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A gram scale selective oxidation of 5-hydroxymethylfurfural to diformylfuran in the presence of Oxone and catalyzed by 2-iodobenzenesulfonic acid

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In the present work, an alternative system of 5-hydroxymethylfurfural (HMF) oxidation was studied, in an attempt to avoid the use of expensive metal catalysts, polluting systems and high pressures. In this context, the partial oxidation of the hydroxyl group on the HMF molecule leads to the formation of the corresponding aldehyde, 2,5-diformylfuran (DFF). This reaction was catalyzed by 2-iodobenzenesulfonic acid in the presence of Oxone. Under optimized experimental conditions, the HMF conversion was found to be 100%, while the DFF yield and selectivity were almost 90%.

Introduction

Biomass, as a source of chemicals, represents a sustainable alternative to fossil fuel. It is composed of 75% of carbohydrates, which are the main carbon source in biorefineries. However, carbohydrates are highly oxygenated molecules Cn(H2O)n and must be deoxygenated to regain similar properties to those of petroleum compounds. The dehydration of C5 and C6 carbohydrates leads to the formation of furan derivatives such as furaldehyde^{1,2,3} and 5hydroxymethylfurfural 4,5,6 (HMF). The latter compounds are therefore platform molecules and represent a major interest in the context of sustainable development. These molecules are already used and valued in many ways, mainly by reduction or oxidation. Numerous applications, towards bio-based solvents, lubricants, bio-based polymers or fine chemicals, are being developed nowadays.^{7,8,9,10,11} Transformations by selective oxidation of furfural and HMF are particularly studied because they lead to bifunctionalized molecules of interest like maleic anhydride or diacids¹² such as succinic acid, levulinic acid, furanedicarboxylic acid (FDCA) or diformylfuran (DFF).13,14

Numerous oxidation methods of HMF to DFF have been reported in the literature, mainly in heterogeneous phase using noble or heavy metals in the presence of oxygen or other oxidants.^{15,16,17,18,19,20,21} Very often, these methods however require the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or its derivatives as an oxidation mediator. These methods are sometimes very effective but may require the preparation of a complex catalyst or multi-component mixture, long reaction times, high boiling solvents and a large excess of oxidant. The old methods with conventional oxidants can also be very effective, for example, the use of barium manganate gives 93% yield of DFF, however these methods suffer from the use of dangerous compounds and the generation of significant amounts of waste.^{22,23,24,25} These reactions are also often carried out in very dilute media making these methods difficult to exploit with the aim of changing the production scale from milligrams to kilos.

Hypervalent iodine derivatives such as 2-iodoxybenzoic $acid^{26,27}$ (IBX) or Dess-Martin reagent²⁸ (DMP) are well known for effective and selective oxidation of primary alcohols to aldehydes (Scheme 1).

These compounds offer an interesting alternative to the use of metal catalysts, which can make the processes more sustainable and less expensive, without the need of extraction, purification and recycling or treatment of metals that are often rare and/or toxic. This strategy has already been used to oxidize HMF into DFF. Lee et al. reported the use of a polymer bearing group similar to IBX, leading under optimal conditions to quantitative yields of DFF.²⁹ However to use this strategy in a viable process, major constraints need to be overcome. Indeed, the polymer contains only a low concentration of oxidant 1.02 mmol.g⁻¹, and it must be prepared in its oxidative form with a large excess of tetrabutylammonium oxone (5 equiv.) in the presence of methanesulfonic acid in dichloromethane for 12 hours followed by filtration before use.



Scheme 1. Hypervalent lodine derivatives used to oxidize selectively primary alcohols to aldehydes.

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Scheme 2. One step preparation of hypervalent iodine compounds from 2-iodobenzoic acid or 2-iodosulfonic acid and Oxone, leading to highly selective oxidant species of primary alcohol, IBX and IBS.

