



Microwave-assisted acylation of aromatic compounds using carboxylic acids and zeolite catalysts

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ABSTRACT

Acylation of aromatic compounds with carboxylic acids smoothly proceeded at 190–230 °C in the presence of zeolite catalysts under microwave irradiation to give aromatic ketones efficiently. H–Y (SiO₂/Al₂O₃ = 30–80) and H–beta (25) zeolites were active for the acylation reaction, giving the aromatic ketones in good yields. Carboxylic acids such as hexanoic and butyric acid smoothly underwent the acylation, while propionic acid showed somewhat lower reactivity. Anisole gave the *para*-acylation products nearly selectively. Anisole, 2,3-dihydrobenzofuran, and thiophene were reactive aromatic compounds. 2,3-Dihydrobenzofuran also reacted at the *para* position to the oxygen atom predominantly to give the corresponding ketones as the major products. The microwave reactions were generally faster than the conventional oil bath reactions and gave higher yields of the acylation products. Activation energies for the reaction of anisole with butyric acid by microwave and by oil bath heating were also estimated on the basis of the Arrhenius plots.

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1. Introduction

Aromatic ketones are principal compounds in organic chemical industry. Friedel–Crafts type acylation reactions of aromatic compounds with acyl halides or carboxylic anhydrides have been generally utilized for the preparation of aromatic ketones. Concerning the catalysts, utilization of solid acids such as zeolites, heteropoly acids, etc. has also been investigated because of the merit of easy separation and/or recyclability of the catalysts [1–3]. Although the method using acyl halides or carboxylic anhydrides has wide applicability, it has a drawback that equimolar amounts of hydrogen halides or carboxylic acids are concomitantly formed. To overcome the drawback, acylation reactions by carboxylic acids have been investigated using some solid acid catalysts such as zeolites [4–13], heteropoly acids or related compounds [14–20], acidic clays including metal cation-exchanged montmorillonites [21–24], and a *p*-toluenesulfonic acid/graphite system [25]. The method using carboxylic acids has an advantage that the co-product is only water, thus providing an environmentally benign method for the preparation of aromatic ketones. However, the rates and/or the yields of the acylation reactions using carboxylic acids has not been necessarily high in comparison with those using acyl halides or carboxylic anhydrides.

On the other hand, microwave-assisted chemical processes have attracted increasing interests with hoping to improve the efficiency of organic reactions [26–28]. In the course of our study on the microwave-assisted chemical reactions, we have found that an intramolecular Friedel–Crafts type dehydrative acylation reaction using solid acid catalysts has been effectively accelerated by microwave irradiation [29]. Meanwhile, an interesting microwave-assisted acylation of anisole with carboxylic acids has been recently reported by Bond et al. using solid acid catalysts of a silica-supported heteropoly acid, a sulfated zirconia, and a La-exchanged Y zeolite [30]. To know the efficiency of proton-type zeolite catalysts in the microwave-assisted acylation reaction, we have investigated the acylation with carboxylic acids using some commercially available zeolite catalysts. Herein are reported the results of the acylation reaction including a consideration on the kinetics of the reaction.

2. Experimental

2.1. Instruments and reagents

Microwave irradiation experiments were carried out with a CEM Discover instrument (single mode type, microwave max power 300 W) using closed Pyrex glass tubes (ca. 10 mL) with Teflon-coated septa. The reaction temperature was monitored by a radiation thermometer attached to the microwave instrument. The temperature measured by the radiation thermometer was calibrated by a fiber optic thermometer and standard mercury ther-

