

In Situ Observation of Nonequilibrium Local Heating as an Origin of Special Effect of Microwave on Chemistry

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We successfully observed the phenomenon of “nonequilibrium local heating” occurring to the DMSO molecules in proximity of the Co particles under microwave irradiation by real-time in situ Raman spectroscopy. This phenomenon was induced only under microwave irradiation but not by conventional heating. This nonequilibrium local heating can be realized by the input of the power more rapid than that of the heat loss induced by the temperature difference between the heated microdomains and the surrounding domains. We have demonstrated the enhancement in the dehalogenation reaction of the C(sp³)–Cl bond of 2-chloroethylbenzene and 4-phenylbutyl chloride caused by the “nonequilibrium local heating” of the surface of the Co and/or Fe particles under microwave irradiation.

1. Introduction

Microwave-driven syntheses have been widely applied for obtaining organic molecules and materials for pharmaceuticals, opto-electronics, and electronics in the laboratory scale experiments, because microwave irradiation has been known to be an effective method for promoting effectively chemical reactions.^{1,2} Microwave effects^{1–12} observed as accelerated reaction rates, increased reaction yields, and controlled reaction selectivities in chemical reactions can at least partially be attributed to the characteristic heating modes through the interaction of oscillating electric and magnetic fields with the substances contained in the reaction systems. However, nobody has obtained a full understanding of microwave-driven chemistry yet. In order to apply microwave-driven chemistry to various chemical reactions, it is essential to understand the mechanism for the promotion of chemical reactions observed under microwave irradiation and to systematize the obtained knowledge as a microwave-driven chemistry. One of the most important characteristic heating modes should be “nonequilibrium local heating”, which has been suggested by some reports.¹² Sato et al. reported the thermally nonequilibrium state in a gas–solid system under microwave irradiation. However, no one obtained experimental evidence of the phenomenon of “nonequilibrium local heating” in a liquid–solid system. “Nonequilibrium local heating” is defined as the phenomenon of heating domains at much higher temperatures than a bulk solution temperature only induced under microwave irradiation. This phenomenon never occurs by conventional heating in principle. The phenomenon of “nonequilibrium local heating” seems to be less difficult for investigating directly and experi-

mentally than the other hypothesis raised before: the stabilization of the transition states in reactions by the interaction with an oscillating electric component proposed by Loupy et al.¹ as the polar mechanism, where increase of the polarity accompanied by the conformational conversion from the ground state toward the transition state results in an enhancement of reactivity by lowering the activation energy. Now, we have made up our minds to focus on observing “nonequilibrium local heating” and obtained experimental evidence of the phenomenon.

“Nonequilibrium local heating” can lead to microwave effects as accelerated reaction rates. The reaction rate constant is dependent on the two factors based on the Arrhenius reaction rate equation ($k = Ae^{-E_a/RT}$):^{1,2,6} the pre-exponential factor representing the frequency of the collisions between reacting molecules (A) and the exponential factor representing the fraction of the molecules that overcome the activation energy barrier ($e^{-E_a/RT}$). Judging from the second factor ($e^{-E_a/RT}$), molecules encountering “nonequilibrium local heating” would be expected to lead to increment of their reaction rates by 10–1000-fold. However, up until now, there had been no reports on direct observation to verify “nonequilibrium local heating”.

In order to observe “nonequilibrium local heating” under microwave irradiation, we have selected a heterogeneous system containing metal particles and an organic solvent for the following reasons: (1) Co particles as ferromagnetic metal having strong interaction with the magnetic field of microwave,^{13–16} (2) dimethylsulfoxide (DMSO) as a solvent for dispersing the particles. Our strategy is to in situ measure the temperatures of the DMSO molecules in proximity to the surface of the Co particles heated through the magnetic interaction with microwave. Furthermore, we have selected Raman scattering measurements^{17,18} as the most suitable method for in situ and real-time observation of “nonequilibrium local heating” occurring under microwave irradiation, because the DMSO molecules show strong Raman scattering which can be a probe for measuring the temperatures of the molecules.

