HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 30. pp. 207 - 210 (2002)

ALKYLATION OF BIPHENYL WITH 1-HEXEN BY USING A CATALYST

S. VELI

(*Department of Environmental Engineering,* University of Kocaeli,41300, Izmit-TURKEY)

Received: July 26, 2002

Alkylation of biphenyl with 1-hexen by using a catalyst was investigated experimentally in this study. $((Al + C_3H_7Cl) + C_2H_4)$ was used as catalyst and mono-, di- and poly- alkyl- biphenyls were formed at the end of alkylation. The influences of temperature, mol ratio of biphenyl to 1-hexen, reaction time and catalyst concentration on alkylation process were investigated. Also the influences of these parameters on the formation of the obtained alkylbiphenyls were observed.

Experiments show that alkylbiphenyl concentration in alkylat increases with temperature. It was observed that the selectivity of monohexylbiphenyl increases by increasing of reaction time and catalyst concentrations. Experiments showed that the selectivity of monohexylbiphenyls reached to its maximum value at a ratio of biphenyl to 1-hexen of 1:1. On the basis of these results, optimum conditions were determined for mono-, di- and polyhexylbiphenyls.

Key Words: alkylation, biphenyl, 1-hexen, $((Al + C_3H_7Cl) + C_2H_4)$ catalyst, selectivity

Introduction

Aromatic hydrocarbons are a proper raw material for the processes of petro-chemical syntheses. As a simple compound of bicyclic aromatic hydrocarbons, biphenyl has both the properties of polycyclic compounds (high thermodynamic stability) and the properties of aromatic compounds (high reaction formation). Alkylation of biphenyl by using different catalysts have been widely discussed in the literature [1-3]. Especially the investigations of alkylation of biphenyl by olefins [1-7] and alcohols [8-9] have played the most important role to understand many problems in catalyst chemistry and chemical industry.

The aim of this paper is to investigate alkylation of biphenyl with 1-hexen by using a catalyst $((Al + C_3H_7Cl) + C_2H_4)$. At the experiment, biphenyl and 1-hexen at 99.9 % purity were used. Experimental results showed that biphenyl is alkylated with 1-hexen easily and different alkyl derivatives of biphenyl are formed. The effects of some parameters (temperature, molar ratio of biphenyl to 1-hexen, reaction time and catalyst concentration) on the process and on the formation of alkylbiphenyls were investigated.

Experimental

Materials

$((Al + C_3H_7Cl) + C_2H_4)$ was used as catalyst in the experiment. Biphenyl and 1-hexen (with 99 % purity) were used as raw matter. Boiling point, density and index of refraction of 1-hexen were 62-63 °C, 0.673 g/cm^3 and 1.388, respectively. 99 % pure ethylene and pure nitrogen were also used.

Catalytic reaction is as follows:

$$C_2H_4 + 4C_3H_7Cl + 2Al = 2Al(C_3H_7)_2Cl + C_2H_4Cl_2$$

Experiment

Alkylation of biphenyl with 1-hexen was carried out in a laboratory device (*Fig.1*). It consists of a reactor of 1.5 l (1) and a flowmeter (5) connecting liquid monometers with the reactor. Reactor was equipped with a mixer (2), a heater (6), manometer (3),