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mometers. Centrifugation was performed by a Porta Centrifuge and a Hsiangtai CN-2060. The yields of the products were analyzed using gas liquid chromatography (GC) with a Shimadzu GC-17A system equipped with a capillary column (Zebtron ZB-50, 0.25 mm i.d. \times 30 m, an internal standard of dodecane), and a flame ionization detector (FID). Identification of the products was made by gas chromatography/mass spectrometry (GC/MS) analyses with a Shimadzu GCMS-QP2000plus system. Complex dielectric constants of liquid compounds and zeolite catalysts were measured by a perturbation method [31] with a system of Kanto Electronic Application and Development Inc. comprising of a vector network analyzer of Agilent 8720ES and a 2.45 GHz cylindrical cavity of TM₀₂₀ mode using Teflon-type sample tubes. Confirmation of the structures of the authentic samples for the acylated products was made on the basis of ¹H and ¹³C nuclear magnetic resonance (NMR) spectra measured by a Jeol JNM-LA600 instrument using chloroform-*d* solvent and Infrared (IR) spectra recorded on a Jasco FT/IR-660plus spectrometer.

Liquid compounds such as anisole (**1a**), 2,3-dihydrobenzofuran (**1b**), thiophene (**1c**), hexanoic acid (**2a**), butyric acid (**2b**), propionic acid (**2c**), and 1,2-dichlorobenzene were used after drying with molecular sieve 4A. Zeolite catalysts were the commercial products of Tosoh Co., Ltd., UOP, Ltd., and Zeolite International. Their properties were summarized in Table 1. These zeolite catalysts were used after heating at 500 °C for 5 h under air. An activated carbon (AC) was obtained from Wako Pure Chem. Ind., Ltd. and used after heating at 200 °C for 2 h.

2.2. Authentic samples of **3**

Authentic samples of 1-(4-methoxyphenyl)-1-butanone (**3b**), 1-(4-methoxyphenyl)-1-propanone (**3c**), 4,4'-dimethoxybenzophenone (**3g**), and 4-methoxybenzophenone (**3h**) were purchased from Tokyo Chemical Industry Co., Ltd. On the other hand, authentic samples of 1-(4-methoxyphenyl)-1-hexanone (**3a**) [32], 1-(2,3-dihydrobenzofuran-5-yl)-1-butanone (**3d**) [33], 1-(2,3-dihydrobenzofuran-5-yl)-1-hexanone (**3e**), and 1-(2-thienyl)-1-hexanone (**3f**) [34] were obtained by the reactions of the corresponding aromatic compounds with suitable carboxylic anhydrides at 80–100 °C using zeolite catalysts; the isolated yields (reaction conditions) of **3a**, **3d**, **3e**, and **3f** were respectively 79% (**1a** 60 mmol, hexanoic anhydride 10 mmol, CBV760 200 mg, 80 °C, 1 h), 57% (**1b** 10 mmol, butyric anhydride 10 mmol, CBV760 300 mg, 100 °C, 2.5 h), 68% (**1b** 10 mmol, hexanoic anhydride 10 mmol, CBV760 200 mg, 100 °C, 1 h), and 55% (**1c** 12 mmol, hexanoic anhydride 10 mmol, CBV720 200 mg, 100 °C, 3 h). The NMR data of the prepared authentic samples were in good agreement with the reported data or with the proposed structures. The NMR, IR, and GC–MS spectral data for **3d** and **3e** and the GC–MS data for their isomeric products **3d'** and **3e'** are as follows.

3d: ¹H NMR (600 MHz, CDCl₃): δ 0.99 (t, J = 7.3 Hz, 3H, CH₃), 1.75 (sextet, J = 7.3 Hz, 2H, CH₂CH₂), 2.88 (t, J = 7.3 Hz, 2H, CH₂CO), 3.24 (t, J = 8.8 Hz, 2H, OCH₂CH₂), 4.65 (t, J = 8.8 Hz, 2H, OCH₂), 6.80 (d, J = 8.4 Hz, 1H, aromatic H), 7.80 (d, J = 8.4 Hz, 1H, aromatic H), 7.85 (s, 1H, aromatic H); ¹³C NMR (151 MHz, CDCl₃): δ 13.9, 18.1, 29.0, 40.3, 72.1, 108.9, 125.3, 127.6, 129.9, 130.6, 164.2, 199.0; IR (KBr): ν (cm⁻¹) 1672, 1604, 1492, 1439, 1364, 1305, 1285, 1239, 1141, 1120, 1095, 980, 942, 909, 808, 751; GC–MS: m/z (relative intensity) 190 (M⁺, 13), 147 (100), 119 (12), 91 (21), 65 (15).

