

Effects of Microwave Irradiation on Activation Energy and Reaction Rate of Synthesis of Dodecylmethyldihydroxyethyl Ammonium Bromide

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Abstract. The reaction kinetics of the synthesis of quaternary ammonium salt under two sets of different reaction conditions, including microwave irradiation condition and conventional heating condition, were studied. In order to make sure that the microwave would not be interrupted, the reaction temperature was maintained at the boiling point of reaction solvents. The results showed that the reaction was a first-order reaction under both set of conditions and microwave irradiation changed the value of the activation energy of the reaction, indicating a change in the reaction mechanism. The activation energy was 41.44 kJ/mol under microwave irradiation condition, and 61.21 kJ/mol under conventional condition.

Introduction

Microwave irradiation has become a widely used technique in chemical reaction engineering. The irradiation not only significantly speeds up chemical reactions from hours or days to minutes but also enables “new” chemistry. In many studies, microwave has been shown to lead to dramatically reduced reaction times, increased product yields and enhanced product purities by reducing unwanted side reactions when compared to the case of conventional method of heating.

However, the exact reasons why and how microwaves enhance the chemical reaction processes are still not fully understood. Several researchers have speculated on the existence of the so-called “non-thermal effects”. Such non-thermal effects could be the consequence of specific electromagnetic wave - material interactions, leading to a decrease in the activation energy or an increase in the pre-exponential factor in the Arrhenius law due to the orientation effects of polar species in an electromagnetic field. Other researchers strictly denounced the existence of non-thermal effects. The effect of microwave irradiation in chemical reactions is a combination of thermal effects, hot-spots and selective heating [1-4]. Therefore, there is an urgent need to address the question of microwave effects. This is even more important if this technology is to move from small scale laboratory work to pilot- or production-scale instrumentation.

In the study of the microwave effect, the commonly used method is contrastive analysis of the different effects by microwave irradiation and conventional heating [5-9]. To elucidate the influence of microwave irradiation on chemical reactions kinetics, a few conditions should be carefully controlled and measured [10]. In addition, based on the characteristics of microwave reactor, when the system temperature attains the set point temperature, the temperature automatic control system will cut the microwave power source off. In this case, the microwave cannot effect on the reaction system continuously, and the reaction was effected by the temperature not by the microwave.

In this paper, a quaternary ammonium salt synthesis reaction was carried out at the boiling point temperatures of the reaction solvent mixtures. The reaction temperature was controlled by changing the ratio of solvents to make sure that the microwave irradiation was uninterrupted. The activation energy of the chemical reaction was obtained under the traditional heating and microwave conditions. The research results provided some evidence for the existence of the non-thermal effects.

Experimental

The experimental procedure was as follows: 2.39 g (0.01 mol) N-Methyldiethanolamine (MDEA) and 4.98g (0.01 mol) bromododecane were placed in a round bottomed flask, adding 10 ml solvent (methanol and n-butanol). According to the different ratios of methanol and n-butanol, the reaction was conducted at 371K, 381K, 391K and 401K. All experiments were performed under temperature control (1 °C accuracy) with invariable microwave power of 600 W for a period of 40 min. In order to investigate the kinetics of the reaction, the concentrations of MDEA were determined by using the method of chemical titration. Comparison experiments were carried out under the conventional conditions.

Results

The relationship between the concentration of MDEA and time under conventional condition (A) and under microwave condition (B) at given temperature is depicted in Fig. 1. All the conversion curves for both conventional and microwave conditions were similar in shapes.

