MICROWAVE ACTIVATION OF HOMOGENEOUS AND HETEROGENEOUS CATALYTIC REACTIONS

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

Microwave heating was applied in homogeneous and in heterogeneous reactions and the results were compared from the point of view of activation of chemical reactions. Reactions including the addition of halo compounds to alkenes catalyzed by copper and ruthenium complexes in different solvents and NaY zeolite catalyzed alkylation of secondary amine in the absence of solvent were studied as model reactions to compare possibilities of microwave activation of reactants and catalysts. Rate enhancement of over one order of magnitude in homogeneous reactions was caused mainly by thermal dielectric heating effect which resulted from the effective coupling of microwaves to polar solvents. Activation of reactants and catalysts was very low if any. In heterogeneously catalyzed alkylation reactions highly efficient activation of zeolite catalyst was recorded. The results indicated that the best reaction conditions were in experiments when both activation of catalyst and performance of reaction were carried out under microwave conditions. Rate enhancement was most probably caused by "hot spots" or by "selective heating" of active sites. In both homogeneous and heterogeneous reactions non-thermal activation (specific effect) was excluded.

Key words: Microwave activation; Catalysis; Addition of halo compounds; Alkylation of secondary amines; NaY zeolite as catalyst.

In recent years increasing number of papers concerning acceleration of chemical reactions by microwave irradiation have been reported. However, satisfactory explanation of drastic reduction of reaction time by microwave irradiation in comparison with conventional heating methods has yet not been reported. According to our opinion and in agreement with some other authors, two models of the mechanism of microwave activation of chemical reactions can be proposed. The first can be called *thermal activation* resulting from mass heating, *i.e.* dielectric heating, and the second *non-thermal activation*, *i.e.* specific activation resulting from non-thermal interactions by microwave irradiation.

The first assumes that whilst the reaction time is drastically reduced, the kinetics or mechanism of the reaction is not altered. This proposal assumes that the rate enhancement is simply due to thermal dielectric heating effect.

The second alternative assumes that there is a specific activation effect due to microwave irradiation that operates in addition to the dielectric heating.

Thermal interactions of microwave irradiation can include the following categories:

1. Reaction rate enhancement due to "hot spots" (localized heating effects).

2. Reaction rate enhancement due to superheating (superheating effect).

3. Reaction rate enhancement due to improved transport properties of organic molecules (diffusion enhancement).

4. Reaction rate enhancement due to selective heating (active sites heating, heterogeneous catalysis).

5. Changes of selectivity of chemical reactions (fast heating).

Specific microwave activation has been a debated concept which actually refers to a unique interaction, reaction or activation, specific to the microwave irradiation. Some of the speculation about non-thermal microwave effect appears to have stemmed from a widely held misconception that microwave at 2.45 GHz can excite rotational transitions. It is necessary to point out that when a compound absorbs microwaves at 2.45 GHz, dielectric heating accounts for the temperature rise and the irradiation does not directly excite the molecule to higher vibrational or rotational energy levels. Moreover, the energy carried by microwaves at 2.45 GHz is too small (0.3 cal/mol) to split off chemical bonds. It means that direct molecular activation such as in photochemistry is evidently improbable. On the other hand if we assume that there can be some non-conventional effect which results in kinetic, yield or selectivity improvement, true microwave activation may occur.

The published results indicated that strong differences exist when microwave heating is applied in reactions carried out under homogeneous or under heterogeneous conditions[1]. The aim of this study was to examine microwave heating effects in homogeneous and heterogeneous catalytic reactions and to compare possibilities of microwave activation of reactants and catalysts.

EXPERIMENTAL

Methods

The reactions were carried out in Philips Whirlpool ovens, M 306 (600 W, mode stirrer) for homogeneous reactions and AVM 902 (1 000 W, turntable, double emission) for heterogeneous reactions. GC analysis was performed on an HP 5890 A instrument with HP Ultra-1 capillary column, ^{1}H NMR spectra of the products were measured on a Varian XL 200 spectrometer with $CDCl_3$ as solvent.