Contact information: E-mail: sevilv@kou.edu.tr

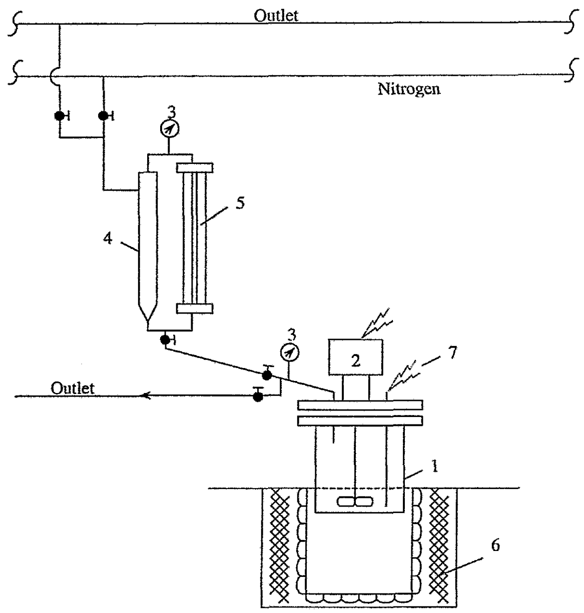

Fig.1 Scheme of the laboratory device (1-reactor, 2-mixer, 3-manometer, 4-1-hexen cup, 5-difmonometer, 6-heater, 7-thermocouple channel)

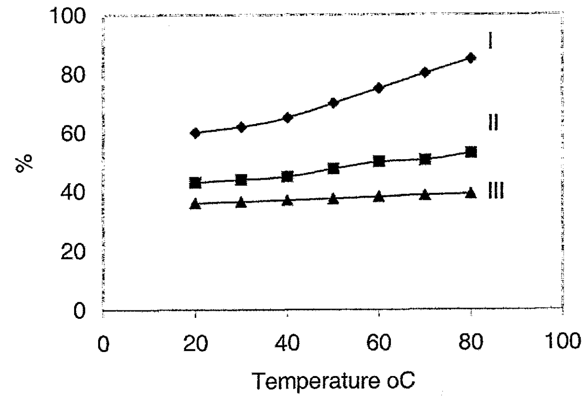

Fig.2 The effect of temperature on the variation of the biphenyl conversion and selectivities of alkylbiphenyls ; I-biphenyl conversion, II- selectivity of monohexylbiphenyl, III-selectivities of di- and polyhexylbiphenyls. Reaction conditions: reaction time 60 min., molar ratio of biphenyl to 1-hexen 1:1, mass ratio of catalyst to biphenyl 1,5 %

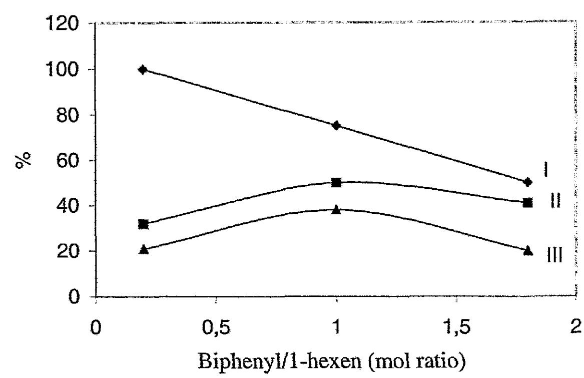

Fig.3 The effect of molar ratio of biphenyl to 1-hexen on the variation of biphenyl conversion and the amounts of obtained alkyl biphenyls; I-biphenyl conversion, II- amount of monohexyl biphenyl, III- amounts of di- and polyhexyl biphenyls. Reaction conditions: reaction temperature 60 ^{0}C, reaction time 60 min., ratio of catalyst to biphenyl 1,5 %

thermocouple channel (7) and inlet and outlet valves. flowmeters and reactor are made of stainless steel.

For the experiment, catalyst and biphenyl at certain amounts were added to reactor. Air in the reactor was removed by nitrogen. Then reactor was heated and, started to be mixed when biphenyl was liquefied. After that, nitrogen application was continued and by the time reaction conditions was reached, 1-hexen at sufficient amounts was added into the reactor by flowmeter (5) under nitrogen pressure. Alkylation was carried out by continuous mixing. At this time temperature was lowered by water bath. After the reaction was completed, the reactor was cooled by water bath to room temperature and opened. Finally samples were taken and prepared for alkyl biphenyl analyzis.

Results and Discussion

Biphenyl is alkylated by different compounds. The alkylation process of biphenyl with olefins is one traditional methods to produce alkylbiphenyls. Therefore alkylation of biphenyl with 1-hexen in the presence of a catalyst has a high importance.