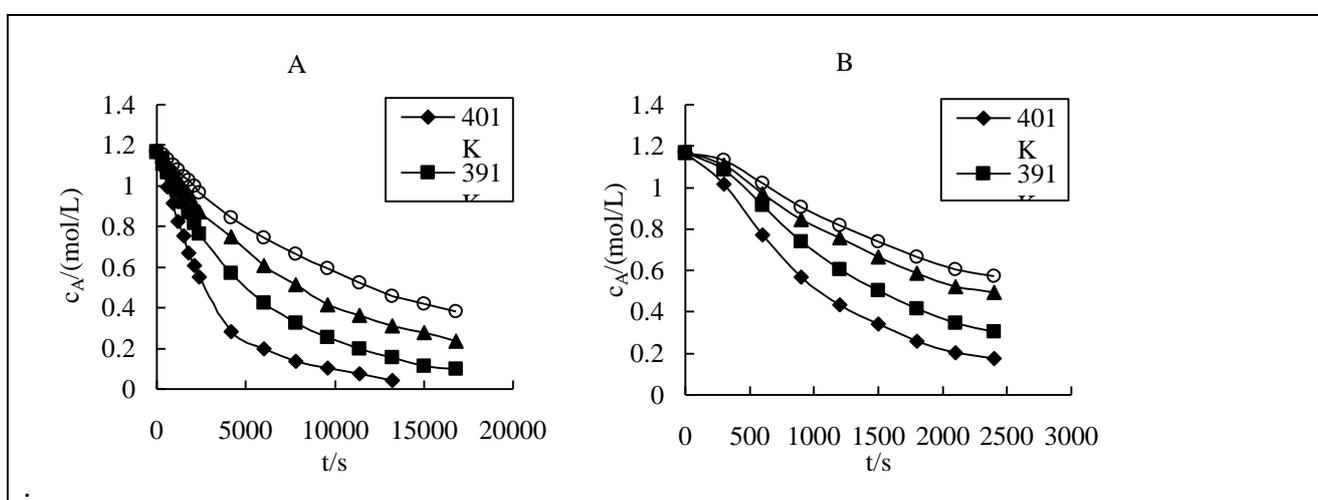


Fig. 1 Dependence of c_A upon t under (A) conventional conditions and (B) microwave conditions

To determine the order of the reaction, the following n th-order reaction rate equation was used:

$$-\frac{dc_A}{dt} = kc_A^n \quad (1)$$

By taking the logarithm of Eq. (1) and by using differential method of analysis of data on reactant concentration variations with time, we obtain:

