



Effects of different reaction conditions on the synthesis of 2, 4 - dihydroxybenzophenone (UV-214)

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ABSTRACT

Resorcinol reacted with resorcinol in water to produce 2, 4 - dihydroxybenzophenone (UV-214). The quality of 2, 4 - dihydroxybenzophenone (UV-214) was significantly improved by adding the phase transfer agent, such as methanol, N, N- dimethyl formamide, dimethylformamide, acetic acid, positive ion surfactants, negative ion surfactants, polyethylene glycols and emulsifiers. Effects of different reaction conditions on the synthesis of 2, 4 - dihydroxybenzophenone were discussed. The experimental results showed that the purity and yield of 2, 4 - dihydroxybenzophenone by adding 0.4 g octadecyltrimethylammonium bromide into the reaction mixture reached 99.4 % and 95.7 %, respectively. It was pale yellow and was used as UV absorber without refinery. It was found that octadecyltrimethylammonium bromide was an ideal phase transfer agent.

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KEYWORDS

2, 4 -
dihydroxybenzophenone;
Resorcinol;
Benzotrichloride;
UV-214;
Phase transfer method.

INTRODUCTION

The requirement of polymer aids is increased with the development of three synthetic material industries. 2, 4 - dihydroxybenzophenone (UV - 214) and its derivative as UV absorber are one of additive of high polymer materials. 2, 4 - dihydroxybenzophenone is used in polyethylene (PE), polystyrene (PS), epoxy resin, unsaturated polyester, coating, synthetic rubber^[1]. UV - 9, UV - 531^[2,3], UV - 1200^[4] and UV - B^[5] are got by using 2, 4 - dihydroxybenzophenone as the feedstock. The traditional synthesis methods of 2, 4 - dihydroxybenzophenone are listed as follows: (1) 2, 4 - dihydroxybenzophenone is got by using resorcinol and benzoyl chloride as the feedstock and Lewis acid (AlCl_3 or ZnCl_2) as the catalyst. The purity of 2, 4 -

dihydroxybenzophenone is very high, but the capital of resorcinol and benzoyl chloride is very high and the yield of 2, 4 - dihydroxybenzophenone is very low. The catalyst of Lewis acid must be added equivalent to that of 2, 4-dihydroxybenzophenone. The catalyst of Lewis acid has to be taken off from this reaction system after the reaction is done. (2) Resorcinol reacts with benzotrichloride under the condition of the given temperature and the selected solvent. The cost of feedstock is cheap and easily gets and the yield of the product is high but the purity of the product is very low. The main by-product (xanthene), whose color is orange, has an obvious effect on the quality of the product as the high polymer material^[6]. A lot of researchers mainly study on how to obtain the higher purity of the product by using activated carbon^[7,8] and vacuum distillation^[9]. In this pa-

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per, effects of different reaction conditions on the synthesis of 2, 4 - dihydroxybenzophenone were discussed.

EXPERIMENTAL

Feedstock and surfactant

Resorcinol (Germany product, purity > 99.5%); benzotrichloride (Germany product, purity > 99.5%); methanol (analytical pure, Beijing Defu Chemical Plant); N, N - dimethyl formamide (analytical pure, Kaifeng Fat Industry); dimethylformamide (analytical pure, Benxi Chemical Plant); acetic acid (analytical pure, Tianjing Organic Plant); octadecyltrimethylammonium bromide (analytical pure, Shandong Jining City Chemical Industry Institute); 1827 (octadecyldimethylbenzylammonium chloride, industry product, Dalian Huaxin Chemical Product LTD, purity > 80.5%); tetrabutylammonium bromide (industry production, Beijing Daxing Fine Chemistry Institute); hexadecylpyridinium bromide (industry production, Dalian Huaxin Chemical Plant); industrial pure emulsifiers T-85 (polyoxyethylene sorbitan tall oil ester); 2000# (polyester sulphate); L-62 (polyester); El-40 (polyoxyethylene caster oil); P-75 (polyester); OP-10 (nonylphenol polyoxyethylene ether); PEG-400 (polyethylene glycol-400); PEG-1000 (polyethylene glycol-1000); PEG-1500 (polyethylene glycol-1500); PEG-6000 (polyethylene glycol-6000); PEG-10000 (polyethylene glycol-10000).