Effect of reaction temperature

Results showed that temperature is one of the main factors affecting the reaction rate. Its effect on the alkylation was observed between 20-80 °C. It was observed that the conversion of biphenyl increases with temperature. In this case, the amounts of mono-, di- and polyhexylbiphenyls obtained were also increased. The results of the experiment were shown in *Fig.2*.

Effect of molar ratios

The effect of molar ratios of biphenyl to 1-hexen was observed at the ratios of 1/5; 1/1 and 1.8/1. Experiments showed that molar ratios of monomers have a significant effect on alkylation process. As the molar ratio of biphenyl to 1-hexen increases, conversion of biphenyl decreases. At the same time, selectivity of monohexyl biphenyl increases while the amounts of di- and polyhexylbiphenyls decreases. Experimental results are shown in *Fig.3*.

As shown in *Fig.3*, maximum amounts of monohexyl biphenyl was observed at the 1:1 molar ratio of monomers.

Increasing the biphenyl ratio in the process caused biphenyl conversion to decrease. Simultaneously the concentration of monohexyl biphenyls increased, while the other alkylbiphenyls decreased.

According to these results, it is suggested that as the biphenyl concentration in the process increases, the

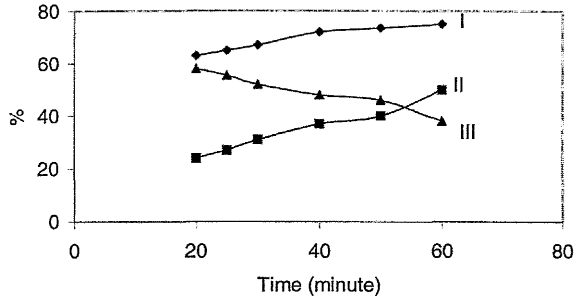

Fig.4 The effect of reaction time on the variation of biphenyl conversion and the amounts of obtained alkyl biphenyls; I- biphenyl conversion , II- amount of monohexyl biphenyl, III- amounts of di- and polyhexyl biphenyls. Reaction conditions: reaction temperature 60 ^{0}C, ratio of catalyst to biphenyl 1,5 %, molar ratio of biphenyl to 1-hexen 1:1

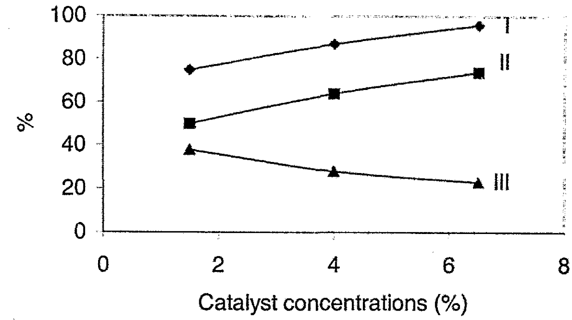

Fig.5 The effect of catalyst concentration on variation of the of biphenyl conversion and the amounts of obtained alkyl biphenyls; I-biphenyl conversion , II- amount of monohexyl biphenyl, III- amounts of di- and polyhexyl biphenyls. Reaction conditions: reaction temperature 60 ^{0}C, reaction time 60 min., molar ratio of biphenyl to 1-hexen 1:1

bounding of one 1-hexen molecule to biphenyl molecule separately occurs easier than the bounding of two 1-hexen molecules to one biphenyl molecule. On the other hand, since all biphenyl molecules could not be alkylated, the amount of biphenyl molecules that are not reacted, increase and therefore the biphenyl conversion decreases.

Effect of reaction time

The effect of reaction time on the alkylation process was examined between 20-60 minutes.

The effect of reaction time on the process is shown in *Fig.4*.

As shown in *Fig.4*, biphenyl conversion and monohexyl biphenyl concentration in alkylat increases as the reaction time increases, while di- and polyhexyl biphenyl concentrations decrease. These results suggest that as the reaction time increases, the dealkylation reaction, parallel reaction of alkylation, accelerates. This leads to a decrease in the di- and polyhexyl biphenyl amount in alkylat, as well as an increase in the amount of monohexyl biphenyl.