$$\ln\left(-\frac{dc_A}{dt}\right) = \ln k + n \ln c_A \quad (2)$$

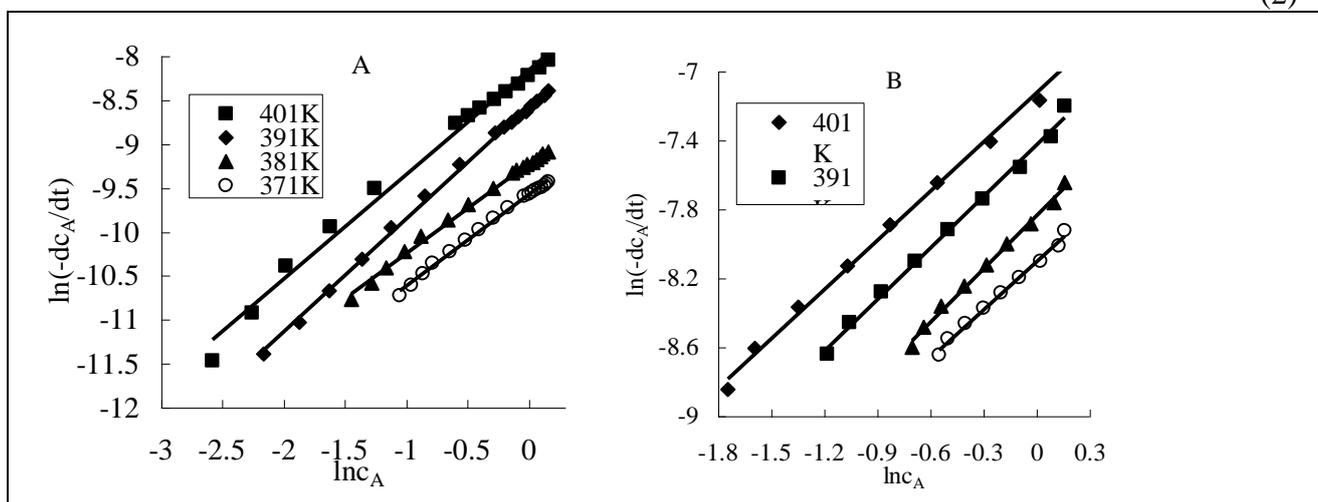


Fig. 2 Dependence of $\ln(-dc_A/dt)$ on $\ln c_A$ under (A) conventional condition and (B) microwave condition

Eq. (2) is a linear equation which enables the determination of the kinetic parameters of the reaction, i.e., the rate constant of the reaction (k), and the order of the reaction (n). In Fig.2, the linear dependence of the function $\ln(-dc_A/dt)$ vs $\ln(c_A)$ is observed, where the reaction order is determined from the slope, and the value of k is determined from the intercept. According to the results shown, one can see that the reaction was first order. The $\ln k$ values under different temperature are given in Table 1 below.

Table 1 $\ln k$ values at different temperatures under conventional condition and microwave conditions

Temperature K	Microwave process	Conventional process
401	-7.1322	-8.143
391	-7.4221	-8.5598
381	-7.8328	-9.2159
371	-8.1121	-9.5742

According to the Arrhenius expression $k = k_0 \exp(-\Delta E_a/RT)$, we obtain $\ln k = \ln k_0 - E_a/RT$ by taking the natural logarithm. The activation energy of the reaction can be determined by the slope of the plot $\ln k$ versus $1/T$, which is shown in Fig. 3. The activation energy for the reaction under microwave condition was $E_a=41.44$ kJ/mol, which is 1.5 times lower than the E_a of the process under conventional condition ($E_a=61.21$ kJ/mol). This indicated that the proportion of activated molecules in the microwave process was more than that with conventional heating. Therefore, the non-thermal effects existed in microwave irradiated reaction.

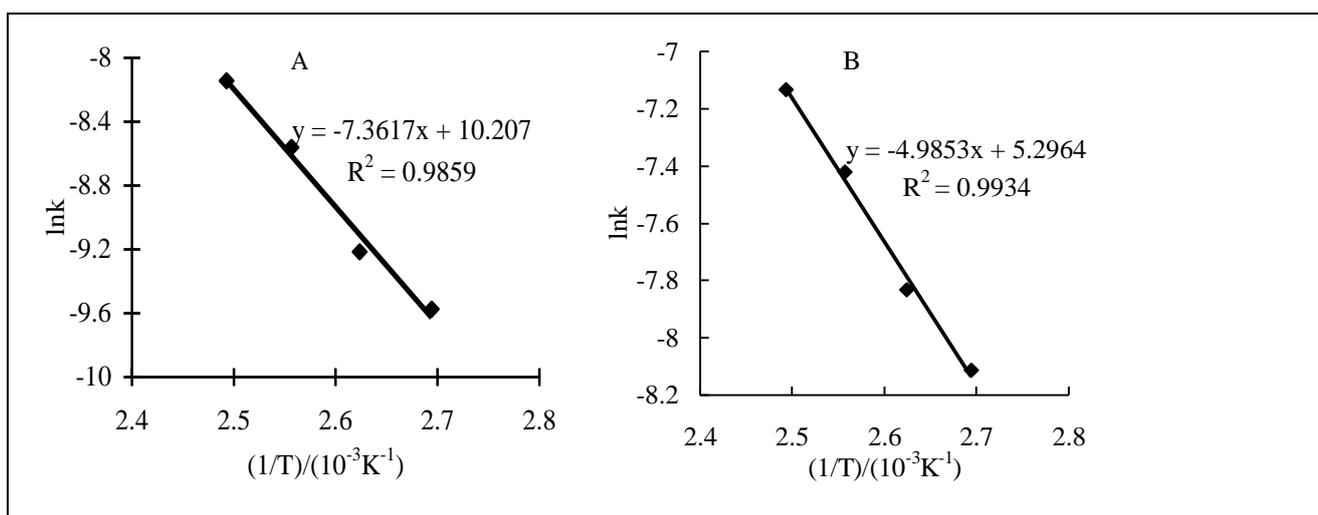


Fig. 3 The plot of $\ln k$ VS $1/T$ under (A) conventional condition and (B) microwave condition