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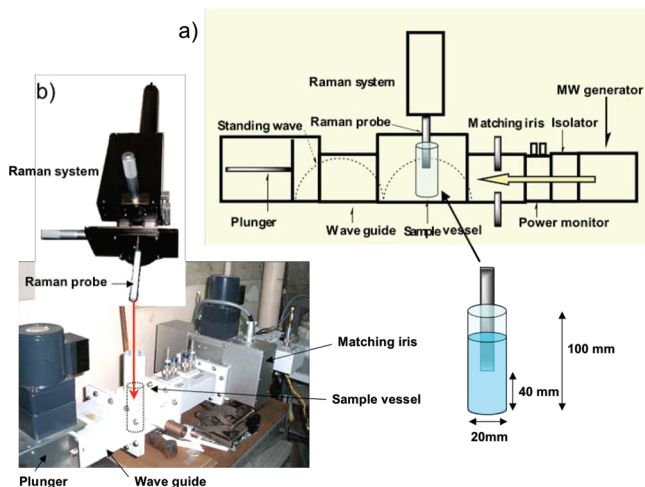


Figure 1. Single-mode microwave apparatus and in situ Raman system. Schematic illustration (a) and photo (b) of the experimental single-mode microwave apparatus equipped with a microwave generator, an isolator, a power monitor, a matching iris, a plunger, and an experimental Raman system equipped with the Raman probe. A standing wave of microwave was tuned by the matching iris and the plunger. A cylindrical sample vessel (20 mm in diameter and 100 mm in height) was placed in a single-mode cavity installed at the middle of the waveguide, as shown in part a. The plunger and the matching iris were placed at the extreme end of the waveguide and at the input side, respectively. The Raman probe was set to the sample vessel and was located at the center position of the vessel and at a height of 60 mm from the bottom of the vessel. The sample vessel was located in a single-mode cavity under the well controlled magnetic (H) fields. MW heating was performed at the constant input power (P_F : 150 W) and the reverse power (P_R : 60–80 W) monitored by the power monitor.

Here, in order to demonstrate the enhancement in the chemical reaction caused by the “nonequilibrium local heating”, we have constructed a heterogeneous reaction system containing the ferromagnetic metal particles such as Co and Fe. Dispersed ferromagnetic particles should act as an electron donor and/or a catalyst and provide with their surface as a reaction field.

In this paper, we report the observation of “nonequilibrium local heating” occurring to the DMSO molecules in proximity of the Co particles under microwave irradiation probed by real-time in situ Raman scattering measurements. Furthermore, we have demonstrated the enhancement in the dehalogenation reaction of the $C(sp^3)$ –Cl bond of 2-chloroethylbenzene and 4-phenylbutyl chloride caused by the “nonequilibrium local heating” of the surface of the Co and/or Fe particles under microwave irradiation.

2. Experimental Section

2.1. Material. DMSO was purchased from Aldrich Co., USA. 2-Chloroethylbenzene and 4-phenylbutyl chloride were purchased from Tokyo Chemical Industry. Fe (av. 150 μm), Fe_3O_4 (av. 45 μm), Fe_2O_3 (av. 45 μm), and Co (0.1–3.0 μm) particles were purchased from Kishida Chemical Co., Ltd. CoO (50–75 μm) and NiO (av. 3 μm) particles were purchased from Wako Pure Chemical Industry Co., Ltd. Ni (av. 3 μm) and FeO (4–40 μm) particles were purchased from Aldrich Co., Ltd. and TERADA CHEMISCHE FABRIK, respectively.

