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Salt-assisted acid hydrolysis of starch to D-glucose under microwave irradiation

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Abstract

The effect of inorganic salts on the hydrolysis of starch in a microwave field was investigated and it was found that some inorganic salts can effectively accelerate the acid hydrolysis of starch. The yield of D-glucose reached 111 wt% (equal to the theoretical yield). © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Salt-assisted; Acid hydrolysis of starch; Microwave irradiation; D-Glucose

1. Introduction

The effect of microwave heating has long been studied in polymer chemistry and is used industrially in vulcanization processes.[1] However the application of microwave heating in organic chemistry appeared only at the end of the 1980s, with the pioneering work of Gedye and Gigere.[2,3] Since then, microwave chemistry has become a rapidly developing branch in organic synthesis.

Microwave dielectric heating dissipates heat inside the medium and raises the energy of the molecules rapidly, and this heating mode is thus quite different from conventional heating. Consequently, under microwave dielectric heating, more molecules become energized, and this usually results in higher reaction rates and greater selectivity.

Some papers have reported the hydrolysis of starch in a microwave field.[4–10] Yu et al. showed that starch (10%) in dilute hydrochloric acid (0.5 M) was completely hydrolyzed with 5 min microwave irradiation without formation of colored byproducts. Some investigators noted that the presence of a large number of ions, which can frequently enhance effects of dielectric loss and microwave coupling, could produce superheating.[11] The addition of salts to solvents can increase their conductivity and has a dramatic influence on their rate of heating.[12] The present study was conducted to examine the effect of inorganic salts on the acid hydrolysis of starch under microwave irradiation. We found that inorganic salts could be coupled with microwave irradiation to accelerate the reaction rate, and that different kinds of salts manifest different effects. The yield of D-glucose obtained reached 111 wt% (equal to the theoretical yield) after the addition of inorganic salts. When compared with conventional heating, the reaction rate for the hydrolysis of starch to glucose was accelerated 100 times under microwave irradiation.

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2. Experimental

Materials and equipment.—Soluble starch was purchased from the Shanghai Chemical Reagents Plant, and a domestic microwave oven of 2.45 GHz was used.

Methods.—Reaction of the starch with hydrochloric acid under microwave irradiation. In a 70 mL thick-walled Teflon with a screw-cap transparent to microwave radiation, 200 mg of starch granules (water content was 11.6%) was suspended in 2 mL of 0.05% (w/w) HCl, and 1 mL of a solution of inorganic salts containing 0.15 mol/L [Cl^-] (or [SO_4^{2-}]) was added. The container could withstand pressures up to 1.2 MPa. The reactor was irradiated in a microwave field for different lengths of time. The solution was then brought to pH ~ 7 with 5% (w/w) NaOH. The amount of D-glucose in the resulting solution was determined by glucose oxidase analysis.[13–15]

Reaction of the starch with HCl with oil-bath heating at 145 °C. In a glass vessel, 200 mg of starch granules (water content 11.6%) was suspended in 2 mL of 0.05% (w/w) HCl, and then 1 mL of a solution of inorganic salts containing 0.15 mol/L [Cl^-] (or [SO_4^{2-}]) was added. The vessel was sealed and heated in an oil-bath at 145 °C for 5 h. The solution was then brought to pH ~ 7 with 5% (w/w) NaOH. The amount of D-glucose was determined by glucose oxidase analysis.

Table 1
The yield of D-glucose in the acid hydrolysis of starch in the presence of metal halides under microwave irradiation [a]

Entry	Metal halide	Yield of D-glucose (wt%) [c]			
		120 s	180 s	240 s	600 s
1	[b]	0	0	0	78.37
2	LiCl	24.0	105.8	85.1	
3	NaCl	88.5	96.0	81.1	
4	KCl	61.9	99.2	60.4	
5	$MgCl_2$	88.0	96.5	83.4	
6	$CaCl_2$	59.0	91.1	90.0	
7	$BaCl_2$	21.7	111.0	70.1	
8	$FeCl_3$	108.6	45.1		
9	$AlCl_3$	0.1	25.6	4.4	
10	NaBr	60.0	92.3	69.3	
11	KBr	83.9	90.1	82.6	
12	KI	89.2	77.7	48.8	

[a] Reaction was carried out with 200 mg of soluble starch, 2.00 mL of 0.05% (w/w) hydrochloric acid, and 1 mL of 0.15 mol/L [Cl^-] under 800 W of microwave power irradiation.