The synthetic method

11 g resorcinol and 30 ml distilled water and 0.25 g surfactant or solvent are put into 100ml conical beaker which is heated to 40 °C with stirring. 19.55 g benzotrichloride is gradually added into the conical beaker and the bath's temperature is kept at between 40 °C and 50 °C. After benzotrichloride is done, the bath's temperature is heated to 70 °C. And it continues to stir the conical beaker about one hour. The product is cooled, filtered, washed to neutral and dried 36 hours at 90 °C. The melting point of the product measured with the capillary melt point measurement contrasts with that of the analytical pure of 2, 4 -

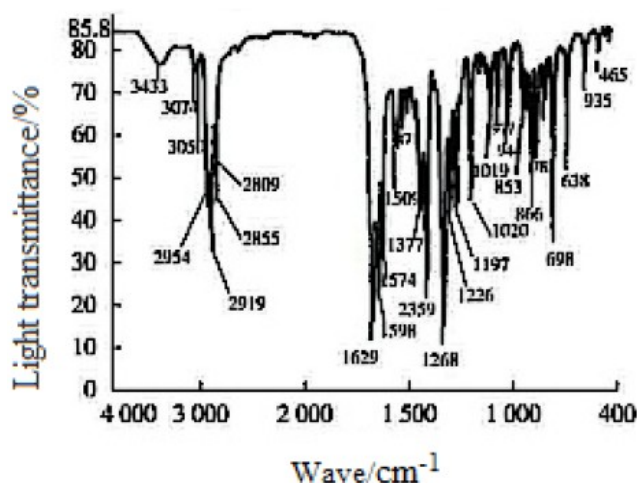


Figure 1 : The infrared image of the product

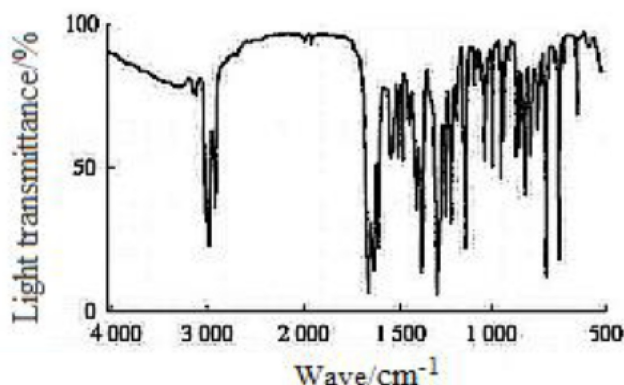
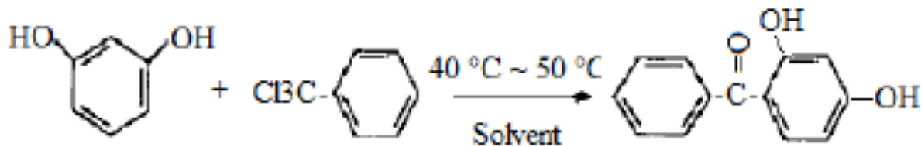


Figure 2 : The infrared image of pure 2,4 - dihydroxybenzophenone

dihydroxybenzophenone (the melting point is between 45°C and 146 °C). The infrared image of 2, 4 - dihydroxybenzophenone are done on TJ-273-30 Infrared Spectrophotometer. The infrared images of 2, 4 - dihydroxybenzophenone and pure 2, 4 - dihydroxybenzophenone are shown in Figure 1 and 2, respectively. The peak of 1450 cm⁻¹~1600 cm⁻¹, 1624 cm⁻¹ and 3184 cm⁻¹ are the skeletal shake of benzene ring, the carbonyl absorbing peak and the hydroxyl absorbing peak, respectively.

The reaction mechanism

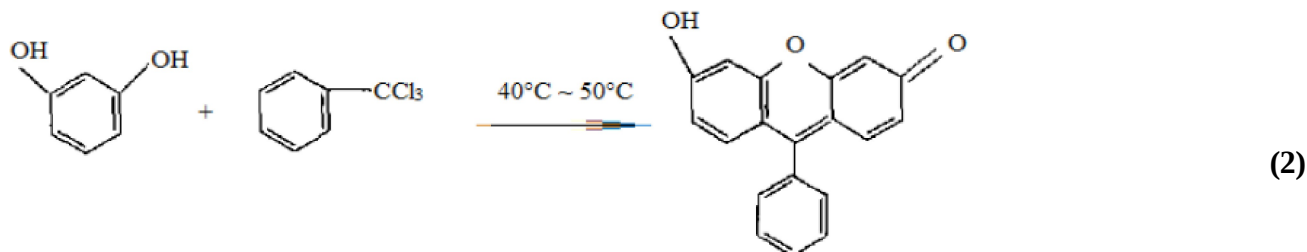
Resorcinol in the distilled water system reacts with benzotrichloride to produce 2, 4 - dihydroxybenzophenone with solvents. The reaction Eq. (1) is listed as follows:



(1)

Resorcinol in the distilled water system doesn't react with benzotrichloride to produce 2, 4 -

dihydroxybenzophenone without any solvent. The reaction Eq. (2) is expressed as follows:



Because the melting point of 2, 4 - dihydroxybenzophenone ranges between 145 °C and 146 °C, the melting point of the product is between 154 °C and 260 °C. Although 2, 4 - dihydroxybenzophenone can be obtained by adding dimethyl formamide or glacial acetic acid, its purity and yield are very low.