Other teams have prepared IBX supported on polymer which prove to be very effective for the oxidation of alcohols (not HMF), nevertheless, the same usage constraints are encountered, in particular the numerous stages of preparation of the catalyst, the very low molar fraction of iodine hypervalent on the polymer and generally its activation in the organic phase by tetrabutylammonium oxone.^{30,31,32,33}

Among the iodine derivatives used for catalytic oxidation, Ishihara et al have demonstrated that 2-iodoxybenzenesulfonic acid (IBS, scheme 1) is a particularly selective and effective catalyst for this type of oxidation.³⁴ Furthermore, it has been demonstrated that it is possible to generate the catalytic species of hypervalent iodine in situ from 2-iodobenzene carboxylic or sulfonic acids in the presence of Oxone® (2KHSO5, KHSO4, K2SO4) as co-oxidant (Scheme 2). This makes it possible to avoid the preparation of the hypervalent iodine species in stoichiometric proportions and to handle these compounds reported to be shock-sensitive.^{35,36} This strategy has been reported for the selective oxidation of primary alcohols by Vinod et al., Giannis et al. and Ishihara et al.^{34,37,38}

Compared to oxygen and hydrogen peroxide, which are well responding oxidants to the principle of atom economy, Oxone[®] provides an inert and useless mass for oxidation. However the processes using oxygen or hydrogen peroxide require special precautions related to the management of gas pressure or the risk of concentration and rapid decomposition of hydrogen peroxide.³⁹ Oxone[®] has, moreover, many advantages, it is a solid oxidant which can be easily transported and handled, it has a non-toxic nature and doesn't produce polluting by-product, and it is rather economical.⁴⁰ Considering some of these criteria, it can be classified among green oxidants.³⁷

In this work, we report the metal free oxidation of HMF into DFF in the presence of Oxone[®] as a co-oxidant and 2iodobenzenesulfonic acid as a catalyst.

Results and discussion

During our preliminary tests, we evaluated the efficiency of the hypervalent iodine derivatives formed "*in situ*" during the transformation of HMF into DFF, and compared the two catalysts, 2-iodobenzenecarboxylic acid and 2-iodobenzenesulfonic acid. As we can see in table 1, the two catalysts lead to the formation of DFF selectively but IBS is particularly more effective. In addition, Ishihara et al. have proved that IBS is a selective and effective catalyst for this type of oxidation and more active than IBX.³⁴

View Article Online DOI: 10.1039/D0NJ01653E avidation of HMF to DFF



Reaction conditions: 200 mg (1.6 mmol) of HMF, 1.17 g Oxone, equivalent to KHSO₅/HMF mol ratio = 1.2, 30 mg of catalyst in 6 mL of nitromethane, 70°C, 4h.

With these very encouraging results, we decided to explore the reaction conditions of the transformation with IBS.

Polar aprotic solvents often show good properties for the oxidation of HMF to DFF, DMSO, for example, has frequently been reported as the best solvent for this type of transformation.^{13,41} However, exposure to DMSO sets problems of toxicity because of its ability to easily dissolve the chemical substances that can be absorbed through the skin, moreover it has a very high boiling point (191 °C), which complicates its separation or recycling in the processes. To this purpose, we carried out a solvent screening for this transformation in order to find an alternative to DMSO. (Table 2)

The same procedure was used with all solvents (same conditions of concentration, agitation speed and temperature), by mixing the Oxone[®] previously ground using a mortar with the hydroxymethylfurfural and the 2-iodoxybenzensulfonic acid as catalyst. The set temperature is 70 °C. The solvents having a boiling point below this temperature (chloroform, DCM, THF and acetone) were heated under reflux (entries 10, 11, 13, 3, table 2).

