ELSEVIER

Journal of Molecular Catalysis A: Chemical 160 (2000) 383–392

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Microwave activation of catalytic transformation of *t*-butylphenols

Milan Hájek *, Marilena T. Radoiu [1]

Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 16502 Prague 6-Suchdol, Czech Republic

Received 1 September 1999; received in revised form 5 April 2000; accepted 15 April 2000

Abstract

Kinetics of catalytic transformation of 2- and 4-*t*-butylphenol (2TBP and 4TBP) in the liquid phase on a heterogeneous KSF catalyst has been studied in detail under conventional and microwave conditions. The process includes dealkylation, isomerization and transalkylation reactions. Its kinetics has been described using the method of initial reaction rates. It was found that microwaves affect both the reaction rate and the selectivity. The results were explained in terms of “microwave-induced polarisation” assuming an interaction of microwaves with a highly polarised reagent molecule in adsorbed state on the acidic active site. Temperature and solvent effects were also examined. The reaction mechanism of *t*-butylphenol transformation is discussed on the basis of electrophilic aromatic substitution via bimolecular reactions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Microwaves; Catalysis; Clays; Phenols; Transalkylation

1. Introduction

In recent years it has been found that heterogeneous reactions taking place on the surface of solid catalyst are more likely to show microwave activation of catalytic reactions than homogeneous reaction in solution where possibilities of activation are rather limited [1–5]. Most of the reported heterogeneous reactions have been carried out under solvent-free (dry) conditions where significant differences in conventional and microwave heating (MW) have been recorded [6]. We have found that higher reaction rates observed under microwave conditions were in most cases probably caused by localised superheating, i.e. by creating hot zones frequently called “hot spots” [7]. When solid catalytic material was efficiently stirred, temperature gradients were eliminated and differences in reaction rates between microwave and conventional heating (CH) were also eliminated. These results indicated that specific activation of chemical reaction by microwaves has not occurred.

The aim of this study was to examine heterogeneous catalytic reactions in the liquid phase

---

* Corresponding author. Tel.: +420-2-230-90-111; fax: +420-2-209-206-61.

E-mail addresses: hajek@icpf.cas.cz (M. Hájek), radoiu@ifin.nipne.ro (M.T. Radoiu).

[1] On leave from the National Institute for Lasers, Plasma and Radiation Physics, R-76900 Bucharest, P.O. Box MG-36, Romania. Tel.: +401-780-6925; fax: +401-423-1791.

1381-1169/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(00)00256-9

where formation of temperature gradients in a stirred suspension of fine powdered catalyst is rather limited. Catalysts and reactants have been examined from the point of view of their activity, reactivity and selectivity. The results obtained under conventional and microwave conditions were compared. Transformation of *t*-butylphenols has been chosen as a model reaction because it gives a mixture of different products. The second reason was that the course of this transformation under microwave conditions has not yet been described, although it has been reported that transformation of *t*-butylphenols proceeds readily in the presence of some natural clays and zeolites under CH [8,9]. We have decided to study these reactions in more detail because clays and zeolites possess a convenient loss factor when exposed to microwave field. Montmorillonite KSF has been chosen as a representative solid acidic catalyst.

2. Experimental

The *t*-butylphenols were provided by Sigma-Aldrich and had the following characteristics: 2-*t*-butylphenol (2TBP) 99.6%, bp 224°C; 4-*t*-butylphenol (4TBP) 99.3%, mp 98–101°C, bp 236–238°C; Phenol (P) 99.0%, bp 182°C, mp 40–42°C; hexane and heptane were supplied by Lachema Brno. They were used as obtained. Montmorillonite KSF catalyst (Sigma-Aldrich), surface area 251 m^2 g^{-1}, micropores 66.8 m^2 g^{-1}, mezopores 151.2 m^2 g^{-1}, particle size 10–15 μm, porosity (Hg porosimeter) ml/g at nm range: 0.29 at 15,000–1750, 0.53 at 1750–80, 0.13 at 80–14, 0.07 at 14–7.5, acidity determined by TPD (Temperature Programmed Desorbtion) of NH_3 corresponded to 0.29 mmol g^{-1} with one temperature maximum at 109°C. This result represents a weak acidic catalyst of one kind of acidic sites. KSF catalyst was activated by heating to 400°C for 2 h in an electrical oven and before each experiment twice for 10 min in a microwave oven at 200–250°C (750 W).

GC analyses of reaction mixtures were carried out on Hewlett Packard 5890 instrument fitted with a capillary column HP-5, 25 m × 0.2 mm × 0.11 mm with 5% crosslinked phenylmethylsilicone as a stationary phase.

Microwave experiments were carried out in a MILESTONE Lavis 1000 Basic Labstation (Italy) of maximum 1000 W power output and equipped with IR and fibre optic (NORTECH, Canada) thermometers for temperature control and with magnetic stirrer (IKAMAG, Germany).

