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Synthesis of 2-hydroxy-4-n-octaoxybenzophenones (UV-531) with the phase transfer method

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ABSTRACT

2, 4 - dihydroxybenzophenone (UV-214) reacted with 1 - bromododecane in KOH solution to produce 2-hydroxy-4-n-octaoxybenzophenones (UV-531). The quality of 2-hydroxy-4-n-octaoxybenzophenones (UV-531) was significantly improved by adding the phase transfer agent, such as N, N-dimethyl formamide, diethyl ether, methyl sulfate octadecyl trimethyl ammonium, alkyltrimethylammonium chloride, dimethyl cetyl ammonium chloride, ammonium dodecyl benzene sulfonate, octadecyl methyl sulfonate sodium, polyethylene glycols and emulsifiers. The experimental results showed that the purity and yield of 2-hydroxy-4-n-octaoxybenzophenones by adding 0.8% dimethyl cetyl ammonium chloride into the reaction mixture reached 88.5 % and 93.2 %, respectively. It was pale yellow and was used as UV absorber without refinery. It was found that dimethyl cetyl ammonium chloride was an ideal phase transfer agent.

KEYWORDS

2-hydroxy-4-n-Octaoxybenzophenones;
1-bromododecane;
UV-531;
Phase transfer method;
2, 4 - dihydroxybenzophenone (UV-214).

INTRODUCTION

The requirement of polymer aids is increased with the development of three synthetic material industries. 2-hydroxy-4-n-octaoxybenzophenones (UV - 531) and its derivative as UV absorber are one of additive of high polymer materials. 2-hydroxy-4-n-octaoxybenzophenones is used in polyethylene (PE), polystyrene (PS), epoxy resin, unsaturated polyester, coating, synthetic rubber[1]. The traditional synthesis methods of 2-hydroxy-4-n-octaoxybenzophenones are listed as follows: (1) 2-hydroxy-4-n-octaoxybenzophenones is got by using 2, 4 - dihydroxybenzophenone and 1 - bromododecane as feedstocks and KOH as the catalyst. The purity of 2-hydroxy-4-n-octaoxybenzophenones is very high, but the capital of 2, 4 - dihydroxybenzophenone and 1 - bromododecane is very high and the yield of 2-hydroxy-4-n-octaoxybenzophenones is very low. KOH must be added equivalent to that of 2-hydroxy-4-n-octaoxybenzophenones[2]. KOH has to be taken off from this reaction system after the reaction is done. (2) 2, 4 - dihydroxybenzophenone reacts with 1 - bromododecane 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. A lot of researchers mainly study on how to obtain the higher purity of the product by using activated carbon and vacuum distillation. In this paper, effects of different catalysts on the synthesis of 2-hydroxy-4-n-octaoxybenzophenones were discussed.

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EXPERIMENTAL

Feedstock and surfactant

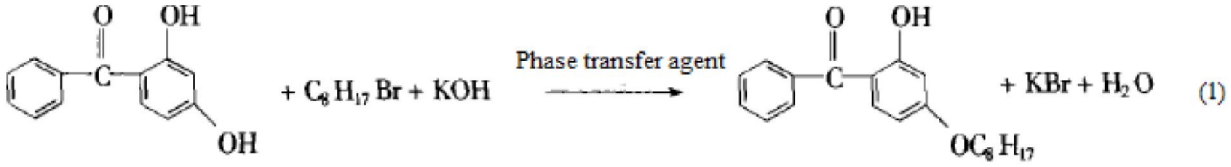
2, 4 - dihydroxybenzophenone (analytical pure, Wuhan Auxiliary Factory); 1 - bromododecane (analytical pure, Shouduang Ocean Chemical Plant); KOH (82%, Shengyang Agent Factory); N, N - dimethyl formamide (analytical pure, Kaifeng Fat Industry); methyl sulfate octadecyl trimethyl ammonium (analytical pure, Liaoning Benxi Xinjian Chemical Plant); alkyltrimethylammonium chloride (analytical pure, Dandong Light Chemical Institute); dimethyl cetyl ammonium chloride (analytical pure, Guangzhou Auxiliary Chemical Plant); ammonium dodecyl benzene sulfonate (analytical pure, Zhejiang Longyou Chemical Plant); octadecyl methyl sulfonate sodium (analytical pure, Dalian Chemistry Physics Institute); industrial pure emulsifiers LAE-9 (fatty acid polyoxyethylene ester (9), Dalian Huaneng Chemical Plant); SG-10 (condensation product of fatty acid and epoxy ethane, Jiangsu Hai'an Petrochemical Plant); LM-102 (xylitol with oleic acid vinegar, Liaoning Lushun Chemical Plant); El-40 (polyoxyethylene caster oil, Shanghai Auxiliary Factory); AEO-4 (C12 fat polyoxyethylene ether (4), Tianjing Auxiliary Factory); OPE-3 (octyl phenol polyoxyethylene (3) ether, Beijing Soaps and Detergent Plants); 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

12.84 g of 2, 4 - dihydroxybenzophenone, 11.58 g of 1 - bromododecane, 4.5 g of distillated water, 4.10 g of KOH and 0.72 g of surfactant or solvent were put into 100 ml conical beaker which was heated to 110 °C with stirring. The bath's temperature was kept at between 110 °C and 120 °C. And it continued to stir the conical beaker about 6 hours. The product was cooled, filtered, washed to neutral and dried 40 hours at 90 °C. The melting point of the product measured with the capillary melt point measurement contrasted with that of the analytical pure of 2-hydroxy-4-n-octaoxybenzophenones (the melting point is between 47°C and 49 °C).