Results are presented in table 2. For most of the solvents, the conversions are high and no trends can be drawn between the nature of the solvent and the HMF conversion. Among these solvents, the best selectivity of HMF to DFF is obtained using nitromethane, acetonitrile, ethyl acetate and acetone. This can be interpreted by 64% and 89% of DFF yield and selectivity using, respectively, acetonitrile and nitromethane that appear to be the most effectives (entries 1 and 8). Furthermore, a 50/50 mixture of acetonitrile and nitromethane leads to a DFF yield equivalent to that carried out in pure nitromethane (data not shown). One should note that DMSO in our case is inefficient. When using solvents that completely dissolve the reactant and catalyst (DMA and water), a complex mixture of products without DFF is detected, and only some of them could be identified, which are mainly diacids such as maleic acid, fumaric acid and dicarboxylic furan. With acidic solvents (entries 6 and 7) the reaction medium rapidly turned dark brown which

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Table 2. Catalytic oxidation of HMF into DFF using different solvents.^a

Entry	solvent	Conversion (%)	Selectivity (%)	Yield (%)	Dielectric constant (20ଅଫ୍ରା: 10 ୫୦ଶିନ/କୁଚ୍ଚଧାନହୀଙ୍କ)		
1	CH ₃ NO ₂	100	89	89	36	101	
2	AcOEt	87	62	54	6	77	
3	Acetone	49	84	41	21	56	
4	MIBK	95	39	38	13	116	
5	DMA	100	0	0	37	164	
6	Formic Acid	100	0	0	58	101	
7	Acetic Acid	100	11	11	6	118	
8	CH ₃ CN	100	64	64	38	82	
9	DMSO	91	0	0	47	190	
10	CHCl ₃	87	23	20	5	61	
11	DCM	100	36	36	9	40	
12	H ₂ O	97	0	0	80	100	
13	THF	53	0	0	7	66	
14	Cyclohexane	100	10	10	2	81	
15	Tert-butanol	100	0	0	12	83	
16	-	97	23	22	-	-	

^a Reaction conditions: 200 mg (1.6 mmol) of HMF, 1.17 g of Oxone[®] (KHSO₅/HMF mol ratio = 1.2), 30 mg of sodium 2-iodobenzenesulfonate (0.36 wt%), 6 mL solvent, 70°C with reflux for solvents having boiling point below this temperature, 4h.

signifies the formation of humin and degradation of HMF. However, acetic acid, which is less dissociating and less acid (Er = 6.2 and pKa = 4.7 at 20 ° C), allows to obtain a small proportion of DFF. These results corroborate the observations already reported that an excessively acidic environment is not favorable and can lead to the degradation of furan derivatives or its polymerization into humin.42,43 Compared with the work of Yoon Sik Lee et al. which reports the best oxidation results in chloroform²⁹, when using chlorinated solvents (entries 10 and 11) only low yields of DFF were obtained. However, with DCM, 35% yield of DFF was obtained which relatively remarkable in view of the relatively low working temperature 40 °C, compared to the other solvents. Regarding the reaction without solvent, which was carried out under the same conditions, almost total HMF conversion is obtained but with a 22% yield of DFF, even though the homogenization of the reaction mixture was difficult to be achieved. This result should be compared with similar ones obtained with non-polar solvents, justifying the hypothesis of complete insolubility of the catalytic oxidizing species of hypervalent iodine in these solvents.

In conclusion, the best solvent for this selective oxidation of HMF to DFF turns out to be nitromethane. The great diversity of results obtained demonstrates the difficulty of being able to predict the efficiency of a solvent according to its physical properties; we can simply note that for this transformation, aprotic polar solvents tend to be more selective towards DFF in the oxidation of HMF. On the base of the proposed mechanism by Santagostino⁴⁴ (Scheme3), we can assume that partial solubilization of the different species produced during the



Scheme3. Different iodine derivatives and supposed catalytic cycle during the selective oxidation of HMF to DFF

oxidation is a necessary but not sufficient condition for the selective oxidation of DFF. Note that, the oxidation depends in particular on the dissociation of the pairs of ions and the solubility of $Oxone^{\oplus}$ in different solvents. Another important aspect of this reaction is that oxidation takes place under partial acid conditions in all cases ($Oxone^{\oplus}$ is a salt of persulfate and hydrogen sulfate pKa = 1.9) and that acidic conditions could lead to the formation of humins.