The identity of the products was confirmed by their NMR and GC-MS spectra and by comparison with authentic specimens. NMR spectra

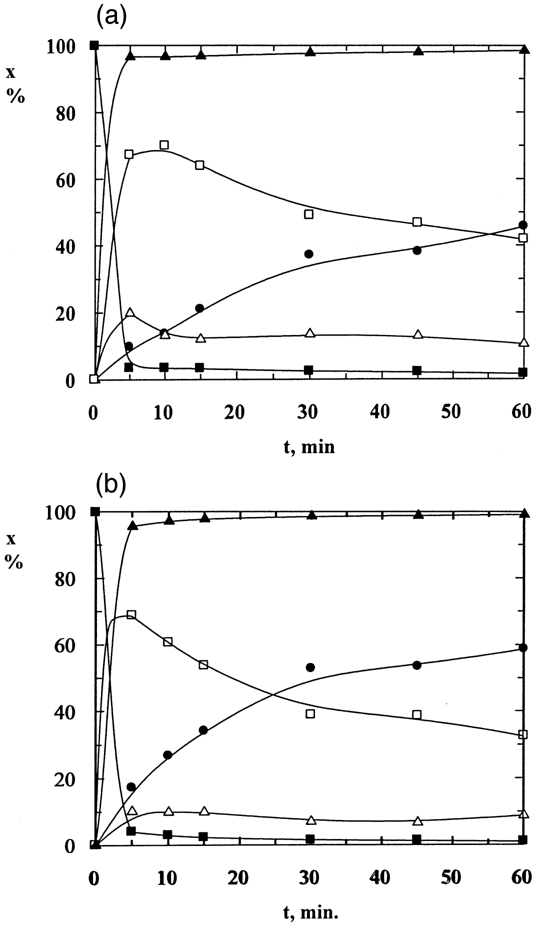


Fig. 1. Transformation of 2-tertbutylphenol (2TBP -■-) catalyzed by montmorillonite KSF catalyst under conventional (CH) (a) and microwave (MW) (b) conditions; -▲- total conversion, (x); -●- selectivity to phenol; -□- selectivity to 4TBP; -△- selectivity to 2,4DTBP at 196–199°C.

were recorded on VARIAN UNITY 200 NMR Spectrometer with $CDCl_3$ as solvent. ^1H NMR spectrum of 4TBP was referenced on a line of hexamethyldisilane ($\delta = 0.04$ ppm) which was added to the solvent in 1% v/v. ^{13}C NMR spectrum was referenced on a central line of solvent triplet ($\delta = 76.99$ ppm). The GC-MS analyses were performed on a capillary gas chromatograph VARIAN, model 3500, equipped with an ion-trap detector Finnigan MAT, model ITD 800 using He as the carrier gas. The maximum temperature of the 30 m column was 250°C. The mass spectrum of di-*t*-butylphenols (DTBP) was in accordance with the published standard spectra (NIST library) of the four existing isomers (2.4, 2.5, 2.6 and 3.5), m.w. 206.

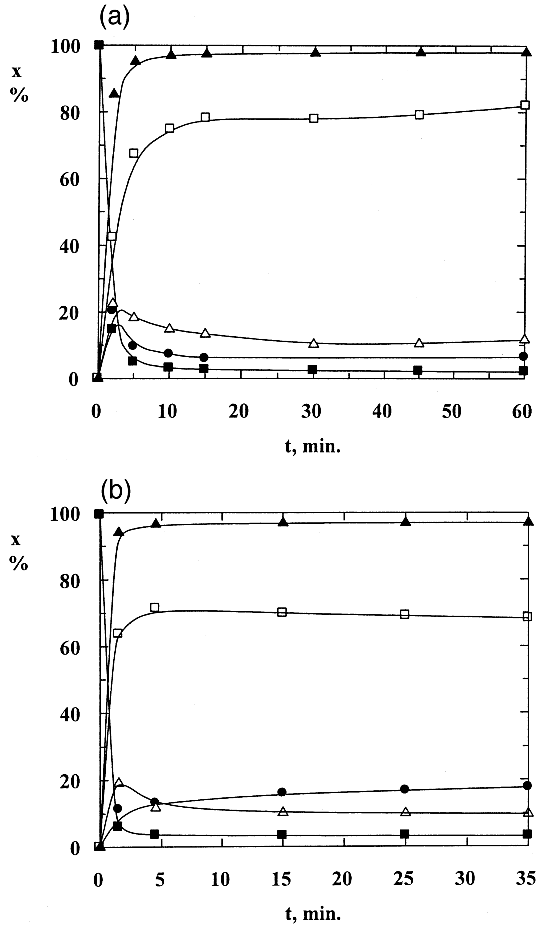


Fig. 2. Same as in Fig. 1 at 105°C.