3d': GC–MS: m/z (relative intensity) 190 (M⁺, 9), 162 (11), 147 (100), 91 (30), 65 (20).

3e: ¹H NMR (600 MHz, CDCl₃): δ 0.86–0.98 (m, 3H, CH₃), 1.30–1.46 (m, 4H, CH₂CH₂CH₂), 1.66–1.76 (m, 2H, CH₂CH₂CO), 2.89 (t, J = 7.3 Hz, 2H, CH₂CO), 3.25 (t, J = 8.6 Hz, 2H, OCH₂CH₂), 4.65 (t, J = 8.6 Hz, 2H, OCH₂), 6.80 (d, J = 8.4 Hz, 1H, aromatic H), 7.80 (d, J = 8.4 Hz, 1H, aromatic H), 7.85 (s, 1H, aromatic H); ¹³C NMR

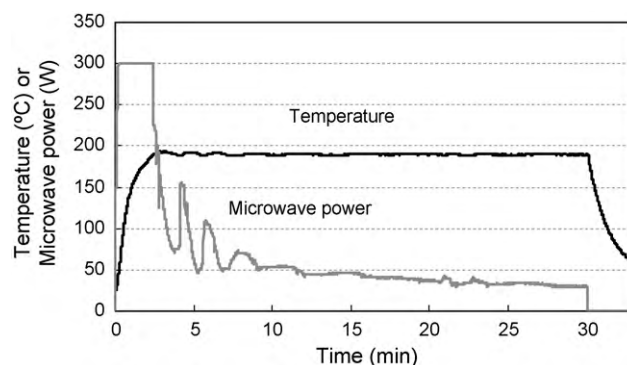


Fig. 1. A monitoring profile for the reaction of **1a** with **2b** (190 °C, 30 min).

(151 MHz, CDCl₃): δ 13.9, 22.5, 24.4, 29.0, 31.6, 38.3, 72.1, 108.9, 125.3, 127.6, 130.0, 130.5, 164.1, 199.2; IR (KBr): ν (cm⁻¹) 1673, 1606, 1587, 1494, 1371, 1324, 1258, 1241, 1205, 1146, 1093, 978, 940, 835, GC–MS: m/z (relative intensity) 218 (M⁺, 6), 162 (53), 147 (100), 119 (12), 91 (22), 65 (14).

3e': GC–MS: m/z (relative intensity) 218 (M⁺, 3), 162 (46), 147 (100), 91 (35), 65 (20).

2.3. Acylation of aromatic compounds with carboxylic acids

A typical procedure for a microwave reaction was as follows. A mixture of an aromatic compound **1** (12.0 mmol), a carboxylic acid **2** (2.0 mmol), a zeolite catalyst (100 mg), an activated carbon (AC, 50 mg), dodecane (internal standard, 50 mg), and a magnetic bar was sealed in a Pyrex test tube (ca. 10 mL). AC was added as a susceptor material to absorb microwave energy efficiently; without AC the rate of the temperature increase of the whole reaction system was lower than that with AC. The mixture was heated by microwave irradiation (microwave max power 300 W) with magnetic stirring under specified conditions shown in Table 2. The reaction mixture was centrifuged (3000 rpm, 2 min), and the supernatant solution was separated. The residual solid was washed with solvents (acetone and toluene, each 2 mL) to extract adsorbed reactants and products. The supernatant solution and the washing were combined, and analyzed by GC and/or GC–MS. Identification of the products **3** was made by comparison with their GC retention times and GC–MS spectral patterns with those of the authentic samples. The conversion of **2** and the yield of the acylation product **3** were estimated by GC.