The reaction mechanism

2, 4 - dihydroxybenzophenone in KOH solution reacted with 1 - bromododecane to produce 2-hydroxy-4-n-octaoxybenzophenones. The reaction Eq. (1) was listed as follows:



RESULT DISCUSSION

Effects of different solvents on yields of 2-hydroxy-4-n-octaoxybenzophenones

1 - bromododecane was maldistribution in the distillated water due to its immiscibility. The touching probability of 2, 4 - dihydroxybenzophenone in KOH solution increased with 1 - bromododecane by adding different solvents. Effects of different solvents on yields of 2-hydroxy-4-n-octaoxybenzophenones were shown in TABLE 1. The quality of 2-hydroxy-4-n-octaoxybenzophenones was significantly improved when different solvents were added into the reaction system. The yield of 2-hydroxy-4-n-octaoxybenzophenones decreased with the increase of the amount of solvents. The experimental results showed that N, N - dimethyl formamide was one of the best catalysts.

TABLE 1 : Effects of different solvents on yields of 2-hydroxy-4-n-octaoxybenzophenones

Solvents	Amount of solvents (ml)	Yield of UV-531	Melting point range (°C)
N, N – dimethyl formamide	30	69.4	41.2 ~ 43.2
	15	75.3	45.2 ~ 46.5
Diethyl ether	30	65.3	38.9 ~ 40.5
	15	73.8	41.5 ~ 42.8

Effects of different surfactants on yields of 2-hydroxy-4-n-octaoxybenzophenones

TABLE 2 presented effects of different surfactants

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on yields of 2-hydroxy-4-n-octaoxybenzophenones. KOH first reacted with UV-214 to produce anion $C_{13}H_9O_3^-$ which dissolved in the water phase. 1 - bromododecane dissolved in the organic phase. 1 - bromododecane slowly reacted with . The quality of 2-hydroxy-4-n-octaoxybenzophenones was improved by adding positive ion surfactants, such as methyl sulfate octadecyl trimethyl ammonium, alkyltrimethylammonium chloride and dimethyl cetyl ammonium chloride. Hyamine has two ends. One end has hydrophilic group and another end has lipophilic group. Hyamine can take in KOH solution into organic phase (1 - bromododecane). 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 dimethyl cetyl ammonium chloride was one of the best positive ion surfactants. Negative ion surfactants (ammonium dodecyl benzene sulfonate and octadecyl methyl sulfonate sodium) did not have phase transfer function due to no positive center, but they had emulsifying ability. The catalytic performance of ammonium dodecyl benzene sulfonate was almost similar to that of octadecyl methyl sulfonate sodium, but yields of 2-hydroxy-4-n-octaoxybenzophenones were very low.

TABLE 2 : Effects of different surfactants on yields of 2-hydroxy-4-n-octaoxybenzophenones

Surfactants	Yield of UV-531	Melting point range (°C)
methyl sulfate octadecyl trimethyl ammonium	89.4	45.7 ~ 46.9
Alkyltrimethyl Ammonium chloride	70.1	43.7 ~ 44.7
dimethyl cetyl ammonium chloride	93.2	46.8 ~ 48.2
ammonium dodecyl benzene sulfonate	67.1	41.5 ~ 42.5
octadecyl methyl sulfonate sodium	66.7	41.1 ~ 42.7

Effects of different emulsifiers or polyethylene glycol (PEG) on yields of 2-hydroxy-4-n-octaoxybenzophenones

Emulsifiers or polyethylene glycol (PEG) had emulsifying ability and moved UV-214 in water phase into 1 - bromododecane in organic phase. TABLE 3 showed effects of different emulsifiers and polyethylene glycol (PEG) on yields of 2-hydroxy-4-n-octaoxybenzophenones. The yield of 2-hydroxy-4-n-octaoxybenzophenones had almost no change with the increase of molecular weight of polyethylene glycol (PEG). Their product qualities were poor. On the other hand, yields of 2-hydroxy-4-n-octaoxybenzophenones were very low when different emulsifiers were added.

TABLE 3 : Effects of different emulsifiers or polyethylene glycol (PEG) on yields of 2-hydroxy-4-n-octaoxybenzophenones

Emulsifiers	Yield of UV-531	Melting point range (°C)
LAE-9	47.6	36.7 ~ 38.0
SG-10	49.7	35.3 ~ 37.3
LM-102	50.3	35.7 ~ 36.7
AEO-4	48.6	33.0 ~ 34.0
EL-10	50.1	32.3 ~ 33.7
OPE-3	48.9	31.7 ~ 32.3
PEG-400	58.5	38.6 ~ 40.0
PEG-1000	56.2	38.0 ~ 39.0
PEG-1500	59.7	36.3 ~ 37.3
PEG-6000	51.6	35.7 ~ 38.7
PEG-10000	52.3	36.8 ~ 38.4

CONCLUSION

Based on the above mentioned results, discussion and review, using 2, 4 - dihydroxybenzophenone (UV-214) and 1 - bromododecane as feedstocks and N, N-dimethyl formamide, diethyl ether, methyl sulfate octadecyl trimethyl ammonium, alkyltrimethylammonium chloride, dimethyl cetyl ammonium chloride, ammonium dodecyl benzene sulfonate, octadecyl methyl sulfonate sodium, polyethylene glycols and emulsifiers as catalysts, effects of different phase transfer agents on yields of 2-hydroxy-4-n-octaoxybenzophenones are discussed. The experimental results show that dimethyl cetyl ammonium chloride was one of best phase transfer agents.

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