2.2. Experimental Setup for In Situ Raman Scattering Measurement under Microwave Irradiation. A microwave apparatus MMG-213VP (Micro Denshi Co., Ltd., 1500 W, 2.45 GHz) equipped with a single-mode cavity was used (Figure 1). A sample vessel made of polytetrafluoroethylene was located

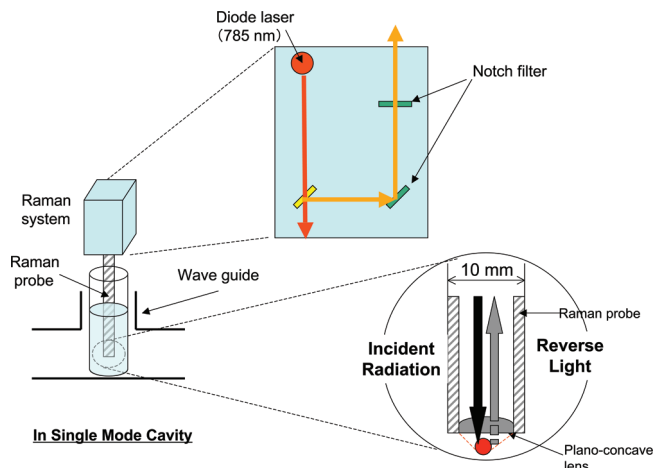


Figure 2. Experimental setup for in situ observation of Raman spectroscopy.

in the maximum magnetic field position in the single-mode cavity. The position of the maximum magnetic field was determined by using a network analyzer (R3767CG, ADVANTEST). We used a Raman spectrometer equipped with a probe and a personal computer. Excitation light generated by a single-mode diode laser (785 nm, 120 mW) was led on the sample through the optical tube and the Raman probe (Figure 2). The laser beam for Raman scattering was focused to 10–20 μm by a lens located at the top of the probe (Figure S1, Supporting Information). The Raman scattered light collected by the lens was passed through the two super notch filters (centered at 785 nm) and focused onto the entrance slit of the Raman spectrometer with the 300 grooves/mm grating (Optometrics Inc.) and a CCD sensor (CCD-30-11, Marconi Applied Technologies Ltd.). Cobalt particles (2.3 g) were introduced in DMSO (15 mL) in the vessel and heated by microwave irradiation for the Raman measurements. Co particles having a small size ($\approx 0.1 \mu\text{m}$) were dispersed in DMSO without stirring, while those of the large size sank to the bottom of the vessel. The probe was inserted into the vessel containing the Co particle dispersion in DMSO. The temperature of the bulk solution was measured with the fiber-optic thermometer inserted directly into the solution (AMOTH TM-5886, Anritsu Meter Co., Ltd.). The Raman spectra of DMSO were collected in the range from -2000 to 2000 cm^{-1} at 0.25 s intervals.

2.3. Apparatus for Microwave-Assisted Chemical Reactions. A focused, single-mode microwave synthesis system (Discover CEM, USA, 2.45 GHz) was used for the chemical reactions. The reaction mixture was stirred using a magnetic stirrer. The temperature of the bulk solution was monitored using an IR sensor in the microwave system, and the validity of the measured temperature was confirmed using a fiber optic thermometer (AMOTH TM-5886, Anritsu Meter Co., Ltd.).

2.4. Measurement. UV–vis spectra were recorded on a JASCO V-570 spectrophotometer in the 200–800 nm spectral range. IR spectra were recorded using a PERKIN ELMER System 2000 FT-IR (Fourier transform infrared spectroscopy) (KBr disk). Gas chromatography was performed using a Shimadzu GC 14A. ^1H NMR spectra were recorded on Joel JNM-GSX-400 spectrometer.

3. Results and Discussion

3.1. In Situ Observation of Nonequilibrium Local Heating. The first point to be discussed should be the validity of the temperatures determined using the in situ Raman scattering