The changes of the reaction rates under microwave reaction condition were compared to those under conventional condition. The relative increase of reaction rates between microwave condition and conventional condition were calculated to show the effect of the reaction rate under the microwave. It was observed that the shorter the reaction time, the higher the relative increase of reaction rates. In addition, the relative increase of reaction rates increased with a decreasing temperature. The reason for this result is that when the concentration of reactants was higher, molecular density of reactant per

unit volume was higher. Therefore, the effective collision between reactants under microwave irradiation was more vigorous. It was also observed that the effect of microwave was more significant at a low temperature than at a high temperature. In addition, the activation frequency of molecules was higher at a high temperature than at a low temperature. When the reaction temperature was lower, activation frequency of molecules was lower and the effect of the reaction rate under microwave was more significant.

Conclusions

Reaction kinetics including the order of reaction and apparent activation energy were determined. The activation energy for the reaction under microwave condition was 41.44 kJ/mol, which was 1.5 times lower than that of the reaction under conventional condition (61.21 kJ/mol). The results showed that the reaction rate was enhanced under microwave irradiation. This indicated that the microwave irradiation may have changed the mechanisms of the reaction. The relative increase of reaction rates between microwave condition and conventional condition was also determined. Further comparative investigations may shed light on the specific nature of the effects of microwave irradiation.

References

- [1] C.O. Kappe, A. Stadler, *Microwaves in organic and medicinal chemistry*, Weinheim: Wiley, (2005).
- [2] K. Huang, X. Yang, The research progress on the non-heat effects of microwave reaction, *Dev. Reprod. Sci.* 3 (2006) 273-279.
- [3] S. Horikoshi, T. Hamamura, M. Kajitani. Green chemistry with a novel 5.8GHz microwave apparatus. Prompt one-pot solvent-free synthesis of a major ionic liquid: the 1-Butyl-3-methylimidazolium tetrafluoroborate system. *Org. Process Res. Dev.* 12 (2008) 1089-1093.
- [4] S. Kalhori, B. Minaev, S. Stone Elander, Quantum chemical model of an S_N2 reaction in a microwave field, *Phys. Chem. A* 106 (2002) 8516-8524.
- [5] A.K. Bose, M.S. Manhas, M. Ghosh. Highly accelerated reactions in a microwave oven: synthesis of heterocycles, *Heterocycles.* (1991) 742-749.
- [6] S.J. Haswell, N. Howarth. Perturbation of a solid phase separation process by a non-thermal microwave effect, *Analytica Chimica Acta.* 387 (1999) 113-120.
- [7] H. Xia, J. Peng, H. Niu. Non-isothermal microwave leaching kinetics and absorption characteristics of primary titanium-rich materials, *Transaction of nonferrous metals society of China.* 20 (2010) 721-726.
- [8] H. Shimizu, Y. Yoshimura, H. Hinou. A new glycosylation method Part III: Study of microwave effects at low temperatures to control reaction pathways and reduce, *Tetrahedron.* 64 (2008) 10091-10096.
- [9] J G P Binner, N A Hassine, T E Cross. The possible role of the pre-exponential factor in explaining the increased reaction rates observed during the microwave synthesis of titanium carbide, *J. Mater. Sci.* 30 (1995) 5389-5393.
- [10] S. Bednarz, D. Bogdal. Influence of microwave irradiation on the rate of complex chemical reactions, *13th Int. Electron. Conf. Synth. Org. Chem.*, (2009) e008:1-4.