted and analyzed by HPLC. The product was also identified by FTIR and ¹H NMR spectroscopy.

Characterization methods

Potassium iodide dosimetry was performed as described in the literature, with a 0.1 mol L⁻¹ KI solution over 30 min.^[33] I₃⁻ formation was monitored by using a UV/Vis spectrophotometer (Evolution 60S from Thermo Scientific) at a wavelength of 355 nm (ε (I₃⁻) = 26303 Lmol⁻¹ cm⁻¹). Each experiment was repeated three times at 22.5 °C, maintained by using the Minichiller cooling system. IR spectra were recorded by using an FTIR PerkinElmer (Spectrum One) using ATR technology. ¹H NMR spectra were recorded by using a 300 MHz Bruker spectrometer using D₂O as solvent and TMS as internal standard.

Glucose and fructose were analyzed by using a Shimadzu HPLC system equipped with a pump system (LC-20AD), an autosampler SIL-10 A, and a controller CBM 20 A. Products were separated by using a Shodex Sugar KS800 300×8.0 mm (size-exclusion chromatography; SEC) column using ultrapure water as eluent and a flow rate of 1.0 mLmin⁻¹, and quantified by a refractor index detector (Shimazu RID-10A). The amounts of gluconic acid and glucose were determined from the HPLC analysis by using the Varian Pro Star HPLC equipped with an ICE-COREGEL 107H column $300\times$ 7.8 mm from Transgenomic, a UV/Vis detector (Varian Pro Star, 210 nm) and a refractive index detector (Varian 356-LC). A H_2SO_4 aqueous solution (7 mm) was used as the eluent with a 0.4 mLmin⁻¹ flow rate. External calibration of the liquid chromatograph was performed using standards of glucose and fructose, and gluconic acid was quantified by the difference between the two HPLC analyses.

Keywords: biomass • heterogeneous catalysis • iron • oxidation • radical reactions

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Efficient and Selective Oxidation of D-Glucose into Gluconic acid under Low-Frequency Ultrasonic Irradiation



Radically oxidized! Low-frequency ultrasound associated with the Fenton system (Fe^{2+}/H_2O_2) can oxidize D-glucose efficiency and selectively into gluconic acid. This sono-Fenton process was demonstrated by studying the effect of hydroxyl radical production on the reaction. This original and eco-efficient method is promising for the further oxidation of chemicals derived from biomass.