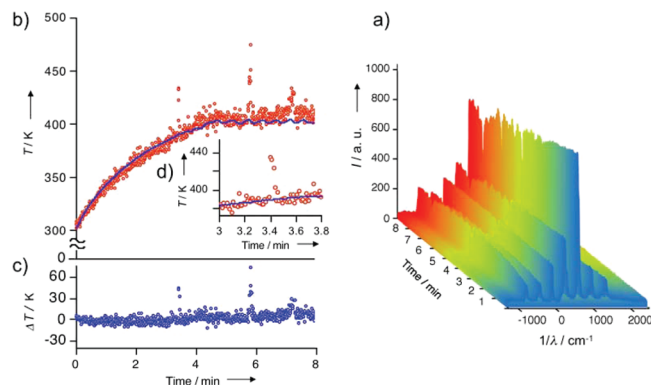


Figure 3. Nonequilibrium local heating induced by microwave irradiation. (a) Time-dependent Raman spectra of DMSO heated by microwave irradiation at 0.25 s intervals for 8 min in the temperature range 300–500 K. (b) T_r (temperatures determined by the intensity ratios of Stokes to anti-Stokes lines using in situ Raman scattering measurements) (red circles) and T_f (temperatures monitored by the fiber-optical thermometer) (blue line) vs t (time) plot. (c) ΔT ($\Delta T = T_r - T_f$) vs t (time) plot. (d) Enlarged view of Figure 3b in the range 3.0–3.8 min.

measurements in our system. In order to prove the validity, we examined the temperatures (T_r) of DMSO determined by Raman spectroscopy and the temperatures (T_f) monitored by the fiber-optic thermometer using silicon oil heated in an oil bath under precise control of the temperatures, as shown in Figure S2 in the Supporting Information. As shown in Figure S2 and SI-text 1 in the Supporting Information, we could determine the precise temperatures of the region (10–20 μm) of the Raman probe for the signal collection by the intensity ratios of Stokes and anti-Stokes lines by the real-time in situ Raman spectroscopy in our system.

Here, we attempted to measure the temperatures of DMSO by Raman spectroscopy under microwave irradiation in order to observe the phenomenon “nonequilibrium local heating”. Figure 3a shows the Raman spectra continuously collected for DMSO heated by microwave irradiation at 0.25 s intervals in the temperature range 300–500 K. As shown in Figure 3a, those Raman intensities were large enough to determine the temperatures.

The T_r and T_f vs t (time) plots are shown in Figure 3b and c. Interestingly, several spikes were observed in the measured temperatures determined by the Raman spectra, indicating the occurrence of abnormally high temperatures at 3.4 min (433 K), 5.8 min (473 K), and 7.3 min (423 K). The determined temperatures at these points were much higher than the bulk temperatures monitored by the fiber-optic thermometer. It should be especially emphasized that the determined temperature at 5.8 min was 473 K, which was above the boiling point of DMSO (bp 462 K). In order to confirm the validity of these plots, the Raman spectra at 3.4, 5.8, and 7.3 min were checked (Figure S3, Supporting Information). As shown in Figure S3 of the Supporting Information, the intensities of the Raman peaks were large enough to reasonably determine the temperatures.

Yoshikawa et al.¹⁴ have reported the heating behavior of ferromagnetic particles such as Ni, Co, and Fe in a single-mode microwave applicator under the well controlled electric (E) and magnetic (H) fields. They have demonstrated that the ferromagnetic metal particles were heated efficiently at the position of the large magnetic field due to the magnetic loss and the eddy current loss mechanism.^{14–16} In the case of our heterogeneous system (DMSO/Co), the solvent (DMSO) was directly heated by dielectric loss and the ferromagnetic metal particles (Co) were directly heated

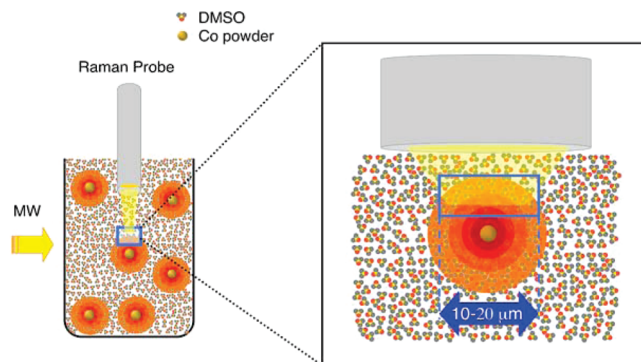


Figure 4. Image of “nonequilibrium local heating”, which is defined as the phenomenon of heating domains at much higher temperatures than a bulk solution temperature induced under microwave irradiation. The laser beam for Raman scattering was focused to 10–20 μm .