[b] With 1.00 mL of H_2O to replace the salt solution to maintain the reaction volume.

[c] The theoretical yield of D-glucose is 111%.

The percent yield of D-glucose was calculated by the following equation

$$\%\ \text{yield} = \frac{\text{mg D-glucose}}{200\ \text{mg} \times (1 - 11.6\%)\ \text{starch}} \times 100$$

3. Results and discussion

Table 1 gives the results of acid hydrolysis of starch in the presence of metal halides in a microwave field. Compared with the results of Entry 1, which showed that the yield of D-glucose was 78.4% in 600 s without added metal halides, the result of other entries show that all metal halides studied accelerated the acid hydrolysis of starch, and the yield of D-glucose was higher than 90%, except for $AlCl_3$, which gave a yield of only 25.6%. Among these metal halides, LiCl, $BaCl_2$, and $FeCl_3$ were the most effective catalysts for starch hydrolysis in a microwave field, and $BaCl_2$ showed the best yield of 111.0% D-glucose in 120 s, indicating that starch was converted completely into D-glucose without any by-products. It suggests that 'selective heating' in a microwave field causes all of the starch molecules to become hydrolyzed in a short time, and efficiently inhibits decomposition of the D-glucose product. This is significantly different from conventional heating. The low efficiency of $AlCl_3$ is probably because it can form $H[AlCl_4]$ with HCl, leading to a decrease of ion concentration, which in turn decreases the microwave coupling of the system.

The results suggest that the metal halide's ability to promote the hydrolysis of starch is due to the salt's ability to cause superheating of the solution. Microwave heat involves a direct interaction with certain classes of absorbing molecules. This direct absorption can lead to a localized introduction of energy to a region from the remote microwave source and raises the solution temperature. It is well established that the superheating effects caused by microwave irradiation can lead to tempera-

Table 2
The yield of D-glucose in the acid hydrolysis of starch in the presence of metal halides with conventional oil-bath heating [a]

Entry	Metal halide	Yield of D-glucose (wt%) [c]
1	[b]	77.8
2	LiCl	94.6
3	NaCl	91.3
4	KCl	88.5
5	$MgCl_2$	95.9
6	$CaCl_2$	76.3
7	$BaCl_2$	71.4
8	$FeCl_3$	95.0
9	$AlCl_3$	61.9
10	NaBr	91.3
11	KBr	95.6
12	KI	97.0

[a] Reaction was carried out with 200 mg of soluble starch, 2.00 mL of 0.05% (w/w) hydrochloric acid, and 1 mL of 0.15mol/L [Cl^-] in an oil-bath at 145 °C for 5 h.

[b] With 1.00 mL of H_2O to replace the salt solution to maintain the reaction volume.

[c] The theoretical yield of D-glucose is 111%.

Table 3
The yield of D-glucose in the acid hydrolysis of starch in the presence of metal sulfates under microwave irradiation [a]

Entry	Metal sulfate	Yield of D-glucose (wt%) [c]			
		120 s	180 s	240 s	600 s
1	[b]	0	0	0	78.37
2	Na_2SO_4	8.0	12.6	9.1	
3	$MgSO_4$	7.7	7.8	4.4	
4	$ZnSO_4$	7.0	6.9	4.7	
5	$Al_2(SO_4)_3$	10.0	66.8	50.9	
6	$Ce(SO_4)_2$	88.9	88.9	80.7	

[a] Reaction was run with 200 mg of soluble starch, 2.00 mL of 0.05% (w/w) hydrochloric acid and 1 mL of 0.15 mol/L [SO_4^{2-}] under 800 W of microwave power irradiation.

[b] With 1.00 mL of H_2O to replace salt solution to maintain the reaction volume.