In the microwave reaction, the irradiation power was automatically adjusted so as to keep the reaction temperature. A typical profile of the changes in the temperature and the microwave irradiation power was shown in Fig. 1 for the reaction of **1a** with **2b** at 190 °C for 30 min. The temperature reached 190 °C for about 2.5 min. The irradiation power was 300 W (max power) for the initial 2.5 min, then decreased to about 50 W by 10 min, and gradually decreased to 30 W by 30 min with maintaining the temperature of 190 °C.

In an oil bath reaction also, a Pyrex glass tube with the same shape as that of the microwave reaction was used. The glass tube containing starting materials, a catalyst, AC, an internal standard, and a magnetic bar was immersed into an oil bath preheated at the specified temperature in Table 2, and heating was continued under stirring for the specified time. In a separate experiment, the rate of the temperature increase of the inside solution was checked by a thermometer. The time for increasing the temperature up to 190 °C was almost the same as that for the microwave reaction.

Experiments of the Arrhenius plots for the microwave and the oil bath reactions of **1a** with **2b** were carried out in the temperature

Table 1
Properties of commercial zeolites used in the acylation reaction.

Zeolite	Product code ^a	SiO ₂ /Al ₂ O ₃	BET surface area (m ² /g)	Na ₂ O (%)	LOI ^b (%)
H-Y (30)	CBV720	28	850	0.03	9.6
H-Y (60)	CBV760	55	910	0.02	9.2
H-Y (80)	CBV780	81	860	0.01	9.6
H-beta (25)	UOP-Beta	25	650	0.5	–
H-beta (40)	CP811C	40	700	<0.01	2.1
H-M (90)	CBV90A	89	570	<0.04	–
H-ZSM-5 (29)	HSZ-830HOA	29	360	<0.01	2.7
H-ZSM-5 (50)	CBV5525	58	460	<0.01	5.5

^a UOP-Beta: UOP, Ltd., HSZ-830HOA: Tosoh Co., Ltd., others: Zeolyst International.

^b Loss on ignition.

range of 160–200 °C. The kinetic constants *k* were derived by taking pseudo first-order kinetics for the carboxylic acid **2b**.

3. Results and discussion

3.1. Catalysts

The reaction of anisole **1a** with hexanoic acid **2a** proceeded at 190 °C in the presence of acidic zeolite catalyst under 2.45 GHz microwave irradiation to give a *para*-acylation product, 1-(4-methoxyphenyl)-1-hexanone (**3a**), along with water (Scheme 1,

Table 2). Survey of the catalyst activity revealed that some H-Y and H-beta zeolites gave relatively high yields for **3a** among the H-Y, H-beta, ZSM-5, and H-mordenite (H-M) zeolites (Fig. 2). H-Y zeolites with the SiO₂/Al₂O₃ ratios being 30:80 gave the best results, forming **3a** in good yields; 61.4% for H-Y (30), 61.7% for H-Y (60), and 57.8% for H-Y (80) (Runs 1–3). In addition to the H-Y zeolites, H-beta zeolites also provided **3a** in reasonably good yields, although the efficiency was lower than the H-Y catalysts; the yields of **3a** using H-beta zeolites were 49.6% (SiO₂/Al₂O₃ = 25) and 40.6% (40) (Runs 4 and 5). In these reactions, formation of small amounts (≤1.2%) of an isomeric product of **3a**, presumably the *ortho*-form