mainly by magnetic loss under microwave irradiation. The Co particles must have been heated efficiently because the sample vessel was located in the maximum magnetic field position in the single-mode cavity under microwave irradiation. The temperature of the DMSO solvent should be heated both by the dielectric loss of the DMSO and by the heat transfer from the Co particles to the DMSO solvent. When the power of the microwave was large enough, a thermal nonequilibrium state was achieved between the microwave energy input and the heat transfer around the Co particles. This thermal nonequilibrium state led to the abnormal phenomenon of “nonequilibrium local heating”, as shown in Figure 3b.

We have successfully observed the phenomenon of “nonequilibrium local heating”, which is defined as the phenomenon of heating domains at much higher temperatures than a bulk solution temperature only induced under microwave irradiation. This phenomenon can be observed only under microwave irradiation but not by conventional heating.

However, the “nonequilibrium local heating” phenomenon could not be observed continuously in these measurements. The temperature difference should be induced between the bottom and the other parts in the solution by the selective heating of Co particles that sank to the bottom. The heat convection induced by this temperature difference should drive the Co particles under microwave irradiation. Therefore, we could observe the “nonequilibrium local heating” phenomenon only when the Co particles were driven into the region (10–20 μm) of the Raman probe for the signal collection by the heat convection (Figure 4). Figure 3d shows the enlarged view of Figure 3b in the range 3.0–3.8 min. The time span estimated by the half width of the peak at 3.4 min was 1.0–1.5 s. Only when the Co particles were driven to the region (10–20 μm) of the Raman probe for the signal collection by the heat convection, we must have observed the high temperature phenomenon of the DMSO molecules. Therefore, the time span should be the time for the Co particles to stay in the region of the Raman probe for signal collection.

3.2. Microwave Special Effect Induced by Nonequilibrium Local Heating for Chemical Reaction. 3.2.1. Construction of Reaction System. The transition-metal-catalyzed dehalogenation reaction is an important protocol in organic syntheses^{19–28} (see SI-text 2 in the Supporting Information).

Our selected reactions would be a model to demonstrate the enhancement in the chemical reaction caused by the “nonequilibrium local heating”. In our report, we focused on the “nonequilibrium local heating” as an origin of the microwave effects. In order to demonstrate the enhancement in the chemical

TABLE 1: Reductive Dehalogenation Conversion of 2-Chloroethylbenzene^a

entry	M	temperature ^b (K)	power ^b (W)	conversion ^c (%)	max temp. (K)
1		523	300	0	450
2	Fe	523	250	100	523
3	Co	523	300	56	507
4	Ni	523	300	41	523
5	Fe ₃ O ₄	523	250	100	474
6	FeO	523	250	100	490
7	Fe ₂ O ₃	523	250	0	458
8 ^d	Fe	523		0	523

^a Reaction condition under microwave irradiation (ramp time + hold time: 20 min). ^b Preset temperature and set power. ^c Products were analyzed using FT-IR and gas chromatography. ^d Conventional heating (ramp time + hold time: 25 min).

reaction caused by the “nonequilibrium local heating”, we have constructed a heterogeneous reaction system containing the ferromagnetic metal particles, which can be extensively heated through the interaction with microwaves. A selected reaction system is a heterogeneous dehalogenation of the C(sp³)–Cl bond of 2-chloroethylbenzene and 4-phenylbutyl chloride with Co and Fe particles functioning as an electron donor and/or a catalyst under microwave irradiation. This selected system has enabled us to demonstrate that the dehalogenation reactions on the surface of the particles were accelerated under microwave irradiation compared to conventional heating conditions even at the same reaction temperatures.