Homogeneous Reactions

In a typical experiment a mixture of a halo compound, alkene, copper or ruthenium catalyst and a solvent in 2.5 : 1 : 0.01 : 5 molar ratio was irradiated for 15–40 min (conversion up to 90%). Screw-tap Teflon closed vessel was used for experiments under microwave conditions (oven) and sealed glass ampoule was used for experiments under conventional conditions (thermostated oil bath). Both reactors were equipped with a septum to take samples for GC analysis and to measure the temperature of reaction mixture. The temperature was measured by quick-response digital thermometer (thin thermocouple was placed inside the needle) immediately after irradiation intervals. Each reaction was carried out both under microwave irradiation (600 W, full power) and conventional heating at the same temperature. The quantity of the reactants and catalysts were kept the same under both sets of reaction conditions. The samples of the reaction mixture were analyzed by GC in regular intervals, and rate constants k_m (microwave heating) and k_c (conventional heating) were determined by known method[2]. The results are presented in Table I.

TABLE I
Rate constants of addition of chloro compounds to alkenes under microwave (k_m) and conventional (k_c) conditions in the presence of $[Cu(2\text{-}PhNH_2)_2Cl]$ catalyst

Run	Alkene	Chloro compound	Solvent[a]	Temperature °C	$k_m \cdot 10^4$ s^{-1}	$k_c \cdot 10^4$ s^{-1}	f[b]
1	$C_6H_5CH=CH_2$	CCl_4	none	30	0.0	0.00	–
2		CCl_4	DCHE	73	1.2	0.37	3.2
3		CCl_4	ACN	72	3.3	0.44	7.5
4		CCl_3COOEt	none	85	9.3	1.30	7.1
5		CCl_3COOEt	DCHE	83	8.7	1.20	7.2
6		CCl_3COOEt	ACN	82	23.0	1.10	21.0
7		CCl_3COOEt	DCHE	85	8.2	6.8	1.2[c]
8	$CH_2=CHCOOMe$	CCl_4	none	51	0.2	0.18	1.1
9		CCl_4	DCHE	74	1.2	0.25	4.8
10		CCl_4	ACN	85	1.9	0.35	5.4
11		CCl_3COOEt	none	88	5.0	0.93	5.4
12		CCl_3COOEt	DCHE	90	4.8	0.85	5.6
13		CCl_3COOEt	ACN	102	5.5	0.83	6.6
14		CCl_3COOEt	B	80	0.7	0.66	1.1

[a] DCHE, 1,2-dichloroethane; ACN, acetonitrile; B, benzene. [b] f, rate enhancement factor (k_m/k_c). [c] $[RuCl(PPh_3)_3]$ catalyst.

Heterogeneous Reactions

NaY zeolite (Aldrich, cat. No. 33, 444-8, powder) was activated[3] both classically (350 °C, 9 h, electric oven) and by microwaves (350 °C maximum, 10 min, 1 000 W, microwave oven). The results are presented in Figs 1 and 2. Activated zeolite was impregnated by dibenzylamine and 2-phenylethyl chloride (1 : 1.5 molar ratio) and exposed to microwave (oven) or conventional (oil bath) heating. The samples of reaction mixture were treated by solution of $NaHCO_3$, extracted 3 times by petroleum ether and analyzed by GC and NMR. NMR spectra of the product were in agreement with published data[4]. Alkylation reaction was carried out at two temperatures 80 and 150 °C, both under microwave and conventional conditions. The temperature of the solid reaction mixture under microwave heating varied in differences ±10 °C. Lower temperatures (70–90 °C) were established by lowering microwave power with a beaker of water (200 ml) to absorb excess microwave energy. Because of varying temperatures which prevented precise kinetic measurements, microwave activation of alkylation reaction was evaluated by the yield of product. The results are presented in Table II.

TABLE II
Alkylation of dibenzylamine under microwave (MW) and conventional (CL) conditions

Run	Activation of zeolite, (350 °C)		Alkylation of dibenzylamine			
	Conditions	Time, h	Conditions	Temperature,°C	Time, h	Yield, %
1	CL	9.0	CL	80	0.5	13.3
2	CL	9.0	CL	80	7.0	23.9
3	CL	9.0	CL	150	0.5	45.3
4	CL	9.0	CL	150	7.0	67.9
5	CL	9.0	MW	70–80	0.5	14.8
6	CL	9.0	MW	140–160	0.5	70.1
7	MW	0.17	CL	80	0.5	15.7
8	MW	0.17	CL	80	7.0	40.0
9	MW	0.17	CL	150	0.5	44.3
10	MW	0.17	CL	150	7.0	66.8
11	MW	0.17	MW	70–90	0.5	47.4
12	MW	0.17	MW	140–160	0.5	69.7
13	–	–	CL	80	7.0	2.7[a]

[a] In the absence of zeolite (Na_2CO_3 solution).