Table 2
Reactions of **1** with **2**.^a

Run	1	2	Catalyst	Method ^b	Temp. (°C)	3	Yield ^c (%)	
							3	Isomer
1	1a	2a	H-Y (30)	MW	190	3a	61.4	0.8
2	1a	2a	H-Y (60)	MW	190	3a	61.7	1.2
3	1a	2a	H-Y (80)	MW	190	3a	57.8	1.2
4	1a	2a	H-beta (25)	MW	190	3a	49.6	≤0.1
5	1a	2a	H-beta (40)	MW	190	3a	40.6	0.2
6	1a	2a	H-M (90)	MW	190	3a	17.2	≤0.1
7	1a	2a	H-ZSM-5 (29)	MW	190	3a	2.8	≤0.1
8	1a	2a	H-ZSM-5 (50)	MW	190	3a	17.6	≤0.1
9	1a	2a	H-Y (30)	OB	190	3a	17.2	0.4
10	1a	2a	H-Y (60)	OB	190	3a	32.5	0.5
11	1a	2a	H-Y (80)	OB	190	3a	19.5	0.6
12	1a	2a	H-beta (25)	OB	190	3a	17.5	≤0.1
13	1a	2a	H-beta (40)	OB	190	3a	28.1	≤0.1
14	1a	2a	H-M (90)	OB	190	3a	14.5	≤0.1
15	1a	2a	H-ZSM-5 (29)	OB	190	3a	2.4	≤0.1
16	1a	2a	H-ZSM-5 (50)	OB	190	3a	10.1	≤0.1
17	1a	2b	H-Y (60)	MW	190	3b	59.6	1.0
18 ^d	1a	2b	H-Y (60)	MW	190	3b	70.9	1.4
19	1a	2b	H-Y (60)	MW	200	3b	74.0	1.4
20	1a	2c	H-Y (60)	MW	190	3c	33.6	0.9
21	1a	2c	H-beta (40)	MW	190	3c	33.2	1.1
22	1a	2c	H-beta (40)	MW	210	3c	44.2	≤0.1
23	1a	2c	H-beta (40)	MW	230	3c	52.0	≤0.1
24 ^e	1a	2c	H-beta (40)	MW	210	3c	52.1	0.9
25	1b	2b	H-Y (30)	MW	190	3d	25.8	1.0
26	1b	2b	H-Y (60)	MW	230	3d	69.6	3.1
27	1b	2a	H-Y (60)	MW	230	3e	57.7	3.7
28 ^{e,f}	1c	2a	H-Y (30)	MW	190	3f	56.8	0.7
29 ^{e,f,g}	1c	2a	H-Y (30)	MW	190	3f	77.8	1.2
30	1a	2d	H-Y (30)	MW	190	3g	29.9	1.1
31	1a	2d	H-Y (30)	MW	230	3g	55.4	2.5
32	1a	2e	H-Y (30)	MW	190	3h	26.3	1.0
33	1a	2e	H-Y (30)	MW	230	3h	49.1	1.8
34	1a	2b	H-Y (60)	OB	190	3b	26.6	0.4
35	1b	2b	H-Y (60)	OB	230	3d	31.4	1.5
36	1b	2a	H-Y (60)	OB	230	3e	25.9	1.7

^a Reaction conditions: **1** 12.0 mmol, **2** 2.0 mmol, catalyst 100 mg, activated carbon (AC) 50 mg, 190–230 °C, 30 min.

^b MW: microwave, OB: oil bath.

^c Estimated by GC.

^d **1a** 24.0 mmol, **2b** 2.0 mmol.

^e 1,2-Dichlorobenzene (0.5 mL) was added.

^f **1c** 4.0 mmol, **2a** 2.0 mmol.

^g 120 min.

dominantly, as observed in the reaction of **1b** with acetic anhydride using solid acid catalysts [35].

In the acylation of benzene derivatives, the presence of alkoxy groups at the aromatic rings significantly promoted the reaction. Exchange of the methoxy group by methyl group resulted in much lower yield; toluene reacted with **2a** to form the corresponding ketone only in a low yield (3.8%) even at a high temperature of 230 °C. This suggested that the electron-donating nature of methyl group was not enough to undergo the present acylation reaction smoothly.

A heteroaromatic compound also underwent the acylation reaction. Thus, thiophene (**1c**) reacted with **2a** (2 equiv.) at 190 °C for 30 min in the presence of the H–Y (30) catalyst under microwave irradiation to form the acylated product, 1-(2-thienyl)-1-hexanone (**3f**), in 56.8% yield (Run 28). The yield was increased up to 77.8% by prolonging the reaction time to 120 min (Run 29). The regioselective acylation of **1c** by zeolite catalysts was previously reported in the reactions of butyryl chloride [36] and acetic anhydride [37].