3.2.2. Reductive Dehalogenation of 2-Chloroethylbenzene.

We first examined the reaction performance of an iron particle during dehalogenation of 2-chloroethylbenzene at 523 K. In this reaction, decaline was used as a solvent. The reaction was allowed to proceed for 20 min under microwave irradiation (3 min of heating to the desired temperature and 17 min at constant temperature). 2-Chloroethylbenzene (0.1 g), decaline (1.9 g) (bp of *trans*-decaline is 460 K and *cis*-decaline is 468 K), and iron particles (0.3 g) were combined in a microwave vial under an inert nitrogen atmosphere. The reaction mixture was irradiated in a CEM Discover microwave synthesizer with stirring. The microwave power was set at 250 W. The products were analyzed using FT-IR and gas chromatography. In this system, dehalo-

genaion using Fe particles (entry 2, Table 1) proceeded smoothly with 100% conversion. 2-Chloroethylbenzene was converted to ethylbenzene and 1,4-diphenylbutane in a decalin solution under microwave irradiation, as shown in Figure 5. For the conventional method, the oil bath was preheated to 523 K and the reaction time was 25 min (5 min of heating to the desired temperature and 20 min at constant temperature). Unlike the results obtained using the microwave reaction system, conventional heating did not yield any product (0% yield) (entry 8). After conventional heating for an extended period of time (120 min), the conversion efficiency was 30%.

The preset temperature, set power, conversion rate, and maximum temperature of each sample are listed in Table 1, and the temperature profiles are shown in Figure S4 and SI-text 3 in the Supporting Information. Without a metal particle, the conversion rate was 0% (entry 1). In the case of Co and Ni particles, 20 min of microwave irradiation led to dehalogenation with 56 and 41% conversion, respectively (entries 3 and 4). The conversion efficiencies for the Co and Ni particle systems were less than that of the Fe particle system. The set microwave power (300 W) for the Co and Ni particle system was greater than that of the Fe particle system. These results indicate that the Fe particle system was more effective than either the Co or Ni particle system.

In the case of the iron oxide particle systems, dehalogenation using either a Fe₃O₄ or FeO particle (entries 5 and 6) proceeded smoothly with 100% conversion for 20 min under microwave irradiation, while dehalogenation using the Fe₂O₃ particles (entry 7) gave an unsatisfactory result (0%), as shown in Table 1. Fe(III) did not show any reducing ability owing to its high oxidative state, while iron species having lower oxidative state, Fe(II) and Fe(0), gave reducing products. These results indicate that the primary determinant of dehalogenation efficiency is the reducing capacity of the metal particle.

To confirm the dehalogenation mechanism, we measured the UV–vis spectra of decaline, 2-chloroethylbenzene, and the product dehalogenated under microwave irradiation with either the Fe or Co particle, as shown in Figure 6. After dehalogenation, the color of the reaction solution turned yellow (M = Fe) or blue (M = Co). After methanol extraction, the absorption spectra of the solutions were measured. The absorption peak