RESULTS AND DISCUSSION

Homogeneous Reactions

$$\text{R–CH=CH}_2 + \text{CXCl}_3 \xrightarrow[\text{Cat}]{\text{MW}} \text{R–CHCl–CH}_2\text{–CXCl}_2 \qquad (A)$$

R = Ph, COOMe; X = Cl, COOEt; Cat = $[Cu(2\text{-}PrNH_2)_2Cl]$, $[RuCl(PPh_3)_3]$

The experiments included combination of polar (ethyl trichloroacetate, methyl acrylate) and non-polar (styrene, tetrachloromethane) reactants, and polar (1,2-dichloroethane, acetonitrile) and non-polar (benzene) solvents with different abilities to absorb microwaves. Transition metal complexes of copper $[Cu(2\text{-}PrNH_2)_2Cl]$ and ruthenium $[RuCl(PPh_3)_3]$ were used as catalysts. Preliminary results indicated that a certain activation of homogeneously catalyzed addition reactions is possible[2]. Because almost no data on application of microwave heating in reactions catalyzed by transition metal complexes was available, we have examined this subject in more detail. The results are summarized in Table I.

Rate enhancement up to 21-fold (run 6) was observed with $[Cu(2\text{-}PrNH_2)_2Cl]$ catalyst when acetonitrile was used as a polar solvent. In non-polar benzene no rate enhancement was observed (run 14). No reaction proceeded with non-polar reactants (styrene, tetrachloromethane) in non-polar media (excess of tetrachloromethane, run 1). This reaction mixture containing homogeneous catalyst did not absorb microwaves and therefore no reaction occurred.

From the values of rate constant under conventional condition can be seen that solvent effect on reaction rate was not too significant (k_c = 0.37–0.44, 0.18–0.35 for tetrachloromethane, runs 2, 3; 8–10 and k_c = 1.10–1.30, 0.66–0.93 for ethyl trichloroacetate, runs 4–6; 11–14). On the other hand reaction rate under microwave condition was much more dependent on the polarity of solvent (k_m = 1.2–3.3, 0.2–1.9 for tetrachloromethane, runs 2, 3; 8–10 and k_m = 8.7–23.0 for ethyl trichloroacetate, runs 4–6) except in the case when both reactants were polar (4.8–5.5, runs 12, 13). In non-polar benzene no rate enhancement was observed (run 14). Ruthenium catalyst was more active than copper catalyst, however, only slight rate enhancement was observed (f = 1.2, run 7) in comparison with copper catalyst (f = 7.2, run 5). Reactivity of reactants followed the same order under conventional and under microwave conditions (styrene > methyl acrylate; ethyl trichloroacetate > tetrachloromethane) as expected.

The highest differences in the rate enhancement by microwave heating were recorded in the presence of polar solvents. Non or low rate enhancement in the absence of polar solvents indicate that activation of reactants and catalysts in homogeneous reactions by microwaves is very low if any. Specific, *i.e.* non-thermal activation of reactants and catalysts which was considered in our previous communication[2] can be excluded. Rate enhancement of over one order of magnitude seems to be caused mainly by thermal dielectric heating effect which resulted from the effective coupling of microwaves to polar solvents.

Heterogeneous Reactions

$$(PhCH_2)_2NH + PhCH_2CH_2Cl \xrightarrow[-HCl]{NaY,\ MW} (PhCH_2)_2NCH_2CH_2Ph \qquad (B)$$

Alkylation of a sterically hindered amine (dibenzylamine) with a low reactive alkyl chloride (2-phenylethyl chloride) in the presence of a solid catalyst (NaY zeolite) was chosen as a convenient model reaction to study possibility of microwave activation. This reaction has not been described in the literature. In an independent experiment we have proved that this reaction almost does not proceed in the absence of catalyst (Table II, run 13).

It was found that activation of NaY zeolite reduced drastically the time from 9 h to 10 min when microwave dehydration method was used in comparison with known conventional heating[3]. The same effect was observed by Roussy[5] and it is explained by direct desorption of water molecules by the electromagnetic field, this process being independent of the temperature of the solid (diffusion enhancement). The results are presented in Figs 1 and 2.

In order to evaluate the effect of microwaves both on activation of catalyst and on heterogeneous reaction, cross-experiments have been carried out by combination of microwave and conventional method of heating. The results are summarized in Table II.