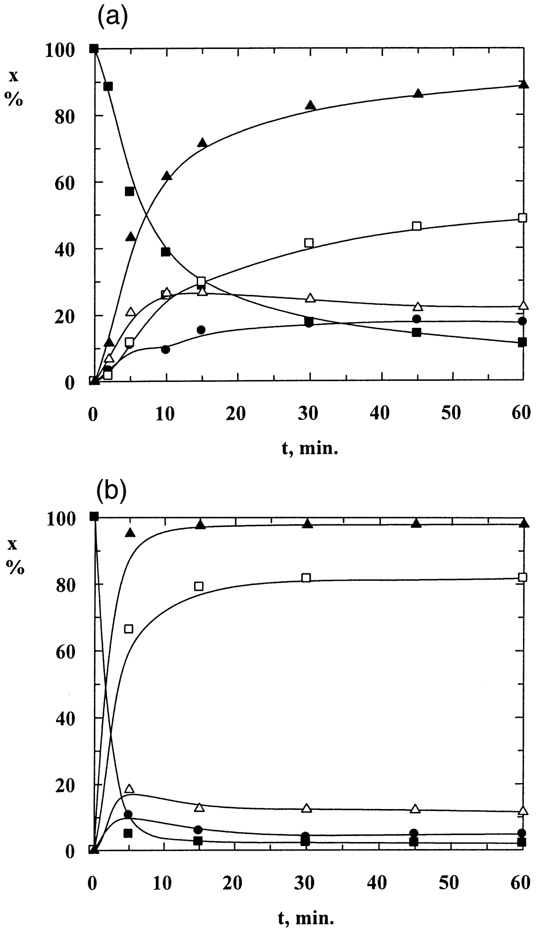


Fig. 3. Same as in Fig. 1 at 75°C.

MS: 191 (100; M-15), 57 (77; butyl group), 192 (43; M-14), 41 (37; propenyl), 206 (26; M), 107 (13), 135 (10), 163 (9.9).

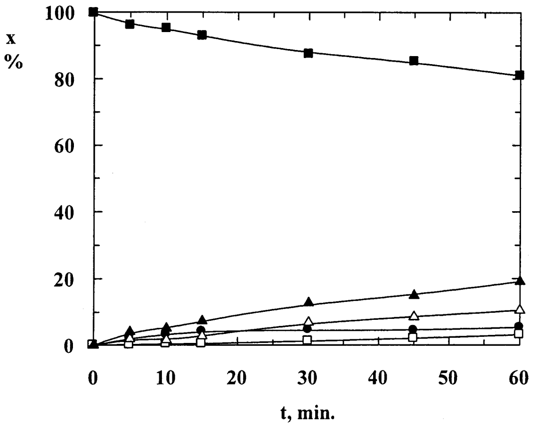


Fig. 4. Same as in Fig. 1a at 22°C.

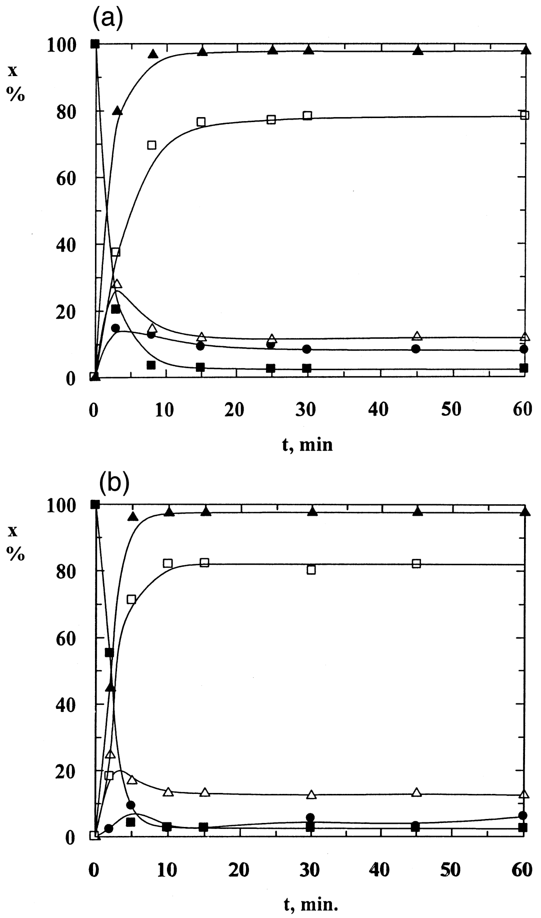


Fig. 5. Same as in Fig. 1 for heptane at 105°C.

The following are examples of typical conventional and microwave experiments.

