Synthesis and Characterization of Itaconyl Chloride

Xueqi Zeng¹, Guojing Xu¹, Pengfei Wang¹, Chuanxing Wang¹*  
¹School of Chemical engineering and technology, Qingdao University of Science and Technology, Shandong 266042, P. R. China.  
*Corresponding author e-mail: Chuan-Xing Wang, wangchxstar@163.com

Abstract. Itaconyl chloride was synthesised using the bio-based itaconic acid (IA) and phosphorus pentachloride (PCl₅) as raw material by a molten method. The effects of various main factors, i.e. The solvent effect on the quality of the product during the purifying process was studied. The ratio of raw materials, the vacuum distillation temperature and vacuum distillation time on itaconyl chloride preparation were investigated. The optimum conditions of synthesis were determined as follows: toluene as purified solvent, n(PCl₅):n(IA)=2.15:1, the vacuum distillation temperature 80 °C, the vacuum distillation time 2 h. The yield of itaconyl chloride could reach 90 % and its purity was more than 98 %. The structure of itaconyl chloride was confirmed by means of Fourier Transform Infra-Red (FT-IR) and Nuclear magnetic resonance hydrogen spectrum (¹H-NMR).

1. Introduction

In recent decades, Cyanuric chloride (2,4,6-trichloro[1,3,5]triazine) as a new type of acyl chloride reagent, had used in different organic transformations, such as dehydration of amides to nitriles, 7 deoxygenation of sulfoxides[1], activation of DMSO for the oxidation of alcohols[2], and conversion of acids to acyl chlorides[3,4]. It was found that CCl₄/FeCl₃ system efficiently chlorinate a wide range of organic acids into the corresponding acyl chlorides with relatively high isolated yield[5,6]. Phosphorus trichloride could be used as acid chloride reagent which prepared acyl chloride with the lower boiling point[7]. The coupling reagent Cl₃CCN/PPh₃ was important since the chlorination of carboxylic acids could be performed efficiently under mild and acid-free conditions that could afford the desired acyl chlorides in high yield[8].

In recent years, the market demand of itaconyl chloride grew with its extensive application in the research and production in amides. The producer price was higher and the waste of raw material was more serious according to the traditional synthetic route. Therefore, the research of synthetic process was valuable, especially an efficient and green one for the synthesis of itaconyl chloride.

An effective method was reported for preparation of itaconyl chloride using IA and PCl₅ as raw material. The effects of main factors, i.e. the ratio of raw materials, the Vacuum distillation temperature and time on itaconyl chloride preparation were investigated. The optimum conditions of synthesis were determined. And the product structure had been characterized.
2. Experimental

2.1. Materials
Itaconic acid (industrial product) was purchased from Qingdao Langyatai Group Co., China. Phosphorus pentachloride (analytical reagent, AR), toluene (AR), Sodium hydroxide (AR), hydrochloric acid (AR) was purchased from Sinopharm chemical reagent Co., Ltd..

2.2. Synthesis of itaconyl chloride
Phosphorus pentachloride and itaconic acid were added into a 250 mL round-bottomed flask which was fitted with a condenser and a drying tube leading the by-products to a gas absorption solution. The reagents were mixed by shaking the flask. After a few minutes, a vigorous reaction commenced and resulted in partial liquefaction of the mixture and copious evolution of hydrogen chloride. At the end of the reaction, a certain amount of toluene was added to solution. The reflux condenser was replaced by a vacuum pump. Phosphorus oxychloride (POCl₃) and a few of hydrogen chloride were removed by rotary evaporation under the vacuum condition with a water aspirator. Determination of the purity of product was using Alkali-soluble neutralization and the yield of product was determined by Gas chromatograph. The equation of chemical reaction for itaconyl chloride was as follows:

\[
\text{H}_2\text{C} = \text{C} = \text{CH}_2\text{COCl} + \text{POCl}_3 \rightarrow \text{H}_2\text{C} = \text{C} = \text{CH}_2\text{COCl} + \text{POCl}_3 + HCl
\]