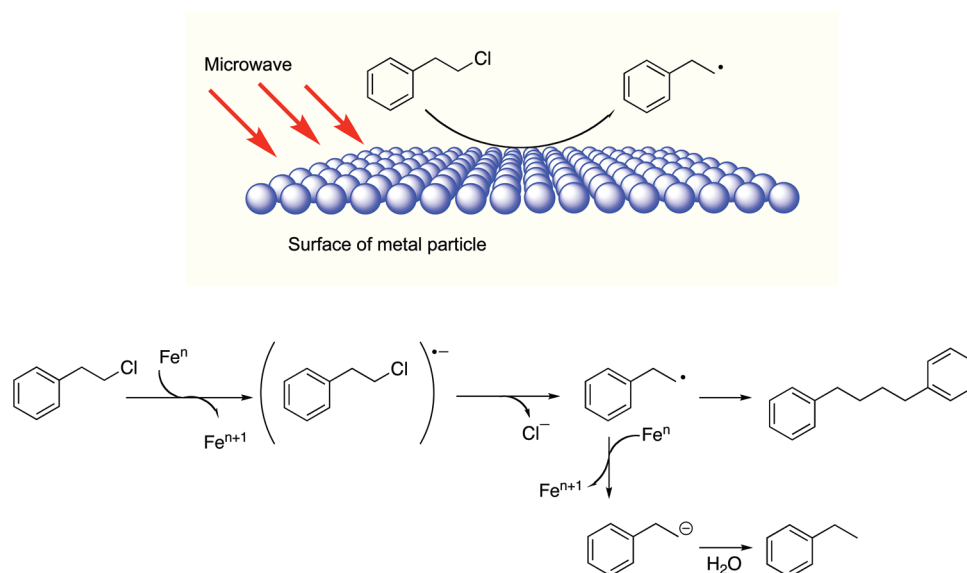


Figure 5. Plausible mechanism of reductive dehalogenation of 2-chloroethylbenzene in the presence of metal particles under microwave irradiation.

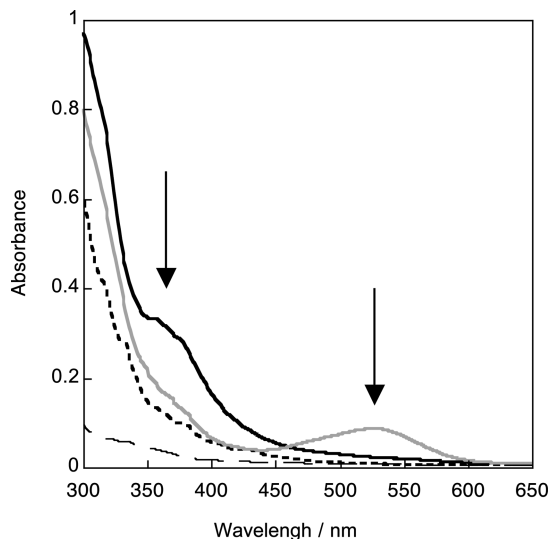


Figure 6. UV-vis spectra of decaline (broken line), 2-chloroethylbenzene (dotted line), and the product dehalogenated under microwave irradiation with either the Fe (solid line) or Co (gray line) particle.

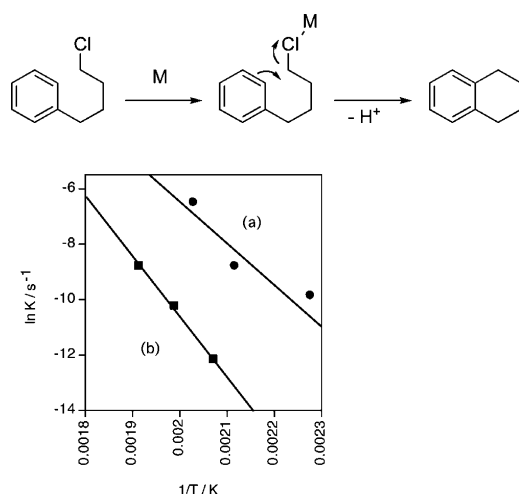


Figure 7. Plausible mechanism of the dehalogenation reaction of the C(sp³)–Cl bond of 4-phenylbutyl chloride and Arrhenius plots for the dehalogenation reaction of 4-phenylbutyl chloride of (a) the microwave system and (b) conventional system.

around 350–400 nm ($M = \text{Fe}$) was assigned to the d–d absorption of Fe^{2+} ions, and the absorption peak around 560 nm ($M = \text{Co}$) was assigned to the d–d absorption of Co^{2+} ions. Furthermore, the measured absorption intensities of the solutions were highly consistent with the absorption intensities estimated from dehalogenation conversion using either the Fe or Co particle system. These results indicate that the color change resulted from reductive dehalogenation using metal particles. Consequently, we have successfully demonstrated the enhancement of the reaction efficiency in the reductive dehalogenation reaction of the C(sp³)–Cl bond of 2-chloroethylbenzene under microwave.

3.2.3. Dehalogenation of 4-Phenylbutyl Chloride. When we examined 4-phenylbutyl chloride as a homologue of 2-chloroethylbenzene, the cyclic compound (1,2,3,4-tetrahydronaphthalene) was unexpectedly obtained. In this case, the transformation was not reduction but Friedel–Crafts type reaction, as shown in Figure 7. We can postulate that the loaded metal activates the C–Cl bond as a Lewis acid and intermolecular cyclization gives the product. This result prompted us to compare the activation energy of the microwave method with that of the

conventional method, because it was a simple reaction system with no byproduct, irreversible, and a first-order reaction.

