

Synthesis of 1, 3-Propane Sultone

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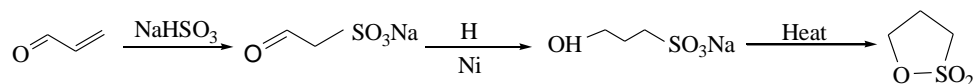
Abstract- 1, 3-propane sultone is synthesized through free-radical addition reaction, acid reaction and intermolecular dehydration reaction from allyl alcohol serving as the starting materials. Compared with other reaction systems, the improved method for preparing of 1, 3-propane sultone has many advantages, such as mild reactive conditions, easy for operation and control, and the yield is up to 95%. The process is applicable to the industrial development for preparation for 1, 3-propane sultone.

Keywords- Allyl Alcohol; 3-Hydroxypropanesulfonic Acid; Synthesis; Characterization; 1, 3-Propane Sultone

I. INTRODUCTION

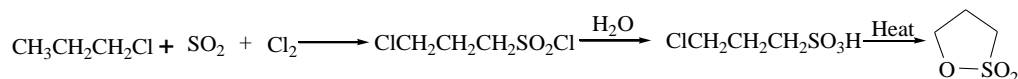
1, 3-propane sultone (PS) is an important reagent for the propylation effect of sulfonic acid, because 1, 3-propane sultone possesses a stronger reaction activity for alcoholysis and aminolysis with alcohols, phenols, mercaptans and amines. The surface properties of the chemical substances can be improved by introducing $-(CH_2)_3SO_3H$ onto the O, S or N of 1,3-propane sultone. Therefore, 1, 3-propane sultone has a wide application in fields of dye, medicine, surfactant [1, 2]. According to different starting materials, there are three practical synthesis routes.

(1) Synthesis process from acrolein [3, 4]



The synthesis needs hydrogenation reduction, and the synthesis is complicated, with a low yield of 79%.

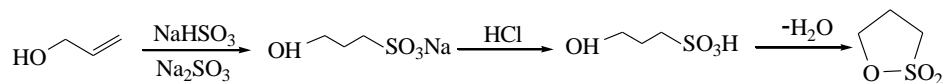
(2) Synthesis process from propyl chloride [5]



The synthesis is also complicated and has lower yield.

(3) Synthesis process from allyl alcohol [6, 7]

1,3-propane sultone is synthesized from allyl alcohol and $NaHSO_3$, through addition reaction, acidification, distillation in vacuum and intermolecular dehydration. The synthesis is as follows:



The reaction is in mild reactive conditions and easy for operation and the yield is 95%.

By comprehensive comparison of the above synthesis routes, the third one is selected and improved in this paper.

II. EXPERIMENTAL

A. Reagents and Instrument

$NaHSO_3$, Na_2SO_3 , allyl alcohol, and ethyl alcohol are all of AR, with purities of 0.995 in mass fraction. The IR spectrum was tested by Shimadzu IR2408. The 1H NMR was tested by Bruker DPX-400 NMR Spectrometer.

B. Preparation for 3-hydroxy-1-propanesulfonic Acid Salt

Solution A was prepared by dissolving 1.83 g $NaHSO_3$ and 12.00 g Na_2SO_3 in 40 ml water. Solution B was prepared by dissolving 5.90 g distilled allyl alcohol in 20 ml water. 0.92 g Na_2SO_3 and 20 ml water were put into a 250 ml three-neck flask with an intense agitation, after which, Solution A and Solution B were simultaneously added in incremental drops at room temperature within 90 minutes, then the reaction temperature was increased and kept at about 90~100°C and the reaction was performed for 3~4 h with the pH is about 7~8. When there was no more the distinctive odor of allyl alcohol, the addition

reaction finished.

The pH of the mixture after the addition reaction was adjusted to 3~4 by adding 10% sulfuric acid to make HSO_3^- and SO_3^{2-} convert to SO_2 , so the impurities could be removed easily; then the mixture was concentrated by a rotary evaporator until the white film appeared. Moreover, 10% sodium hydroxide solution was added to the concentrated mixture to adjust the pH to be neutral, thus, the excessive H_2SO_4 was converted into Na_2SO_4 ; because the inorganic salts were insoluble in alcohol which would be added at the next operation, and then the inorganic salts could be removed by filtration, thus, the purity of 3-hydroxy-1-propanesulfonic acid salt will be greatly increased. Then the neutral mixture was concentrated once again till the white solid appeared, after that, quantitative ethanol was added to the mixture, which was then filtrated and the filtrate was obtained.

C. Preparation for 3-hydroxy-1-propanesulfonic Acid (HPS)

HCl gas was introduced into the filtrate in the stirring condition to make NaCl precipitate completely. Then the suitable amount of anhydrous CaCl_2 was added into the mixture which was then stirred for 2 h, frozen for 12 h, and then filtrated to remove the insoluble salts; the obtained filtrate was concentrated in a rotary evaporator below 75°C to get HPS, a reddish-brown liquid.