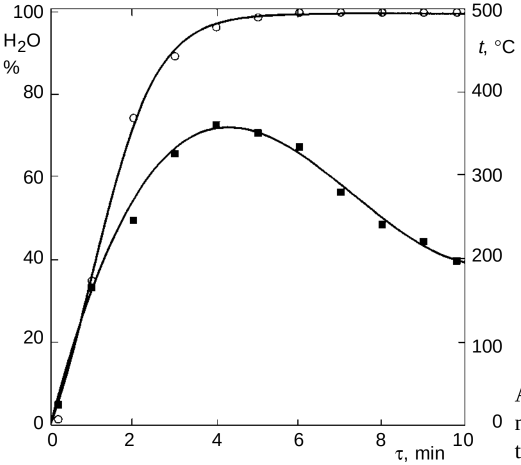

FIG. 1
Activation (dehydration) of NaY zeolite by microwave heating (○) (temperature against time curve designated by ■)

It was found that the activity of zeolite was almost the same irrespective if the catalyst was activated by conventional or by microwave method.

More significant effect of microwaves was found in alkylation reaction especially at higher temperatures. The yield of product was much higher when the reaction was carried out under microwave condition in comparison with conventional method (45.3 → 70.1%, runs 3, 6 and 44.3 → 69.7%, runs 9, 12). To achieve high yield under conventional conditions longer reaction time from 0.5 to 7 h was necessary (runs 4, 10).

The results indicated that alkylation reaction was significantly affected by microwaves. The best evidences were obtained in experiments when the activation of catalyst and the activation of reaction were both carried out under microwave conditions (runs 11, 12).

The explanation for activation of heterogeneous reactions by microwaves seems to be more complex than activation of reaction in solution. It is known that zeolites contain polar active sites (dipoles) on the surface which are mainly responsible for a strong absorption of microwaves and therefore for a fast efficient heating of this material. These sites interact with microwaves and their temperature may be somewhat higher than in the bulk. This is the case of activation by "selective heating". The second possibility is the presence of "hot spots". We have observed temperature gradients up to 20 °C in the samples, the elimination of which is not a simple operation and they can not be totally eliminated even by stirring. These "hot spots" may be therefore always present in the solid sample in the absence of solvent and they may be responsible for acceleration of alkylation reaction.

Both these cases belong to the thermal activation of chemical reactions. The possibility of non-thermal activation may also occur, *e.g.* in the case when reactants ad-

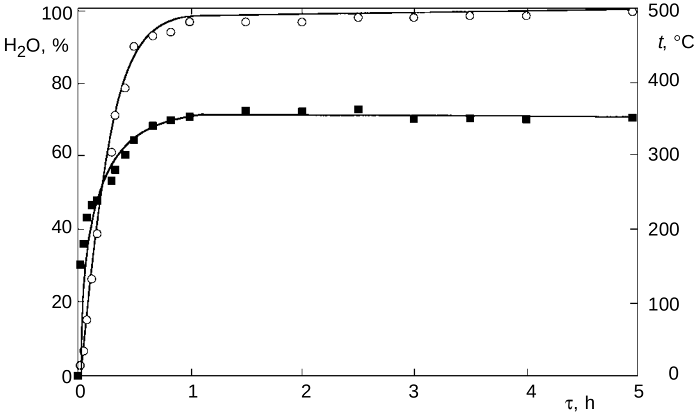

FIG. 2
Activation (dehydration) of NaY zeolite by conventional heating (❍) (temperature against time curve designated by ■)

sorbed on the active sites are activated by microwave energy transfer from the sites to adsorbed molecules. In our described alkylation reaction the rate enhancement was not so high as would be expected (less than one order) and therefore non-thermal activation may be excluded.

It can be concluded that for the study of microwave activation of catalytic reactions heterogeneous reactions taking place on the surface of solid catalyst are more interesting than reactions in solution where possibility for microwave effects is very limited. The results of this study documented that much broader possibilities exist for both thermal or non-thermal activation in heterogeneous reactions in the absence of solvent than for homogeneous reactions in solution where microwave effects are practically reduced to thermal "superheating" effect.

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REFERENCES

1. Bram G., Loupy A., Villemin D.: *Solid Support and Catalysis of Organic Synthesis* (K. Smith, Ed.), p. 302. Ellis Horwood, Chichester 1992.
2. Adamek F., Hajek M.: Tetrahedron Lett. *33*, 2039 (1992).
3. Ipaktschi J., Brück M.: Chem. Ber. *123*, 1591 (1990).
4. Katritzky A. R., Yannakopoulou K., Lue P., Rasala D., Urogdi L.: J. Chem. Soc., Perkin. Trans. 1 *1989*, 225.
5. Roussy G., Zoulalian A., Charreyre M., Thiebaut J. M.: J. Phys. Chem. *88*, 5702 (1984).