2.3. Determination of purity
The purity of product was measured by Alkali-soluble neutralization (Peng CH et al. 2005)[9]. First, appropriate amount of itaconyl chloride (about M×10⁻³ g) was taken into excess of standard solution of sodium hydroxide. The mixture was heated to reflux. Hydrolysis reaction of itaconyl chloride proceeded, and several drops of phenolphthalein solution were added after cooling to room temperature. The amount of sodium hydroxide that reacted with itaconyl chloride was determined by the method of hydrochloric acid standard solution titration. The content of itaconyl chloride could be calculated according to the chemical reaction equation and the free acid was removed through the acid-alkali neutralization titration.

\[
\text{H}_2\text{C} = \text{C} = \text{CH}_2\text{COCl} + \text{NaOH} \rightarrow \text{H}_2\text{C} = \text{C} = \text{CH}_2\text{COONa} + \text{NaCl} + H_2O
\]

The determination of itaconyl chloride content:

\[
c = \left( \frac{c_1V_1 - c_2V_2 - c_3V_3 - c_4V_4}{m_1} \right) \times \frac{M}{4000} \times 100\%
\]

\[
c_1 - \text{Concentration of sodium hydroxide standard solution, mol/L;}
\]
\[
V_1 - \text{The volume of sodium hydroxide standard solution, mL;}
\]
\[
c_2 - \text{Standard solution of hydrochloric acid, mol/L;}
\]
\[
V_2 - \text{Concentration of hydrochloric acid standard solution, mL;}
\]
\[
c_3 - \text{Concentration of sodium hydroxide solution which used for titrating free acid, mol/L;}
\]
\[
V_3 - \text{The volume of sodium hydroxide solution of titrating free acid, mL;}
\]
\[
V_4 - \text{The volume of sodium hydroxide solution in blank test, mL;}
\]
\[
m_1 - \text{Quality of total itaconyl chloride, g;}
\]
\[
m_2 - \text{Quality of itaconyl chloride for titration free acid, g;}
\]
\[
M - \text{Molecular mass of itaconyl chloride, g/mol.}
\]

2.4. Yield of the product
The yield of itaconyl chloride was determined using Gas chromatography (GC-7806, Wenling Beijing Instrument Co., Ltd.). Strong polar chromatographic column (EN 20) was used in the chromatographic analysis, dichloromethane (DCM) as solvent, N₂ as carrier gas with a flow rate of 1 mL/min, column temperature 200 °C, detector temperature 230 °C, injection port temperature 230 °C, retention time 1 min, heating rate 2 °C/min to 230 °C.
2.5. Characterization

$^1$H-NMR Spectroscopy: Chemical structures of PA were characterized by $^1$H-NMR, which was implemented on a BRUKER AV 500 MHz spectrometer at ambient temperature, using Chloroform-d ($\text{CDCl}_3$) as the solvent and the internal standard, respectively.

FT-IR: Fourier Transform Infrared Spectrometer was carried out with a BRUKER TENSOR-27 infrared spectrometer using the pure liquid to confirm the structure.

3. Results and discussion

3.1. Effect of the spin steaming for the content of free acid

In consideration of the reaction mechanism of itaconyl chloride, there was too much hydrochloric acid gas that was produced which made the product contain a large number of free acid. The purity of itaconyl chloride decreased. Adding of the toluene to the reaction could help get rid of the hydrogen chloride gas and POCI$_3$ from itaconyl chloride by rotary evaporation. As shown in Table 1, it was the affection of spin steaming to the free acid content after adding toluene.

As shown in Table 1, the reason, why free acid content of the products decreased significantly after adding toluene, was that the POCI$_3$ would form azeotrope with toluene by the method of spin steaming. And the solubility of hydrochloric gas in toluene was better than the solubility of itaconyl chloride. There was less impurity of hydrochloric gas and POCI$_3$ in the product with rotary evaporation. Thus high purity of itaconyl chloride was obtained.

| Time | 1 | 2 | 3 | 4 | 5 | Average |
|------|---|---|---|---|---|---------|
| Free acid content/\% | With toluene | 12.73 | 15.72 | 10.03 | 12.43 | 13.56 | 12.89 |
| | Without toluene | 1.35 | 1.19 | 1.03 | 1.31 | 1.51 | 1.28 |

3.2. Effect of the ratio of raw materials

As shown in Figure 1, the effect of different mole ratio on the yield and purity of itaconyl chloride was studied when the reaction temperature was 95 °C and the reaction time was 5 h.