[c] The theoretical yield of D-glucose is 111%.

ture 10–30 °C in excess of the conventional boiling point of the solvent. Furthermore, the presence of salts in polar solvents frequently enhances dielectric loss effects and microwave coupling of the solvents. Consequently, superheating effects can be magnified by the addition of such ions as NaCl. Also it is possible that localized superheating effects could lead to a small but significant increase in the reaction rate. The hydrolysis reaction can thus be completed in a short time in the presence of metal halides.

The yield of D-glucose decreased dramatically with 240 s of microwave irradiation because of higher temperature reached by the solution. Under these conditions, D-glucose is not stable at the higher temperature, and undergoes oxidation and decomposes rapidly. In practical applications, it may thus be difficult to control the reaction time for the maximum yield of D-glucose.

Table 2 summarizes the results obtained with conventional oil-bath heating. It is clear that metal halides, except $CaCl_2$, $BaCl_2$ and $AlCl_3$, are effective catalysts for starch hydrolysis. When compared with Table 1, these results suggest that microwave dielectric heating can shorten the reaction time, enhance the chemical yield, and improve the selectivity. In the case of $BaCl_2$, the large difference of catalytic activity between conventional heating and microwave dielectric heating is considered to result from the 'salt-assisted' effects in a microwave field. Barium chloride, which is capable of strong coupling with microwaves, can lead to much higher rates of heating than in the conventional method.

Compared with conventional heating, microwave dielectric heating is an efficient procedure which shortens the reaction time 100-fold.

Further investigations were made on the effect of metal sulfates in a microwave field. As listed in Table 3, Na_2SO_4, $MgSO_4$, and $ZnSO_4$ did not accelerate the acid hydrolysis of starch, and the highest yield of D-glucose was only 12.6% in the presence of Na_2SO_4. However, when $Ce(SO_4)_2$ was employed, the yield of D-glucose reached 88.9%, and thus $Ce(SO_4)_2$ facilitates hydrolysis of starch more than other sulfates in a microwave field. These results suggest that the catalytic activities of sulfates are lower than metal halides, and the presence of sulfates, such as Na_2SO_4, $MgSO_4$ and $ZnSO_4$, even inhibit the acid hydrolysis of starch. The reason is probably that sulfate buffers the pH and decreases the acidity of 0.05% HCl because the hydrogen sulfate ion is a weak acid

Table 4 shows the results with metal sulfates under conventional heating. A maximum yield

Table 4
The yield of D-glucose in the acid hydrolysis of starch in the presence of metal sulfates with conventional oil-bath heating [a]

Entry	Metal sulfate	Yield of D-glucose (wt%) [c]
1	[b]	77.8
2	Na_2SO_4	0
3	$MgSO_4$	0
4	$ZnSO_4$	5.6
5	$Al_2(SO_4)_3$	24.9
6	$Ce(SO_4)_2$	95.6

[a] Reaction was run with 200 mg of soluble starch, 2.00 mL of 0.05% (w/w) hydrochloric acid and 1 mL of 0.15 mol/L [SO_4^{2-}] in an oil bath at 145°C for 5 h.

[b] With 1.00 mL of H_2O to replace salt solution to maintain the reaction volume.

[c] The theoretical yield of D-glucose is 111%.

of 95.6% was obtained in the presence of $Ce(SO_4)_2$. On the other hand, Na_2SO_4, $MgSO_4$ and $ZnSO_4$ inhibited the acid hydrolysis of starch, and no D-glucose was found in the case of Na_2SO_4 and $MgSO_4$ under conventional heating.

Although the yields of D-glucose in the presence of Na_2SO_4 or $MgSO_4$ under microwave irradiation were very low, being 12.6 and 7.8%, respectively, some hydrolysis reaction still occurred.

4. Conclusions

Investigations of the salt-assisted acid hydrolysis of starch have established that hydrolysis is accelerated significantly by the addition of inorganic salts in a microwave irradiation field. It was found that starch could be hydrolyzed to D-glucose completely in a short time by adding metal halides. The maximum yield of D-glucose reached 111 wt% with use of the metal halides, LiCl, $BaCl_2$, and $FeCl_3$, with 120–180 s of microwave irradiation. The difference between metal halides and sulfate salts illustrates that the properties of the salts are very important in affecting the hydrolysis reaction in a microwave field.

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