2.1. CH

The reactions were carried out in a 50 ml two-neck glass round-bottom flask fitted with thermometer, water-cooled condenser and magnetic stirrer. The condenser was connected to a double bubbling flask for monitoring of gas evolution. A mixture of 3 g KSF catalyst and 15 ml 2TBP (or 4TBP) and either no solvent or 15 ml solvent (or 15 or 1 or 0.3 ml water) was magnetically stirred and heated on an oil bath to the desired temperature. The reaction temperatures were maintained using a constant-temperature oil bath. Samples of reaction mixtures were taken in regular intervals and analysed by GC. The results are presented in Figs. 1–8 and Table 1. Occasionally, the hot reaction mixture was freed off the catalyst by filtration, and after cooling the solid product was separated by filtration and washed with hexane. NMR spectra (vide supra) and melting point proved that the product corresponds to 4TBP (mp 101°C, authentic sample mp 98–101°C).

2.2. MW

The reactions were carried out in a 50-ml round-bottom glass flask fitted with optic fibre thermometer, outside water-cooled condenser

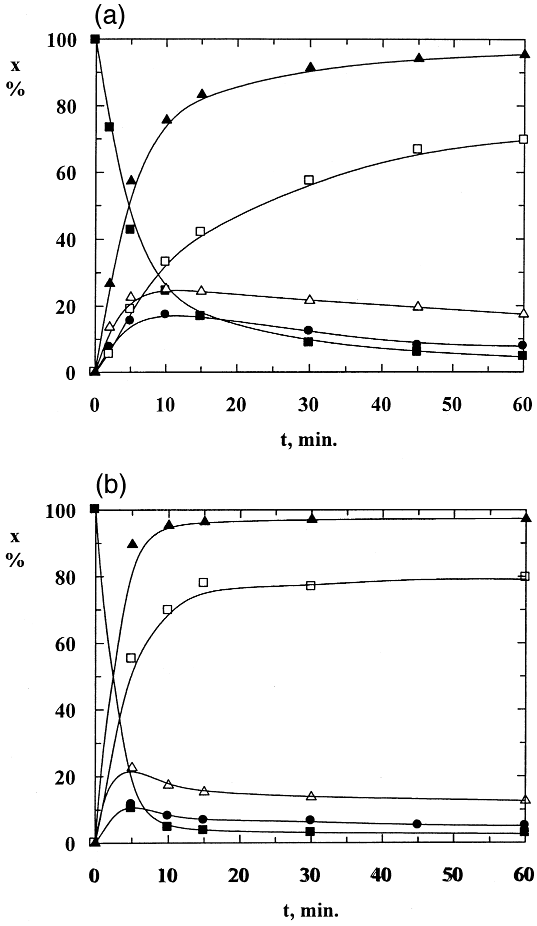


Fig. 6. Same as in Fig. 1 for hexane at 75°C.

and magnetic stirrer. The condenser was connected to a double bubbling flask for monitoring of gas evolution. Mixture of 4 g KSF catalyst, 20 ml 2TBP (or 4TBP) and either no solvent or 20 ml solvent (or 20 or 4 or 0.4 ml of water) was magnetically stirred and irradiated by microwave in the range of power output 400–1000 W. The amplitude of pulses of microwave irradiation were fixed to 1 s; it means that continuous irradiation was performed only at 1000 W. At the lower power than 1000 W, the oven was working by switch on–off regime of 1-s pulses (e.g. 400 W means 1000 W irradiation in 0.4 s switched on and 0.6 s switched off). The reaction temperature was measured and maintained using fibre optic and IR thermometers via PC temperature control. The results are presented in Figs. 1–8 and Table 1.[2]

The comparison of the relative reaction rates under conventional and microwave conditions has been done using the method of initial reaction rates (r^0) because the reaction kinetics of

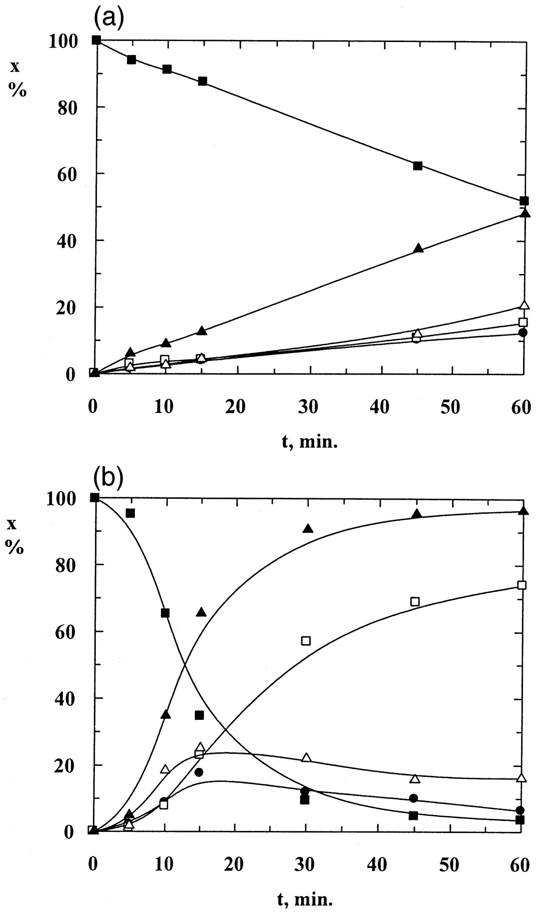


Fig. 7. Same as in Fig. 1 for water 2% at 105°C.