Besides aliphatic carboxylic acids, aromatic acids also reacted with **1a** to give the corresponding diaryl ketones, although the reaction conditions have not been optimized. Thus, treatment of 4-methoxybenzoic acid (**2d**) with **1a** using the H–Y (30) catalyst at 190 °C provided a diaryl ketone **3g** in 29.9% yield (Run 30). Benzoic acid (**2e**) also reacted at 190 °C with **1a** to form the corresponding ketone **3h** in 26.3% yield (Run 32). The yields of **3g** and **3h** were improved to 55.4% and 49.1%, respectively, by raising the reaction temperature from 190 °C to 230 °C (Runs 31 and 33).

Since the zeolite catalyst was easily recovered by centrifugation, reuse of the catalyst was attempted in the reaction of **1a** with **2a** at 200 °C for 30 min using H–beta (25) catalyst. After the reaction was finished, the yield of **3a** was estimated at 51.8%. The catalyst was recovered by centrifugation, washed with acetone and toluene, and reactivated by heating at 500 °C for 5 h. When the reaction of **1a** with **2a** was carried out using the recovered catalyst, however, the yield of **3a** was 27.9%, which was lower than that obtained by the pristine catalyst, 51.8%, showing a significant decrease in the activity of the catalyst. In the present reaction using a batch-type closed vessel, the generated water did not go out of the reaction system, and might cause dealumination of the zeolite to reduce the catalyst acidity, as previously demonstrated by Timken et al. in the steam treatment of a H–beta zeolite (SiO₂/Al₂O₃ = 36) [38]. To reduce the effect of the generated water, a batch-type open system or a flow reaction system, which is able to remove the generated water continuously, may be better than the present closed system.

3.3. Comparison with external heating

As mentioned above for **3a** in Section 3.1, the reactions using external heating by oil bath in place of microwave irradiation significantly decreased the yields of other aromatic ketones **3** as well. Thus, the yield of **3b** in the reaction using oil bath was 26.6%, which was much lower than that obtained by microwave irradiation, 59.6% (Runs 17 and 34, Fig. 3). Similarly, in the reactions of **1b** also, the yields of **3d** and **3e** by oil bath heating were lower than those by microwave irradiation; the yields of **3d** and **3e** were respectively 31.4% and 25.9% (oil bath) and 69.6% and 57.7% (microwave) (Runs 26, 27, 35, and 36). This shows that microwave irradiation more effectively promotes the acylation reaction than the conventional oil bath heating.

In the microwave reaction, it seems important to know the degree of microwave absorption for the chemical materials in the reaction system. For transfer of microwave energy, the dielectric loss factor of the material is a key parameter; the calorific power (P) by microwave absorption is postulated to be proportional to the dielectric loss factor (ϵ''); $P = 2\pi f \epsilon_0 \epsilon'' E^2$, where f is the microwave frequency, ϵ_0 is the dielectric constant of vacuum, and E is the inten-

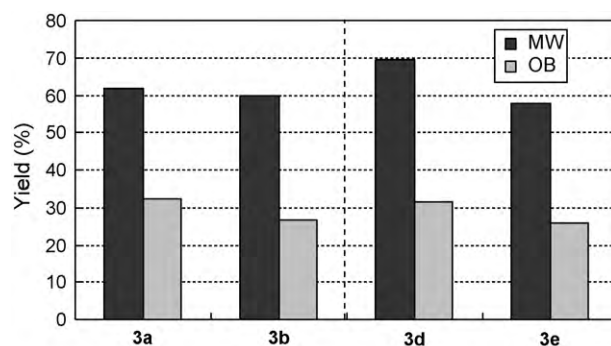


Fig. 3. Comparison of the yields between MW and OB heating in the reactions of **1a, b** with **2a, b** affording **3a, 3b** and **3d, 3e** (**1a**: 190 °C, 30 min; **1b**: 230 °C, 30 min).