![Figure 1](image)  
**Figure 1.** Effect of the ratio of raw materials on purity and yield

Figure 1 showed that purity and yield of products were not the highest when the mole ratio of phosphorus pentachloride to itaconic acid was 2:1. The reason was that there would be a part of the PCl$_5$ sublimating to the reaction system at this temperature so that the reaction mole ratio was less than 2:1. But it could be found from Figure 1 that the mole ratio of PCl$_5$ to itaconic acid mole ratio was not the higher the better. The reason was that with the increase of mole ratio, remaining PCl$_5$ would increase that could hinder the impurity of hydrochloric acid gas discharge in time, the addition
reaction of hydrochloric acid and double carbon bond, which affected the yield and purity of itaconyl chloride. In view of atomic economy and resources, the mole ratio of PCl$_5$ to itaconic acid was determined as 2.15:1 which made the itaconyl chloride yield and purity reach above 90% and 98%, respectively.

3.3. Effect of the Vacuum distillation temperature

After the reaction, the product contained a large amount of impurity POCl$_3$ and a small amount of hydrochloric acid that was dissolved in solution. So, these impurities was removed by vacuum distillation to ensure the quality of itaconyl chloride. And in the process of vacuum distillation, the temperature was one of essential factors to affect the yield and the purity of product. As shown in Figure 2, the pressure was negative 0.1 MPa and the other reaction conditions were kept constant. To investigate the effect of reduced pressure distillation temperature on itaconyl chloride product yield and purity:

![Figure 2. Effect of the Vacuum distillation temperature on purity and yield](image)

As shown in Figure 2, with the temperature was rising, the purity and yield of product were generally increase and then decrease. The reason of low productivity and low purity might be that POCl$_3$ and toluene did not reach the boiling point in the pressure of negative 0.1 MPa. The temperature was too low, which made lots of impurities mixed in the product of itaconyl chloride. On the contrary, if temperature was too high, though impurities and solvent toluene were moved, the double bond of itaconyl chloride could polymerize and generate low polymer. Meanwhile, a small amount of product would be steamed out under the condition of high temperature which would affect the yield of itaconyl chloride. In conclusion, with the temperature of vacuum distillation 80 °C, the yield and the purity of product could reach above 90% and 95%, respectively.

3.4. Effect of the Vacuum distillation time

There was a double bond in itaconyl chloride, the double bond of itaconyl chloride could self-polymerize and generate low polymer in the condition of high temperature and long time that might affect the quality of the product. So it was very important for purity and yield of itaconyl chloride to control the time of vacuum distillation. The results were shown in Table 2.

| t/h  | Purity/% | Yield/% |
|------|----------|---------|
| 1    | 84.90    | 78.65   |
| 1.5  | 85.10    | 71.74   |
| 2    | 98.43    | 90.57   |
| 2.5  | 88.57    | 82.88   |

Table 2. Effect of the Vacuum distillation time on purity and yield
As shown in Table 2. If vacuum distillation time was too short, there would be a part of the residue in the product. And the quality of the product was affected by incomplete reaction. If the reaction time was too long, the double bond of itaconyl chloride could polymerize. The purity and yield of the product decreased. In summary, vacuum distillation time 2 h was the best, while the yield and purity of itaconyl chloride could meet the ideal requirements.

3.5. FT-IR spectrum of itaconyl chloride

The product was determined by the method of liquid membrane. FT-IR spectrum of itaconyl chloride was shown in Figure 3.