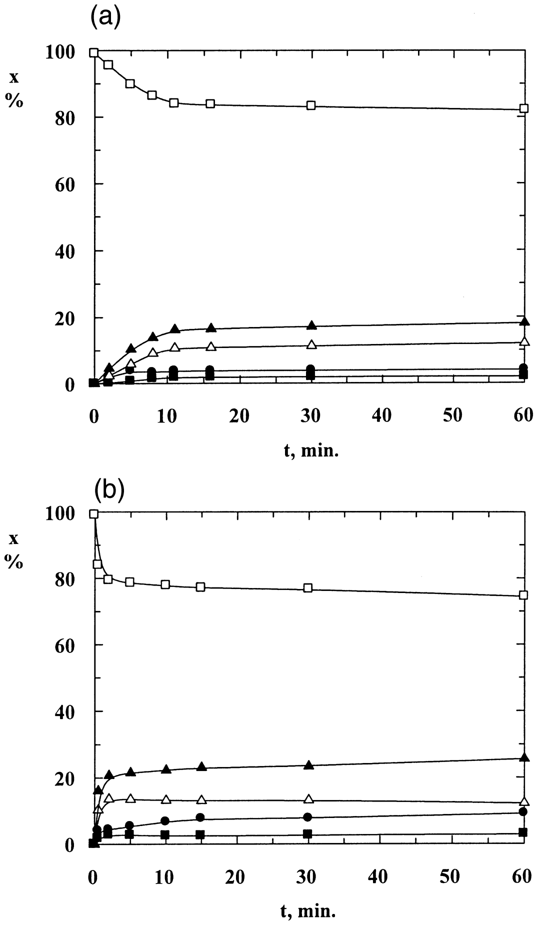


Fig. 8. Transformation of 4-tertbutylphenol (4TBP, -□-) catalyzed by montmorillonite KSF catalyst under conventional (CH) (a) and microwave (MW) (b) conditions; -▲- total conversion, (x); -●- selectivity to phenol; -■- selectivity to 2TBP; -△- selectivity to 2,4DTBP at 110°C.

---

[2] In the case of 4TBP, the solid substrate was at first melted by heating on an oil bath to 110°C and then KSF catalyst was added. The temperature 22°C under microwave conditions was kept by efficient cooling by bath of liquid nitrogen.

Table 1
Initial reaction rates of transformation of *t*-butylphenols catalyzed by montmorillonite KSF catalyst under conventional (r^0_{CH}) and microwave (r^0_{MW}) conditions

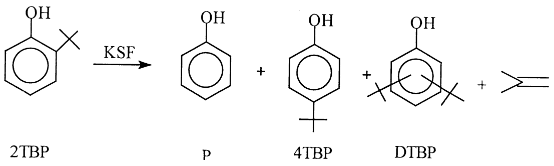
Substrate	Solvent	Temperature (°C)	$r^0_{CH} \times 10^3$ (s^{-1})	$r^0_{MW} \times 10^3$ (s^{-1})	r^0_{MW}/r^0_{CH}
2TBP	–	196–199[a]	20.00[b]	21.00[b]	1.05
	–	105	7.11[b]	10.30[b]	1.45
	–	75	1.21	3.17	2.62
	–	22	0.07	1.51	21.6
	Heptane	105[a]	3.20	3.80	1.19
	Hexane	75[a]	1.90	3.00	1.58
	Methanol	65[a,c]	0.00	0.00	–
	Tetrahydrofurane	75[a,c]	0.00	0.00	–
	Water	105	0.16	0.99[d]	6.19
4TBP	–	110	0.38	5.37	14.13

[a] Reflux.
[b] Too fast to be measured precisely.
[c] The reflux temperature under microwave was ~ 7°C higher because of superheating effect.
[d] Induction period.

the process are too complex due to a great number of the secondary reactions involved.

3. Results and discussion

The transformation of 2TBP is known to provide phenol, isomeric 4TBP and DTBP [6,7], in accordance with the following equation:



Microwave and conventional experiments have been carried out under strictly identical conditions. The results are summarised in Figs. 1–8 and Table 1. It was found that transformation of 2TBP includes isomerization, transalkylation and dealkylation reactions. Their proportions depended on the catalyst, reaction conditions and heating mode.