D. Preparation for 1, 3-propane Sultone (PS)

3-hydroxy-1-propanesulfonic acid (HPS) and water were added into a round bottom flask in an oil bath, then HPS performed vacuum distillation and intermolecular dehydration to synthesize PS in the stirring condition; the product PS of $205\sim 230^\circ\text{C}$ was collected, the yield was 95%.

E. The Characterization of 1, 3-propane Sultone

The IR spectra of 1, 3- propane sultone is shown in Fig. 1. It can be seen that wave 2970 cm^{-1} is the vibration absorption peak of methylene, and waves 1345 cm^{-1} , 1269 cm^{-1} and 1166 cm^{-1} are the characteristic absorption peaks of 1,3- propane sultone.

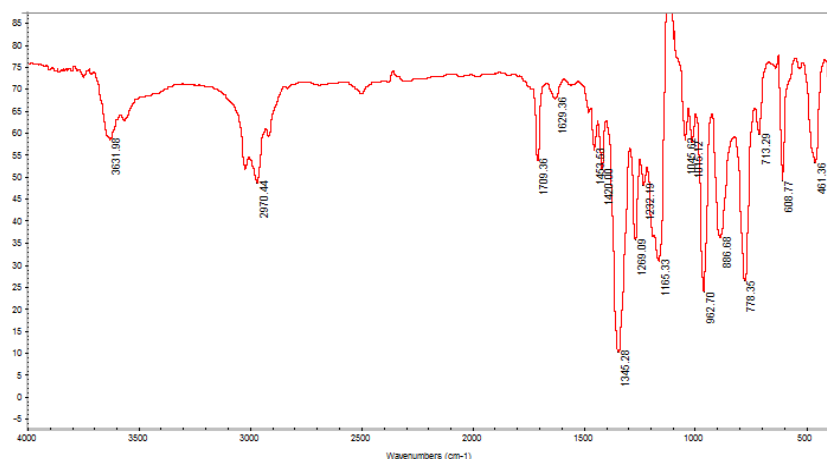


Fig. 1 The IR spectra of 1, 3- propane sultone

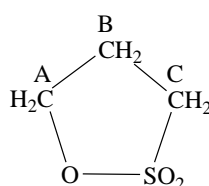
The ^1H NMR spectrum was tested by NMR Spectrometer of Bruker DPX-400 NMR.

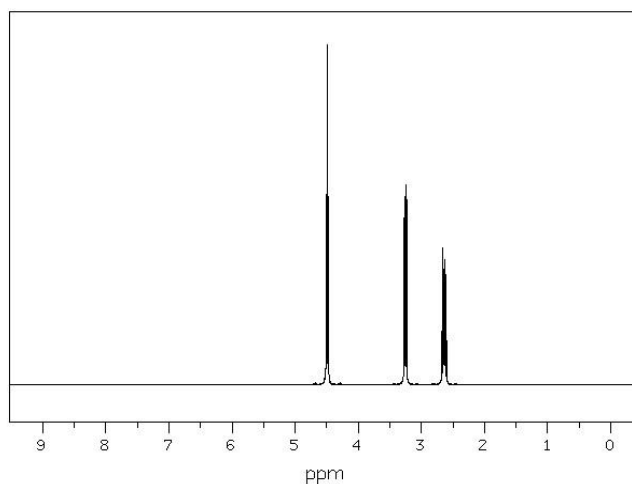
The ^1H NMR spectrum of 1, 3-propane sultone is shown in Fig. 2, and the spectrum analysis results are shown in Table 1.

TABLE 1 ^1H NMR ANALYSIS RESULTS OF 1,7-DIBROMOHEPTANE PREPARED

Characteristic functional groups	Chemical Shift δ , ppm
A	4.49
B	3.25
C	2.64

In Table 1, what do “A, B and C” stand for are as follows:



Fig. 2 The ^1H NMR spectrum of 1,3-propane sultone

III. RESULTS AND DISCUSSION

A. The Effects of the Reactant Ratio between NaHSO_3 and Na_2SO_3 on HPS Yield

When the adding time was 70 minutes, the pH was about 7~8, the reaction temperature was 95°C , and the reaction time was 3.5 h, the effects of reactant ratio between NaHSO_3 and Na_2SO_3 on HPS yield were studied. In the free-radical addition reaction, different reactant ratios result to be different pH values; pH affects the oxidation potential and then further affects the generation of the free radicals, which play a key role in the free-radical addition reaction. Therefore, the reactant ratio plays an important role in the free-radical addition reaction. Several experiments of different reactant ratios on HPS yield had been carried out, and the results are shown in Table 2, which indicates the reactant ratio of 5:1 between NaHSO_3 and Na_2SO_3 is the best, and the yield of HPS is up to 95.7%.