According to the Figure 3, the spectrum showed a broad and strong peak in the region of 2500~3200 cm^{-1} in the FT-IR of itaconic acid. This was the peak of hydroxyl in carboxyl group. The peak was caused by the frequency multiplication and combination frequency of stretching vibration and deformation vibration, which was the most direct proof of the carboxyl group. And in the FT-IR of itaconyl chloride, it could be clearly seen that the peak disappeared which proved that there was no carboxyl group and it had been replaced. In the FT-IR of itaconic acid, the peak of double carbon bond stretching vibration absorption was at 1628 cm^{-1}. In FT-IR of itaconyl chloride, stretching vibration peaks of double carbon bond was at 1665 cm^{-1}. In the FT-IR of itaconic acid, the absorption peak of carboxyl group was at 1703 cm^{-1}, and the position of absorption peak shifted to low wave for the influence of hydrogen bond. In the FT-IR of itaconyl chloride, the absorption peak of carboxyl group was at 1786 cm^{-1}. Due to the conjugate effect of carbonyl and unsaturated groups, the wave number was more than that of the absorption peak of itaconic acid. Thus the synthesis of itaconyl chloride was confirmed.

![Figure 3. FT-IR spectrum of the product](image)

3.6. ^1H-NMR spectrum of itaconyl chloride

The product was characterized by ^1H-NMR with the Chloroform-d (CDCl₃) as solvent. The result was shown in Figure 4.
Figure 4. 1H-NMR spectrum of the product

From the $^1$H-NMR spectrum of compound, it could be seen that the peaks of protons were all in accordance with the characteristic peaks of protons of the target itaconyl chloride. The hydrogen to the double bond was located to the deshielded area. The chemical shift was greater than the chemical shifts of hydrogen in alkane. So there were two peaks at δ=5.91 ppm and δ=6.47 ppm, respectively, which were the hydrogen of itaconyl chloride in the side chain C-H. And acyl halide group was to the electron-donating group, enhance the induced magnetic field which was produced by the extranuclear electron, shielding effect, enhance the nuclear resonance absorption to highly mobile. So the chemical shift value was decreased and the signals at δ=3.59 ppm was -CH$_2$-. The integral curve indicates that the proton number of three groups of peak ratio 1:1:2.

And the molecular structure of the itaconyl chloride was consistent with the characteristics of the spectrum. It could be undoubtedly concluded that the itaconyl chloride were successfully synthesized.

4. Conclusions

In summary, itaconyl chloride was synthesized using the itaconic acid (IA) and phosphorus pentachloride (PCl$_5$) as raw material in a molten method. The results showed that the best conditions were: toluene as purified solvent, the dosage was 15 mL, n(PCl$_5$):n(IA) 2.15:1, Adding the toluene 15 mL, the Vacuum distillation temperature 80 ℃, the Vacuum distillation time 2 h. The yield of Itaconyl chloride could reach 90 % and its purity was more than 98 %.

Acknowledgments
This work was financially supported by National Natural Science Foundation Youth Fund(51872150).

References
[1] Guanti, G.; Narisano, E.; Banfi, L.; et al. Tetrahedron Lett, 1983, 24(8):817-818.
[2] Albright, J. D. J. Org. Chem. 1974, 39: 1977–1979.
[3] Venkataraman, K.; Wagle, D. R.. Tetrahedron Lett. 1979, 20: 3037–3040.
[4] Luo, G.; Li, X.; Poindexter, G. S.. Cheminform, 2003, 34(13):8909-8912.
[5] Chu, C.; Liu, R.. Applide Catalysis B: Environmental. 2011, 101(3):343-347.
[6] Bae, J. W.; Lee, J. S.; Lee, K. H.. Ind. Eng. Chem. Res. 2007, 46, 7057-7065.
[7] Galbraith, A. R.; Hale, P.; Robertson, J. E.. J Am Oil Chem Soc. 1964, 41(2): 104-107.
[8] Puentapanupat, W.; Chantarasiwong, O.; Taboonpong P.; et al. Tetrahedron Lett. 2007, 48(2):223-226.
[9] Peng, C. H.; Chen, Z. X.; Yang, Z. X.. Chemical World , 2005, (2): 86-88.