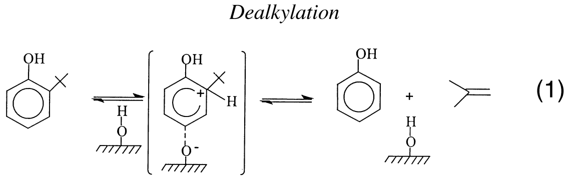
3.1. CH

3.1.1. Temperature effect

According to the literature [8], reactions with 2TBP catalysed by clays were usually carried out under reflux (225–230°C). Under these conditions debutylation and isomerization were reported as the main reactions to proceed. In the presence of a zeolite catalyst (type Y) isomerization of 2TBP proceeded rapidly even at much lower temperature (100°C) [9].

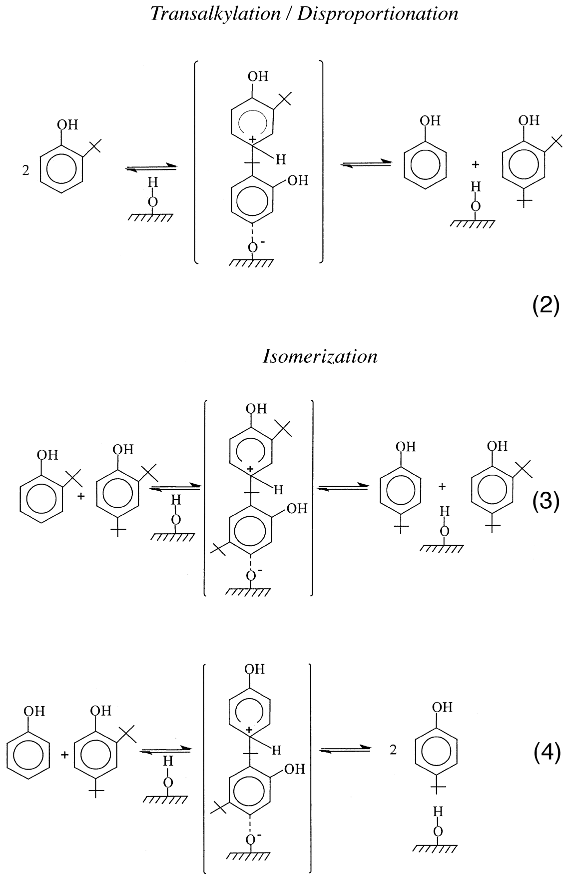
In our study we have used montmorillonite KSF as the catalyst. This clay is known to be an acidic heterogeneous catalyst efficiently used for Friedel–Crafts reactions [10], including phenol alkylation [11]. We have observed that in the presence of KSF catalyst, 2TBP underwent the following transformations.

3.1.1.1. Dealkylation. The reaction forming phenol and 2-methylpropene took place only at reflux temperature 196–199°C (Fig. 1) and is described in Scheme 1, Eq. (1). The lower reflux temperature than bp of 2TBP (224°C) was caused by the formation of the lower boiling phenol (182°C) even in the early stage of



Scheme 1.

the reaction before reaction mixture starts to boil.



Scheme 2.

3.1.1.2. Transalkylation and isomerization. The reactions affording phenol, 4TBP and DTBP proceeded at lower temperatures 105°C, 75°C (Figs. 2 and 3). It was found that the same transformation proceeds at significant reaction rate even at room temperature (22°C) (Fig. 4, Table 1), the isomerization being slower than the transalkylation at lower temperatures (22°C, 75°C) (Figs. 3 and 4). The isomerization of 2TBP using KSF catalyst has been found to occur via transalkylation since the product of isomerization, 4TBP, was detected to occur only in the presence of transalkylation products (Figs. 3 and 4) and never in the absence of transalkylation (vide infra). This observation is consistent with a transalkylation mechanism producing a kinetically controlled product distribution (Scheme 2, Eqs. (2–4)). Similar results were obtained by Bolton et al. [9] using zeolite catalyst where transalkylation was also assumed as an integral part of the isomerization reaction. It means that the amount of 4-isomer steadily increased with time while di-*t*-butyl product is permanently consumed. Bolton et al. [9] claimed that 3-isomer was the main final product. However, in our catalytic reaction 3TBP was formed only in trace amounts (less than 1 mol%) and occurred only after most of the 2-isomer was converted to the 4-form (Scheme 2, Eq. (3)). Thus the isomerization of 4TBP to 3TBP did not occur. As to the dialkyl fraction, there is a strong preponderance of one isomer which is assumed to be 2,4-di-*t*-butylphenol. This compound is a principal intermediate owing to the strong influence of hydroxyl group to 2- and 4-positions. *t*-Butyl group induces a considerable hindrance to the substitution of the two adjacent positions. It is surprising that no dialkyl isomer has been reported in the previous investigation of the isomerization and dealkylation of 2TBP on bentonite and kaoline clays by Saleh and Mahmoud [8]. Moreover, the authors supposed that 4TBP is produced by butylation of phenol with 2-methylpropene. This is improbable according to our results and mechanism proposed (vide infra). We have also observed the formation of tributylphenols, however, to a negligible extent (less than 1 mol%).