At first, we examined the reaction performance of an iron particle for dehalogenation of 4-phenylbutyl chloride. In this reaction, decaline was used as a solvent. 4-Phenylbutyl chloride was converted to 1,2,3,4-tetrahydronaphthalene in a decaline solution, and the reaction time was 30 min (3 min of heating to the desired temperature and 27 min at constant temperature) with a CEM Discover microwave synthesizer. 4-Phenylbutyl chloride (0.1 g), decaline (1.9 g), and iron particles (0.3 g) were combined in a microwave vial under an inert nitrogen atmosphere. The products were analyzed using FT-IR, gas chromatography, and ¹H NMR. In this system, dehalogenation using Fe particles proceeded with 27.4% conversion at 473 K for 30 min under microwave irradiation. For the conventional method, the oil bath was preheated to 483 K and the reaction time was 35 min (5 min of heating to the desired temperature and 30 min at constant temperature). Unlike the results obtained using the microwave reaction system, conventional heating did not yield any product (0% yield).

3.2.4. Calculation of Activation Energy for Dehalogenation of 4-Phenylbutyl Chloride. Arrhenius plots for the conventional heating system and the microwave system are presented in Figure 7. From the slope of the lines in Figure 7, we obtained an activation energy ($E_a(\text{CH})$) of 178 kJ/mol for dehalogenation of 4-phenylbutyl chloride of the conventional system. The pre-exponential factor (A) from the y-intercepts was $\ln(A) = 32$.

In the case of the microwave system, dispersed Fe particles should act as a catalyst and provide with their surface as a reaction field. The Fe particles must have been heated selectively due to the large magnetic loss of the ferromagnetic metal particles resulting in the nonequilibrium local heating under microwave irradiation. The surface of the Fe particles must have provided with the heated surface at much higher temperature than a bulk temperature as the reaction field under microwave irradiation. Thus, in order to calculate the precise activation energy for the microwave system, we have to obtain the precise temperature of the reaction field. However, it is difficult to obtain the reaction field temperature continuously, as discussed in this Article. Here, calculating the activation energy from the bulk solution temperature monitored using an IR sensor, we obtained an activation energy ($E_a(\text{MW})$) of 154 kJ/mol ($\ln(A) = 31$) from the slope of the line in Figure 7 for the microwave system. Estimating from the difference of the activation energy ($\Delta E_a = 24$ kJ/mol) in this dehalogenation reaction, the reaction field temperature for the microwave system can be estimated to be 55 K higher than the bulk solution temperature (473 K) under microwave irradiation. Thus, one special effect of microwave irradiation on chemical reactions has been revealed leading to accelerating reaction rates.

Conclusions

We successfully observed the phenomenon of “nonequilibrium local heating” occurring to the DMSO molecules in proximity of the Co particles under microwave irradiation by real-time in situ Raman spectroscopy. This phenomenon was caused only under microwave irradiation but not by conventional heating. Furthermore, we have successfully demonstrated the enhancement in the dehalogenation reaction of the C(sp³)–Cl bond of 2-chloroethylbenzene and 4-phenylbutyl chloride caused by the “nonequilibrium local heating” of the surface of the Co particles under microwave irradiation. It must be inferred from these results that the phenomenon is an origin of “special effects of microwave on chemical reactions”. The elucidation of

“nonequilibrium local heating” would open up a new field of microwave-driven chemistry.

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Supporting Information Available: Figures showing the temperature detecting range of the Raman probe and the fiber-optical thermometer, Raman spectra, and temperature profiles and descriptions of the validity of the temperatures determined using the in situ Raman scattering measurements, the details about refs 19–28, and the differences of the temperature profiles under microwave irradiation with metal and metal oxide particles among the samples of dehalogenation of 2-chloroethylbenzene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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