In view of the good results obtained in nitromethane and their potential optimization, we studied, in this solvent, the effects of the various reaction parameters of the transformation. First, we evaluate the influence of the temperature over a 4 h reaction (Figure 1). The conversion of HMF is larger than 90% at 40°C; however, this value is 100% at temperatures above or equal to 70°C.

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The catalyst's stability was also verified by preheating it at 90°C for one hour then introducing it into the reactor for 4 hours of oxidation at 70°C. Despite this, a DFF yield of 90% was still Nevertheless, these results also demonstrate once again the instability of the formed DFF towards temperature. Thus, the best results are obtained for a moderate heating at 70°C over 4h. This is in accordance with the known instability of DFF (storage at low temperature is recommended to avoid its degradation). In conclusion, increasing the temperature increases the reaction rate of DFF formation and its

For the purpose of verifying a potential acceleration of the reaction with the increase of the catalyst quantity, we investigated the effect of its concentration (Figure 3). It is observed that in the absence of catalyst, the HMF conversion reaches only 60% without leading to the formation of DFF. The obtained brownish yellow mixture signifies the decomposition of furan derivatives into humins due to the acid characteristics of Oxone. With increasing the amount of catalyst at 70 °C in 4 hours, the conversion reaches 100 % and the yield of DFF attain a maximum using 0.36 wt% of the catalyst before decreasing to values around 50 to 40%. In order to further investigate these results, we compared the formation of DFF with time at 0.36 and 0.73 wt% of catalyst (Figure 4). Even though an acceleration of the DFF formation is observed during the two first hours using more catalyst it quickly appears that during time the DFF degradation becomes preponderant. Therefore, it could reasonably be hypothesized that increasing the quantity of catalyst is detrimental to DFF stability and formation, probably due to the acidic nature of the catalyst leading to DFF degradation. To conclude, the best compromise is a reasonable 70°C heating over 4h with 0.36 wt% of catalyst. In order to maximize the production of DFF by limiting the

production of wastes, we studied the effect of the amount of co-oxidant Oxone[®] and the HMF concentration on the yield of DFF. We know that these factors can have a significant impact on the transformation.

room temperature (21 °C) after 4 hours of reaction, it was interesting to note that around 50% of HMF have been converted to unknown products (probably intermediate species) that could not be identified by our GC method. DFF yield and selectivity varied similarly with the reaction temperature reaching a maximum for 70°C. Furthermore, above 70 °C, the conversion rate of HMF is total, but the yield of DFF gradually drops, demonstrating its instability at high temperatures. At 101 °C, the boiling point of nitromethane, only 18% of the DFF can be measured in GC after 4 hours of reaction. The degradation products have been identified as being mainly maleic acid and furan dicarboxylic acid (NMR analysis, SI).

Despite the fact that there were no traces of DFF formation at

In order to verify the hypothesis of DFF degradation at temperatures above 70 °C, we performed reaction monitoring at 70°C, 80°C and 90°C (Figure 2).

These experiments show that high yield of DFF could be reached rapidly at higher temperature, 80% at 90°C in half an hour (Figure 2). This also indicates that the catalyst presents a good stability at higher temperature and could play its full role without inconvenience.







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Figure 3. Effect of the catalyst weight sodium 2-iodobenzenesulfonate (wt%) on HMF conversion and DFF selectivity. HMF 1.6 mmol, Oxone 1.17g, sodium 2-iodobenzenesulfonate 0 to 1.44 wt%, 6 mL nitromethane, 70°C.