From Figs. 2–4, which show the course of the reaction at different temperatures, it is evident that in the absence of dealkylation reaction, the reaction mixture composition reaches equilibrium, e.g. the final content of 4TBP is close to the value in the range 70–80 mol% and 1–2 mol% for 2TBP. Isomerization of 2TBP to 4TBP is very fast at high temperatures, sometimes almost instantaneous. When 4TBP was used as the starting compound, the final composition reached the same value, i.e. 76–82 mol% 4TBP and 20 mol% 2TBP (Fig. 8), indicating equilibrium concentration. Disproportionation of 2TBP to phenol and 2,4-di-*t*-butylphenol should provide the equal product ratio. The differences in concentration between phenol and di-*t*-butylphenol from theoretical 1:1 molar ratio might be explained by dealkylation of 2TBP and 4TBP or by transalkylation of phenol and 4TBP by trialkylphenols.

3.1.2. Solvent effect

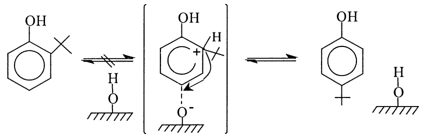
We have also examined solvent effects on the transformation reaction of 2TBP using both polar (methanol, tetrahydrofuran) and nonpolar (hexane, heptane) solvents. The reason was to examine the influence of dilution of the reaction mixture by inert solvents of different loss factor on the reaction rate and to compare the effect of microwaves on the reaction rate and selectivity in absorbing and non-absorbing media. The results of the experiments carried out in refluxing hexane or heptane (75°C and 105°C) showed a decrease in reaction rates by dilution $7.1 \rightarrow 3.20 \times 10^{-3}$ s^{-1} at 105°C and a slight increase $1.21 \rightarrow 1.90 \times 10^{-3}$ s^{-1} at 75°C (Table 1).

In the presence of polar solvents like methanol and tetrahydrofuran, the reaction did not proceed. This was attributed to the stronger adsorption of polar solvents compared to phenols. It was proved that 2TBP does not react without adsorption. Water has also been found to have a strong inhibitory effect on the reaction rate (Fig. 7, Table 1), but did not totally inhibit the catalytic activity of KSF catalyst at low concentrations (10 p.w. related to the catalyst).

3.1.3. Reaction mechanism

The results confirmed that the transformation of *t*-butylphenols includes at least three types of reaction: dealkylation, isomerization and transalkylation. The reaction path can be represented by Schemes 1 and 2. The dealkylation reaction was observed only at reflux temperature (196–199°C) in the absence of solvent and is represented by Scheme 1.

The isomerization has been found to proceed via a transalkylation process which satisfactorily explains the experimental results. The mechanism of transalkylation step involves a bimolecular intermediate formed by coupling of two monoalkylphenols that subsequently yields phenol and dialkylphenol. Since adjacent *t*-butyl groups are not readily formed, the 2,4-isomer was deduced from the transalkylation mechanism as the main product. Experimental results on the isomerization of *t*-butylphenols show that the mechanism proposed for positional isomerization via transalkylation satisfactorally accounts for the occurrence of transalkylation products. We believe that the experimental results obtained in this study are in close agreement with the reaction paths represented in Scheme 2.



(5)

Scheme 3.

An intramolecular rearrangement by 1,2-shift mechanism has been discounted (Scheme 3).

3.2. MW

When transformation of 2TBP has been carried out under microwave conditions, significant differences in reaction rates and in reaction course have been recorded. The results are summarised in Table 1.

3.2.1. Rate enhancement

As can be seen from Table 1, the rate enhancement of 2TBP transformation (expressed by the relative ratio of initial reaction rates) in the presence of microwave irradiation was in the range of 1.05–21.6 in the absence of solvents at temperatures 22–199°C. The reaction rates under both microwave and conventional conditions at reflux temperature were too high to be measured precisely. When the reaction mixture was heated at lower temperature or diluted with an inert solvent transparent to microwaves (hexane or heptane), the differences between the reaction rates under conventional and microwave conditions were more significant. The rate enhancement had the highest value at the lowest temperature up to 21.6 times at room temperature. When the effect of water on the reaction rate had been examined, 6.19 times rate enhancement was achieved by microwave irradiation in spite of the strong inhibition effect of water (Table 1). The observed induction period (Fig. 4) indicates that microwaves efficiently remove the water adsorbed on the surface of the catalyst and then the reaction is accelerated. This observation is very important for the reactions where water is obtained as the reaction product and indicates that it should be quickly removed from the catalyst (or from the reaction mixture). 4TBP was less reactive than 2TBP; however, the rate enhancement was also higher (14.13) for MW.