Effect of catalyst concentration

The rate of alkylation reaction also depends on the catalyst concentration as all reactions do. The effect of catalyst was examined at three ratios of catalyst used to biphenyl 1,5 %, 4 % and 6,5 %.

Fig.5 shows the results of the experiment.

As shown in the *Fig.5*, as the catalyst concentration increases, alkylation reaction accelerates and then, conversion of biphenyl and amounts of obtained monohexyl biphenyl increase while amounts of di- and polyhexyl biphenyls decrease. The decreasing of di-, and polyhexyl biphenyls is explained that the catalyst used was a catalyst of both alkylation and dealkylation. Therefore, as the catalyst concentration increases, dealkylation also increases and di- and polyhexyl biphenyls are transformed to monohexyl biphenyl by dealkylation. As a result, the ratio of monohexyl biphenyls to alkyl biphenyls increases.

The experiments showed the high activity of the catalyst used in alkylation of biphenyl with 1-hexen. That activity causes the alkyl biphenyls to be formed with a higher selectivities as compared to other catalysts.

Consequently, after examining the effects of these parameters on the process, the optimum conditions for the formation of mono- , di- and polyhexyl biphenyls can be determined. Optimum conditions for the formation of monohexyl biphenyls were found as follows:

– Reaction temperature	60 °C
– Reaction time	60 min
– Molar ratio of biphenyl to 1-hexen	1:1
– Ratio of catalyst to biphenyl	6.5 %

On the other hand, optimum conditions for the formation of di- and polyhexyl biphenyls were determined to be as follows:

– Reaction temperature	60 °C
– Reaction time	20 min
– Molar ratio of biphenyl to 1-hexen	1:1
– Ratio of catalyst to biphenyl	1.5 %

Conclusions

The alkylation of biphenyl with 1-hexen by a catalyst produces alkyl biphenyls with high efficiency and selectivity. Activity of the catalyst was studied in different intervals of temperature, molar ratio, reaction time and catalyst concentration. It was showed that increasing the temperature accelerates the process and leads to an increase in the amount of alkyl biphenyls obtained. Additionally, optimum conditions for the production of mono- and dialkyl biphenyls were determined.

Acknowledgement

The author wishes to express his thanks to Prof. Dr. Asker Hüseyinov for the helpful discussions and suggestions.

REFERENCES

1. MATSUDA T., URATA T. and KIKUCHI E.: Appl.Catal.A-Gen., *1995,* 123, 205-215
2. MATSUDA T., URATA T., SAITO U. and KIKUCHI E.: Appl.Catal.A-Gen., *1995*, 131, 215-224
3. BUTRUILLE J. R. and PINNAVAIA T. J.: Propene alkylation of biphenyl catalyzed by alumina pillared clays and related acidic oxides, *1992*, 12, 187-192
4. SUGI Y., MATSUZAKI T., HANAOKA T., KUBOTA Y., KIM J. H., TU X. and MATSUMOTO M.: Catal.Let., *1994*, 26, 181-187
5. MATSUDA T., KIMURA T., HERAWATI E., KOBAYASHI C. and KIKUCHI E.: Appl.Catal.A-Gen., *1996*, 136, 19-28
6. VERGANI D., PRINS R. and KOUWENHOVEN H. W.: Appl.Catal.A-Gen., *1997*, 163, 71-81
7. AGUILAR J., CORMA A., MELO F. V. and SASTE E.: Catal.Tod., *2000*, 55, 225-232
8. AGUILAR J., MELO F. V. and SASTRE E.: Appl.Catal.A-Gen., *1998*, 175, 181-189
9. HORNIAKOVA J., MRAVEC D., FABOKOVA S., HRONEC M. and MOREAU P.: Appl.Catal.A-Gen., *2000,* 203, 47-53