Figure 4. Effect of the amount of catalyst on DFF yield as a function of time. HMF 1.6 mmol, Oxone[®] 1.17g, sodium 2-iodobenzenesulfonate 0.36wt% (red) and 0.73wt% (green), 6 mL of nitromethane, 70°C.

We carried out a first series of experiments by keeping the quantities of catalyst and Oxone® constant and varying only the HMF mass. This, therefore, implies a variable Oxone/HMF ratio ranging from 2.4 corresponding to 100 mg to 0.6 corresponding to 400 mg of HMF introduced (Figure 5, red line (□)). We observe that the Oxone® used in excess, corresponding to 2.4 eq, leads to a loss of selectivity and yield of DFF (Figure 5 (\Box) , point at 100 mg). While it is used as a limiting reagent, we observe a quantitative yield compared to the Oxone® which is totally consumed to oxidize the HMF to DFF (Figure 5 (
), points at 300 and 400 mg of HMF). Furthermore, in the latter two cases, the remaining expected HMF is no longer visible, demonstrating its transformation along unknown reaction path. During a second series of experiments, we maintained the Oxone/HMF ratio at 1.2, keeping the other parameters constant (Figure 5 (Δ), Green curve). In this case, the constant amount of catalyst (30 mg) mainly affects the yield of DFF, there is a slight decrease in the yield at low HMF concentration (point at 100 mg), and a loss of activity when the HMF concentration increases with respect to the amount of catalyst.



Figure 5. Effect of the amount of HMF (from 100 mg to 400 mg) on the yield of DFF with various oxone to HMF ratio and catalyst to HMF ratio, 6 mL of nitromethane, 70°C, 4h. (\Box): The mass of Oxone is kept constant to 1,17 g and catalyst to 30 mg, Oxone/HMF ratio= 2.4 (100 mg of HMF), 1.2 (200 mg of HMF), 0.8 (300 mg of HMF) and 0.6 (400 mg of HMF), (Δ): Oxone/HMF ratio = 1.2, catalyst/HMF ratio = 0.12 (100 mg of HMF), 0.06 (200 mg of HMF), 0.04 (300 mg of HMF) and 0.03 (400 mg of HMF), (\diamond): Solvent volume is invariable i.e. 6 mL, the ratio Oxone/HMF = 1.2 and catalyst/HMF ratio = 0.06, (o): HMF conversion as a function of HMF mass.

Finally, during a final series of experiments, the volume of solvent is kept as the only constant parameter, *i.e.* 6 mL. The Oxone/HMF ratio is maintained at 1.2 and the Catalyst/HMF ratio at 0.06.

In this case, it is interesting to note that the yield obtained in DFF remains very high, close to the maximum yield under optimal conditions. Thus, with 1.3wt%, 3.4wt% and 4.2 wt% of HMF corresponding to a mass of 100 mg, 300 mg and 400 mg, the corresponding DFF yields are 85%, 86 % and 84% (Figure 5 (\diamond), yellow curve). These last results are very important because they confirm the possibility of working at higher HMF concentrations without significantly affecting the production of DFF.

For effective industrial utilizations of heterogeneous catalysts, the lifetime, stability and reusability is an important parameter. Hence, the recyclability test of 2-iodobenzenesulfonic acid was investigated on the oxidation of HMF to DFF under the optimized experimental conditions. After the catalytic test, the catalyst was recovered by simple filtration and extensively washed with ethyl acetate. After being dried under vacuum, 14 mg of catalyst precipitates were obtained (around 50% of initial mass). This exact amount was reused for the next reaction, instead of 30 mg, and a DFF yield of 50% was obtained.

Note that, at the end of the reaction, the catalyst is present in different forms with different oxidation degrees (+I, +III and +V) more or less soluble in the washing solvent. This could explain the loss of around 50% of the catalyst.

Thus, the catalyst recovery is a feature to improve, but it appears that the recovered catalyst is still active and permit to perform the reaction as efficiently.