3.2.2. Course of the reaction and its selectivity

The following differences as to the selectivity and reaction course have been observed under microwave conditions.

(1) In spite of slight difference in the reaction rates at reflux temperature, there was a great difference in the evolution of 2-methylpropene. While under CH 2-methylpropene was not released, it was vigorously evolved under microwave conditions. The question of whether 2-methylpropene is the result of prevention of its polymerisation or of changes in mechanism is under investigation.

(2) From Figs. 1–8 it can be seen that the product distribution in the course of reaction always differs more or less when microwaves are used for accelerating the reaction. However, quantitative description of differences in the selectivity is difficult because transalkylation process is very complex and includes a great number of secondary reactions. It is clear that microwaves do have a certain selectivity effect on the transformation of alkylphenols.

3.2.3. Microwave effect

Finally, the question arises: how to explain differences in reaction rates and selectivity when reactions are carried out under microwave irradiation?

An increase in reaction rates by microwave irradiation as compared to CH has very often been attributed to the *local superheating* of the catalyst, to the formation of *hot spots* and to the *selective heating of active sites* [2–5,12]. However, until now no direct evidence has been provided to prove the existence of one or more these effects. It was assumed that a catalyst could have a steady state temperature, somewhat higher than the surrounding liquid medium [12]. If the existence of microwaves effect is thought about on molecular level, one can conclude that there exists a very small or no difference between the selective heating of active sites, hot spots or localised superheating effects, taking into consideration the adsorption state of the reactant molecule. Instead of speculating on what kind of microwave effect is responsible for the rate enhancement and selectivity changes, our attention was focused to the interaction of microwave energy with species adsorbed on the surface of catalyst, particularly on the polarised molecule in the transition state. We believe that adsorbed 2TBP molecules are more affected by microwave irradiation than solely by CH. This interaction may result in great changes in both reaction rates and selectivity. We explain this effect by a “microwave-induced polarisation”. It is evident that such a microwave effect can operate when the transition state involves a significantly polarised or charged intermediate species. According to the reaction mechanism, it seems most likely that the transformation of alkylphenols involves this type of effect.

4. Conclusions

Despite the fact that transformation of alkylphenols is a complex process, it was established that microwaves had a strong effect on both the reaction rate and the selectivity. We believe that the effect of microwaves involves the interaction of microwave energy with highly polarised reagent molecules during their adsorption on active sites in transition state. We explain this effect by a “microwave-induced polarisation”. However, more data are needed to support these conclusions. For that reason, the research which includes adsorption study, different catalysts with different kinds of active sites and polar and nonpolar alkylaromatic reagents has already started in our laboratory. The results will be published in a subsequent paper.

Acknowledgements

Authors thank Dr. K. Jiratova for acidity measurements and Dr. O. Solcova for surface area measurements of the KSF catalyst. Financial support of this work by the Grant Agency of the Czech Republic (203/97/1175) is gratefully acknowledged.

References

[1] M. Hajek, Collect. Czech. Chem. Commun 62 (1997) 347.

[2] R.N. Gedye, Proc. Int. Conf. on Microwave Chemistry, Prague, Czech Republic, 6–11 September, 1998, plenary lecture No. 3.

[3] R.N. Gedye, Ceram. Trans. 80 (1998) 165.

[4] R.N. Gedye, M. Shaw, Proc. 33rd Microwave Power Symposium, Chicago, USA, 12–15 July, 1998, paper No. 71.

[5] F. Chemat, M. Poux, S.A. Galema, J. Chem. Soc. Perkin Trans. 2 (1997) 2371.

[6] A. Loupy, Proc. Int. Conf. on Microwave Chemistry, Prague, Czech Republic, 6–11 September, 1998, plenary lecture No. 2.

[7] H. Richterova, M. Hajek, Proc. Int. Conf. on Microwave Chemistry, Prague, Czech Republic, 6–11 September, 1998, paper No. 4.

[8] S.A. Saleh, S.S. Mahmoud, React. Kinet. Catal. Lett. 64 (1998) 373.

[9] A.P. Bolton, M.A. Lanewala, P.E. Pickert, J. Org. Chem. 33 (1968) 3415.

[10] J.H. Clark, Catalysis of Organic Reactions by Supported Reagents, VCH Publishers, New York, 1994, p. 41.

[11] J.H. Patinkin, B.S. Friedman, in: G.A. Olah (Ed.), Friedel–Crafts and Related Reactions vol. 2 Interscience Publishers, New York, 1964, p. 75, Part I.

[12] F. Chemat, D.C. Esveld, J. van Haveren, Proc. Int. Conf. on Microwave Chemistry, Prague, Czech Republic, 6–11 September, 1998, paper No. 17.