RESULT AND DISCUSSION

Effects of different solvents on yields of 2, 4 - dihydroxybenzophenone

Benzotrichloride was maldistribution in the distilled water due to its immiscibility. The touching probability of resorcinol in the distilled water system increased with benzotrichloride by adding different solvents. Effects of different solvents on yields of 2, 4 - dihydroxybenzophenone were shown in Figure 3. The quality of 2, 4 - dihydroxybenzophenone was significantly improved when different solvents were added into the reaction system. The yield of 2, 4 - dihydroxybenzophenone increased with the increase of

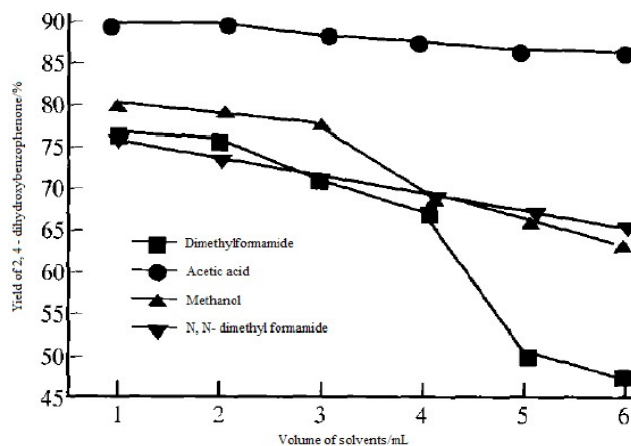


Figure 3 : Effects of different solvents on yield of 2, 4 - dihydroxybenzophenone

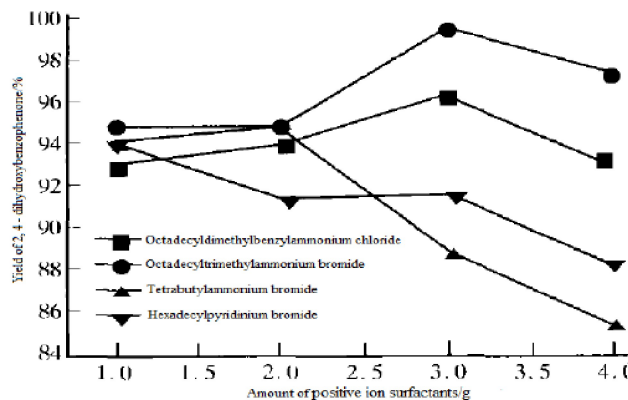


Figure 4 : Effects of different positive ion surfactants on yields of 2, 4 - dihydroxybenzophenone

the amount of solvents. The experimental results showed that acetic acid was one of the best catalysts.

Effects of different positive ion surfactants on yields of 2, 4 - dihydroxybenzophenone

Octadecyltrimethylammonium bromide is an ideal phase transfer catalyst because the melting point of the product almost reaches the theoretical value and the purity of the product arrives at 99.7% based on liquid chromatographical analysis. Hyamine has two ends. One end has hydrophilic group and another end has lipophilic group. Hyamine can take resorcinol in the distilled water system into organic phase (benzotrichloride). Resorcinol fully touches with benzotrichloride so it prevents xanthenes producing. The length of chain of lipophilic group has an obvious effect on the purity and yield of the product. The longer is the chain of lipophilic group and the more active is the catalytic property. The experimental results showed that octadecyltrimethylammonium bromide was one of the best positive ion surfactants.

Effects of different negative ion surfactants on yields of 2, 4 - dihydroxybenzophenone

Negative ion surfactants (sodium dodecyl sulfate

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and 1- dodecane sulfonic acid sodium salt) did not have phase transfer function due to no positive center, but they had emulsifying ability. They made benzotrichloride distribute small particles. Benzotrichloride could fully

touch with resorcinol. The phase transfer property of 1-dodecane sulfonic acid sodium salt was better than that of sodium dodecyl sulfate. The yield and purity of UV-531 were not very high^[1].