TABLE 2 THE EFFECTS OF THE REACTANT RATIO ON HPS YIELD

No.	NaHSO_3 , mol	Na_2SO_3 , mol	HPS yield, %
1	0.10	0.01	70.1
2	0.12	0.02	87.6
3	0.10	0.02	95.7
4	0.12	0.03	91.7
5	0.10	0.05	90.6

B. The Effects of Adding Time on HPS Yield

When the reaction conditions are as follows: the reactant ratio between NaHSO_3 and Na_2SO_3 was 5:1, the pH was about 7~8, the reaction temperature was 95°C , and the reaction time was 3.5 h, the effects of adding time on HPS yield were studied. Solution A and Solution B were added in incremental drops simultaneously. While adding too fast, it is easy for allyl alcohol itself to perform polymerization; in contrast, while adding too slowly, sulfite is probable to be oxidized. So adding time is important to HPS yield and the results are shown in Table 3, from which, it can be seen that 90 minutes is the optimum, and the yield of HPS is up to 94.6 %..

TABLE 3 THE EFFECT OF THE ADDING TIME ON HPS YIELD

Adding time, min	50	70	90	110	130
HPS yield, %	63.3	82.4	94.6	92.7	83.6

C. The Effects of the Reaction Time on HPS Yield

When the reactant ratio between NaHSO_3 and Na_2SO_3 was 5:1, the adding time was 90 minutes, the pH was about 7~8, and the reaction temperature was 95°C , the effects of reaction time on HPS yield were studied. The addition reaction of allyl alcohol and NaHSO_3 is an important step which depends mainly on the reaction time and the reaction temperature. The effects of the reaction time on HPS yield are shown in Table 4. As seen in Table 4, with the increase of the reaction time, the yield increases. When the reaction time is up to 3 h, the yield is higher, and then, with the increase of the reaction time, the yield keeps constant. So the optimum reaction time is 3 h. The reaction time should be appropriate; longer reaction time may result in the negative reactions and by-products, which will reduce the yield. On the contrary, shorter reaction time may cause an incomplete reaction.

TABLE 4 THE EFFECT OF THE REACTION TIME ON HPS YIELD

Reaction time, h	1	2	3	4	5
HPS yield, %	68.7	85.6	93.7	93.6	93.6

D. The Effects of the Reaction Temperature on HPS Yield

When the reaction conditions are as follows: the reactant ratio between NaHSO_3 and Na_2SO_3 was 5:1, the adding time was 90 minutes, the pH was about 7~8, and the reaction time was 3 h, the effects of the reaction temperature on HPS yield were studied. The effects of the reaction temperature on HPS yield are shown in Table 5. It indicates that the reaction temperature has a little effect on the yield. However, when the reaction temperature is 90°C , the yield is higher. The reason is that higher temperature can speed up the reaction rate, but when the temperature continuously increases, there will be side effects, such as the self-polymerization of allyl alcohol.

TABLE 5 THE EFFECT OF THE REACTION TEMPERATURE ON HPS YIELD

Temperature, $^\circ\text{C}$	70	80	90	100	110
HPS yield, %	90.6	92.7	94.1	94.1	94.0

E. The Effects of HPS Concentration on PS Yield

When the reactant ratio between NaHSO_3 and Na_2SO_3 was 5:1, the adding time was 90 minutes, the pH was about 7~8, the reaction temperature was 90°C , and the reaction time was 3 h, the effects of HPS concentration on PS yield were studied. Intermolecular dehydration of HPS is the key process for the synthesis of PS. It will be easy and beneficial for agitation and esterification when the right amount of water is added to HPS before the intermolecular dehydration reaction; therefore, the concentration of 3-hydroxy-1-propanesulfonic acid in the vacuum distillation has great influence on the yield of PS. The results are shown in Table 6. When the concentration of HPS is 80 %, the yield of PS is higher.

TABLE 6 THE EFFECTS OF HPS CONCENTRATION ON PS YIELD

HPS concentration, %	70	75	80	85	90
PS yield, %	83.3	90.2	94.6	91.2	83.7

IV. CONCLUSIONS

1, 3- propane sultone is synthesized through free-radical addition reaction, acid reaction and intermolecular dehydration reaction from allyl alcohol as the starting materials, and the yield is 95%. The process is applicable to the industrial development for preparation of 1,3-propane sultone.

The yield and purity of 1, 3-propane sultone have been greatly improved by several improvements. Firstly, the pH value after the free-radical addition reaction is adjusted to 3~4 with 10% sulfuric acid, to make HSO_3^- and SO_3^{2-} convert to SO_2 , so the impurities can be removed easily. Secondly, the pH value of the concentrated mixture is adjusted to be neutral with 10% NaOH solution after the first concentration by the rotary evaporator, thus, the excessive H_2SO_4 is converted into Na_2SO_4 ; because the inorganic salts are insoluble in alcohol and can be removed by filtration, then the purity of 3-hydroxy-1-propanesulfonic acid salt increases. Thirdly, in the vacuum distillation, the remaining inorganic salts in 3-hydroxy-1-propanesulfonic acid have side-effects on the synthesis of 1, 3-propane sultone, so these inorganic salts must be removed. Therefore, after the acid reaction, the suitable amount of anhydrous CaCl_2 is added to the solution, which is then continuously stirred for 2 h and frozen for 24 h, the formed precipitations containing CaSO_4 and NaCl are filtered, thus, the impurities of SO_4^{2-} and NaCl are removed.

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