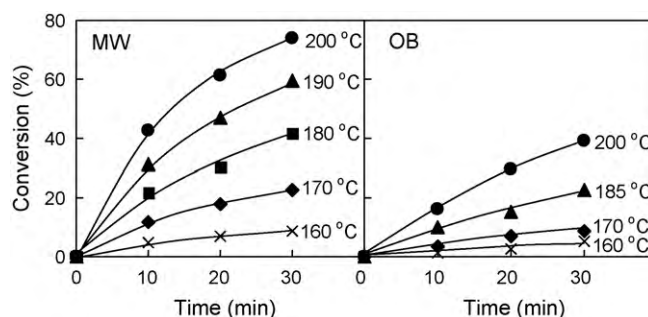


Fig. 4. Time dependency of the conversion of the carboxylic acid in the microwave (MW) and oil bath (OB) reactions of **1a** with **2b** using H–Y (60) catalyst in the range of 160–200 °C; the conversion was estimated on the basis of the yield of the acylated product.

sity of electric field [39]. In this sense, the dielectric properties of the starting compounds were analyzed by a perturbation method using a 2.45 GHz cylindrical cavity. As the results, aromatic compounds **1a** and **1b** exhibited relatively large values of the dielectric loss factors (0.289 and 1.007, respectively), while the values of the carboxylic acids **2a** and **2b** were moderate or small (0.135 and 0.071, respectively). The values of **1a** and **1b** were much larger than those of normal hydrocarbons such as toluene and hexane (0.012 and 0.0008, respectively). The large values of **1a** and **1b** indicate that starting aromatic compounds are suitable for absorbing microwave energy. In addition, the water, which is produced as a co-product in the acylation reaction, has a very large value of the dielectric loss factor, 10.1. Activation of water by microwave irradiation may lead to effective desorption of the water from the surface of the catalyst, resulting in acceleration of the acylation reaction. Bond et al. also provided a similar suggestion on the effect of microwave for desorption of water in the solid acid-catalyzed dehydrative acylation reaction [30].

In addition, to make a consideration from a kinetic view point for the microwave-assisted acylation reaction, the Arrhenius plots for the oil bath and the microwave reactions of **1a** with **2b** using H–Y (60) catalyst were derived on the basis of the kinetic data taken in the temperature range of 160–200 °C (Fig. 4, Table 3). Consequently, nearly straight lines were observed in both reactions (Fig. 5). Noteworthy is that the line of the microwave reaction is placed in a upper position with an almost parallel manner to the line of the oil bath reaction. The parallel location means that the activation energy of the microwave reaction is similar to that of the oil bath reaction; the estimated energy is 103.9 kJ/mol for the microwave reaction, which is close to the energy of the oil bath reaction, 102.4 kJ/mol. On the other hand, when the line of the microwave reaction was replotted by modifying the temperature with an increase of 17°, the simulated line was revealed to be close to the line of the oil bath

Table 3
Kinetic data in the reaction of **1a** with **2b**.^a

Method ^b	Temp. (K) [(°C)]	1/temp. (K ⁻¹)	Kinetic constant (k) ^c	ln(k)
MW	473 [200]	0.00211	0.0456	-3.09
MW	463 [190]	0.00216	0.0307	-3.48
MW	453 [180]	0.00221	0.0181	-4.01
MW	443 [170]	0.00226	0.0091	-4.70
MW	433 [160]	0.00231	0.0040	-5.52
OB	473 [200]	0.00211	0.0177	-4.03
OB	458 [185]	0.00218	0.0084	-4.78
OB	443 [170]	0.00226	0.0033	-5.71
OB	433 [160]	0.00231	0.0016	-6.44
MW ^d	490 [217]	0.00204	–	-3.09
MW ^d	480 [207]	0.00208	–	-3.42
MW ^d	470 [197]	0.00213	–	-4.01
MW ^d	460 [187]	0.00217	–	-4.70
MW ^d	450 [177]	0.00222	–	-5.52

^a Reaction conditions: **1a** 12.0 mmol, **2b** 2.0 mmol, H–Y (60) zeolite catalyst 100 mg, activated carbon (AC) 50 mg, 160–200 °C.

