Microwave assisted pyrolysis of urea supported on graphite under solvent-free conditions

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Abstract—The coupling of graphite (support) with microwaves (energy source) is responsible for a high temperature gradient leading to increased reaction rates as compared to conventional procedures. A rapid one-pot preparation of cyanuric acid is described that proceeds from urea by pyrolysis using microwave heating in the absence of water and organic solvents. © 2001 Elsevier Science Ltd. All rights reserved.

Microwave heating is convenient to perform reactions very efficiently in the absence of any organic solvents, so called dry media conditions. The advantages of using dry media conditions reach from faster reactions with a different selectivity to more economical conditions due to the absence of organic solvents. Reactions that normally require many hours at reflux temperature under classical conditions proceed much faster and with higher yields within several minutes under microwave heating.[1–3] Graphite is a chemically inert support able to transmit high thermal energy to the supported reagents.[4] Coupling microwaves (energy source) with graphite (support) by a conducting process is responsible for a high temperature gradient leading to increased reaction rates as compared to conventional procedures.[5]

This paper deals with the contribution of microwave heating to pyrolysis of urea into cyanuric acid under homogeneous and heterogeneous solvent-free media conditions. In all reactions, temperature and pressure are controlled for microwave and conventional experiments.[6,7] When the dissipative solid phase also called 'heat captor' (graphite) is introduced to create a heterogeneous medium, the yield and the rate of the heterogeneous pyrolysis reaction increases with microwave heating as compared to conventional heating under the same conditions.
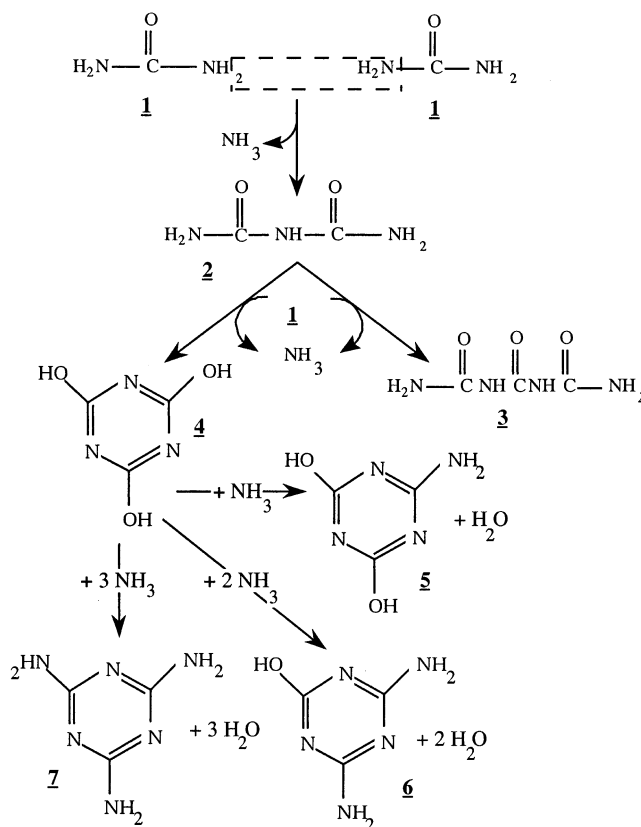
Scheme 1. Detailed mechanism of pyrolysis of urea (urea **1**, biurea **2**, triurea **3**, cyanuric acid **4**, amelide **5**, ameline **6**, melamine **7**).

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Table 1. Microwave assisted pyrolysis of urea under homogeneous and heterogeneous conditions

Phase (reactants)	T (°C)	Time (min)	Yield (%)	Selectivity (%)	Reaction rate (10^3 s^{-1})
Homogeneous phase (urea 20 g)					
Microwave heating	200	30	68.4	73.6	8.8
Classical heating	200	30	67.9	72.2	8.7
Microwave heating	200	1	5.2	20.2	8.8
Classical heating	200	1	4.5	30.3	8.7
Heterogeneous phase (urea 20 g+graphite 5 g)					
Microwave heating	300	3	61.2	93.5	12028
Classical heating	300	3	15.2	45.6	7156
Microwave heating	200	1	9.9	56.3	21.9
Classical heating	200	1	4.6	33.6	8.7

The traditional process of producing cyanuric acid **4** using urea **1** as the starting raw material consists basically in heating urea at 180–300°C to convert it to **4** with evolution of ammonia gas. An excessive heating necessary for converting the intermediates into **4** causes decomposition of the product formed in the mass.[8] Identification of the components of the reaction mixture, initially containing urea, allowed the reaction pathway illustrated in Scheme 1 to be established.

Kinetic studies have been carried out under carefully monitored reaction conditions. Within experimental errors, our results fit with the first order reaction equation. Using Arrhenius equation, the activation energy and the pre-exponential constant were determined for both microwave and conventional heating: E_a (microwave) = 159±3 kJ/mol, E_a (conv. heat) = 160±3 kJ/mol; ln A (microwave) = 35±1, ln A (conv. heat) = 34±1.

Table 1 summarises the effect of the heating mode when the experiments are carried out under homogeneous and heterogeneous conditions. When the reaction is conducted in the homogeneous phase, identical reaction rates and equilibrium yields are obtained with classical heating and with microwave irradiation. The question of a specific non-thermal activation by microwaves has been addressed during the past decade. In our case of the homogeneous pyrolysis, the answer is clearly that there is no non-thermal effect. When graphite is added to the reaction mixture, the yield and the rate of the pyrolysis reaction increases with microwave heating as compared to conventional heating under the same conditions (temperature, concentration and pressure).

The results show an increase yield of 200% when the reaction is conducted in the microwave batch reactor. The increase in reaction rate corresponds to a virtual difference in reaction temperature. Since the bulk temperature is equal for both the conventional and microwave heated systems, there must be an elevated temperature at the local heterogeneous site: the support surface. The apparent temperature of the catalytic site under microwave irradiation can be estimated from the initial reaction rates.

The reaction rate is connected to the temperature by Arrhenius Eq. (1):

$$k = A \exp(-E_a/RT) \tag{1}$$

For two temperatures, the ratio of the respective reaction rates is related to Eq. (2):

$$\ln(k_2/k_1) = (E_a/R) \times (1/T_1 - 1/T_2) \tag{2}$$

From Eq. (2), it follows that the apparent elevated temperature of the graphite support for the batch reactions was calculated to be 11±1 K higher than the measured bulk temperature.

In the steady state, the microwave heat transfer to the support is equal to the heat loss of the support to its surroundings. The resulting ΔT will be linearly dependent on the difference in loss factor and the radius of the support.

In summary, it has been found that heterogeneous reactions, taking place on the surface of a dissipative and/or catalytic solid, are more likely to show microwave activation. Higher yields and reaction rates were in most cases caused by localised superheating, i.e. by creating hot zones frequently called 'hot spots'.[9,10]

Acknowledgements

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cavity is optimised to have a good coupling to a variety of liquids and a homogeneous power distribution. The feeding magnetron operates at 2.45 GHz with a maximum power range of 300 W. The quartz reactor vessel, with a capacity of 10–150 ml, is fitted with a condenser and mixed by a quartz stirrer. The temperature is measured at the bottom of the reactor by an IR sensor and controlled by a feedback to microwave power regulation.

7. In a typical run, 20 g of urea with 5 g of graphite were introduced in the reactor and heated under stirring. The reactor was made of quartz. It was fitted with a thermo-couple for temperature control. At the desired reaction time, the reactor was rapidly cooled down and the resulting mixture analysed by HPLC [Spectraphysics P1500-UV150] with a Hamilton PRP-1 column.

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