At the end of this work, we wanted to verify that this method could be adapted to the preparation of DFF on the scale of several grams. By multiplying by ten the quantities of materials we obtained 1.78 g (87%) of DFF with the same grade of purity

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Scheme 4. Synthesis of DFF by selective oxidation of HMF in gram scale.

(NMR analysis, SI), confirming the possibility of extending our method to this first stage of scale-up. Finally, a gram scale synthesis was performed in the optimized conditions. Starting with 2 g of HMF, a 87% isolated yield of DFF was achieved (Scheme 4), which further highlighted the interest of this catalyst in this oxidation reaction.

In order to highlight the simplicity and the inherent advantages of our process, we have extracted some of the best recent methods of DFF synthesis described in the literature. Although we can see that the yields of DFF can be higher, almost all these methods require the preparation of complex metallic catalyst, the presence of co-catalyst of TEMPO type and/or very dilute reaction media. By comparing these various methodologies, it appears that our process is competitive and could be suitable for the production of DFF (Table 3).

Conclusion

With this work, we demonstrated the possibility of using hypervalent iodine derivatives in the presence of Oxone[®], an economical and non-toxic oxidant with non-toxic byproducts, to carry out the oxidation of HMF to DFF with great selectivity and

yields. The method is particularly simple, because only filtration or extraction of the sulfate salts and the Catalyse and t the reaction are required to obtain the DFF with a high grade of purity. The active oxidizing species obtained "in situ" eliminate the risks associated with the use of iodine derivatives in stoichiometric proportions and reduce the costs of the catalyst. We optimized the reaction conditions by considering the product stability and competitive reactions. The best compromise was obtained for a 4 hours of reaction at 70 °C, using nitromethane. In these conditions, 89% of DFF is obtained as the only product after extraction and filtration. In addition, very good results are also observed over much shorter times, in 30 min at 90 °C, where 80% of DFF is obtained. On the contrary to what was described in literature this method involves no metallic catalyst, uses reasonable concentration of HMF, and we have demonstrated the possibility of extending the method to a gram-scale production of DFF. Therefore, we believe that these results lay the foundation for the development of a larger scale process.

Conflicts of interest

There are no conflicts to declare.

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Table 3. Examples of recent studies about DFF synthesis										
Catalyst wt%	HMF wt%	[HMF] mol.dm ⁻³	Solvent	Oxidant	Mole ratio, Oxidant/HMF	Temp. (°C)	Time (h)	Product(s) (%)	Ref.	
ECS-IL-AI(NO₃)₃ª 3,75% TEMPO 0,37%	5,4	0,5	AcOH	Flow O ₂ 1bar	-	50	5	DFF 98% FDCA 1%	15	
HKUST-1 ^b 0,09% TEMPO 0,09%	0,045	0,004	DMSO	O ₂ 3,4 bar	35	120	3	DFF 96%	17	
MnO2-NRs ^c 0,13% UV Light 375nm	0,008	0,0005	AcN	Air	-	39	4	DFF 99%	16	
TEMPO like nitroxide ^d 0,28%, Collidine 0,3%, NaHCO ₃ 6,6%	3,2	0,4	DCM/H ₂ O	lodine	2	22	1	DFF 93%	45	
Sodium 2-	2,44	0,26	− CH ₃ NO ₂	Oxone®	1,2	70	4	DFF 89%	This work	
iodobenzenesulfonate 0,36%						90	0,5	DFF 80%		
Sodium 2- iodobenzenesulfonate 0,62%	4,2	0,53				70	4	DFF 84%		

^a ECS-IL-Al(NO_3)₃: Expanded corn starch covalently bonded to a ionic liquid with Al(NO_3)₃; ^b HKUST-1: Cu based metal organics frameworks, Cu and 1,3,5 benzenetricarboxylic acid; ^c Manganese Oxide nanorods; ^d TEMPO like: 4-acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl.

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