^b MW: microwave, OB: oil bath.

^c Kinetic constants (*k*) were estimated by taking a pseudo first-order approximation on the basis of the conversion of the carboxylic acid at the reaction times of 10, 20, and 30 min (Fig. 4); the value of *k* for each temperature was calculated as the gradient in the straight line passing through the origin of the coordinates in the graph of ln[100/(100 – conversion)] versus time.

^d The values of Temp. and 1/temp. were calculated by adding 17° to the temperatures in the microwave reaction, while the values of ln(*k*) were the same as those of the original data.

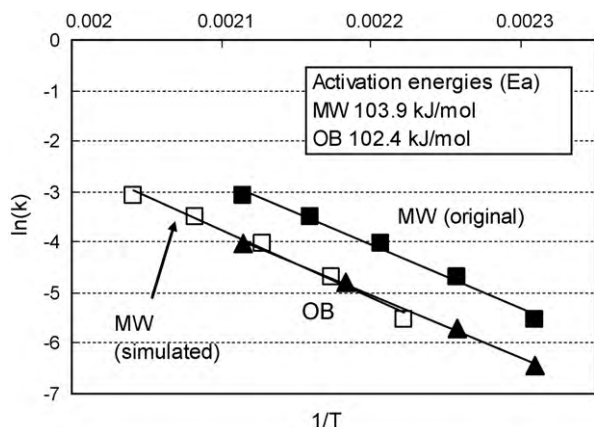


Fig. 5. Arrhenius plots for the microwave (MW, ■) and oil bath (OB, ▲) reactions of **1a** with **2b** using H–Y (60) catalyst in the range of 160–200 °C; the line of MW (simulated, □) was drawn by adding 17° to the temperatures of the MW reaction.

reaction. These results seem to suggest that (1) the reaction pathway by microwave heating is not so different from that by oil bath heating, but (2) the temperature of the catalyst active center in the microwave reaction may be higher than that in the oil bath reaction. Recently, Winé et al. also have provided an assumption that the temperature of the catalyst is higher than that of the solution in the microwave-assisted reaction of anisole with acetic anhydride or benzoyl chloride, catalyzed by a beta/SiC composite system [40]. Concerning the ability of microwave absorption, even if the zeolite catalyst is not a good absorber as a bulk form [40], there would be a possibility that the protic catalytic sites on the zeolite surface can absorb microwaves well because of their polar structures. This may provide an explanation on the increased reaction rate observed by microwave irradiation, although future investigation is necessary to evaluate the microwave absorption of the surface of the zeolite catalyst. On the other hand, heat-transfer is also an important key factor, and we have to think whether non-uniform temperature distribution really exists or not and, if it exists, whether the temperature of the catalytic sites is reasonably high enough to promote the acylation reaction. Although it is difficult to give confirmed ideas at the moment and further study is required to elucidate the origin of the microwave effect, we suppose that selective heating itself is a characteristic nature of microwave irradiation and would some-

how accelerate the catalytic process by specific activation of the catalyst, the reactant, and/or the product molecules in the reaction system.

4. Conclusion

Dehydrative acylation reactions of aromatic compounds (alkoxy unit-containing benzene derivatives, thiophene) with aliphatic and aromatic carboxylic acids smoothly proceeded in the presence of H–Y and H–beta zeolite catalysts under microwave irradiation. The microwave-assisted reactions generally gave higher yields than the conventional oil bath reactions. Further study on the development of efficient chemical reactions using solid acid catalysts and microwave irradiation is under way.

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