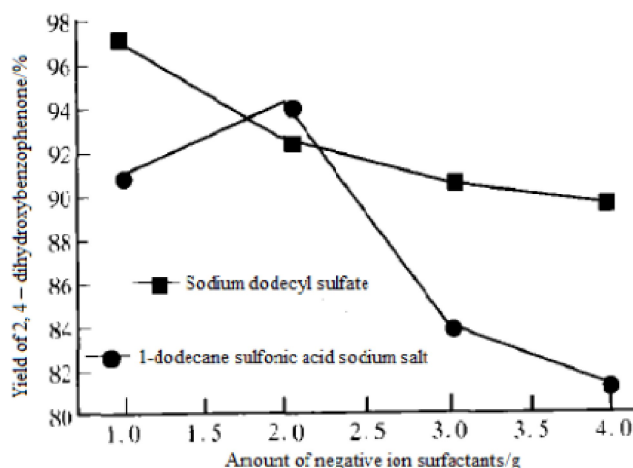


Figure 5 : Effects of different negative ion surfactants on yields of 2, 4 - dihydroxybenzophenone

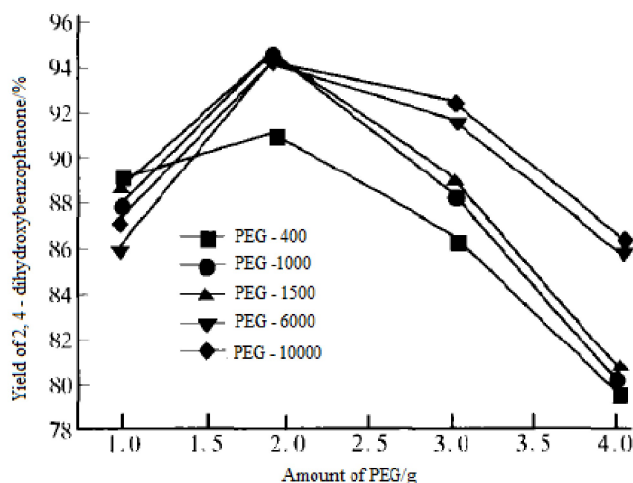


Figure 6 : Effects of different polyethylene glycol (PEG) on yields of 2, 4 - dihydroxybenzophenone

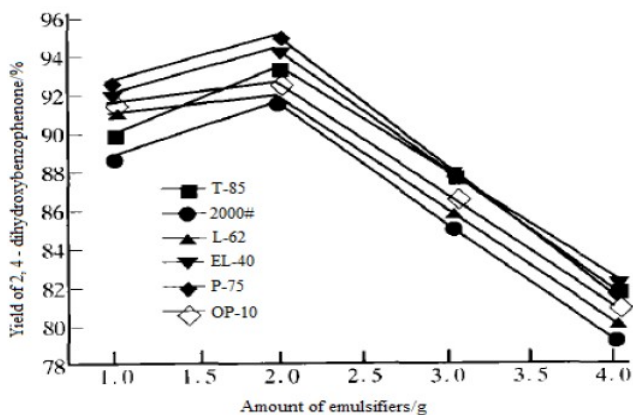


Figure 7 : Effects of different emulsifiers on yields of 2, 4 - dihydroxybenzophenone

Effects of different polyethylene glycol (PEG) on yields of 2, 4 - dihydroxybenzophenone

Polyethylene glycol (PEG) had emulsifying ability and moved benzotrichloride in water phase into resorcinol in organic phase. Benzotrichloride could react with resorcinol. Figure 6 showed effects of different polyethylene glycol (PEG) on yields of 2, 4 - dihydroxybenzophenone. The quality of 2, 4 - dihydroxybenzophenone was not significantly improved and its melting point was low^[1].

Effects of different emulsifiers on yields of 2, 4 - dihydroxybenzophenone

Emulsifiers had emulsifying ability and moved benzotrichloride in water phase into resorcinol in organic phase. Figure 7 showed effects of different emulsifiers on yields of 2, 4 - dihydroxybenzophenone. Yields of 2, 4 - dihydroxybenzophenone first increased and then decreased with the increase of emulsifiers, but the melting point of 2, 4 - dihydroxybenzophenone was very low^[1].

CONCLUSION

Based on the above mentioned results, discussion and review, using benzotrichloride and resorcinol as feedstocks methanol, N, N- dimethyl formamide, dimethylformamide, acetic acid, positive ion surfactants, negative ion surfactants, polyethylene glycols and emulsifiers as catalysts, effects of different reaction conditions on yields of 2, 4 - dihydroxybenzophenone are discussed. The experimental results show that octadecyltrimethylammonium bromide was one of best phase transfer agents.

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