Short Communication

Controlled methyl chloride synthesis at mild conditions using ultrasound irradiation

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ABSTRACT

A new route for the chlorination of methane is described using ultrasound irradiation, which allows for an intrinsically safe process at ambient pressure and temperature. By tuning the gas feed composition methyl chloride yields of up to 19% have been obtained.

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1. Introduction

Methyl chloride is a versatile methylating agent and as such it is an important intermediate in the chemical industry [1–3]. The largest market for methyl chloride is in the production of silicone polymers, which are increasingly applied in traditional non-silicone applications. Other uses of methyl chloride are in the production of a large variety of methyl ethers such as methyl cellulose and methyl amines. Despite its toxicity, methyl chloride does not suffer as much from the stringent environmental legislation that applies to other chlorinated hydrocarbons as there is virtually non-exposure to the general public. Consequently, methyl chloride represents one of the few halogenated compounds for which demand increases.

Currently, the industrial chlorination of methane is performed as a non-catalytic, thermally initiated gas-phase reaction. This route requires elevated pressures and temperatures to obtain a significant yield. Furthermore, the chlorination of methane is an exothermic reaction involving a flammable reactant and such reactions are preferably performed under diluted conditions, resulting in improved reaction heat removal and reduction of potential explosion hazards. Development of a more sustainable production process should therefore aim at mild reaction conditions, preferably in an aqueous environment [4,5].

In many systems ultrasound irradiation is known to successfully increase conversion, shorten reaction times, and minimize waste production and as such it is an important tool in green chemistry [6–9]. These effects primarily derive from acoustic cavitation, i.e. the sound-induced growth and adiabatic collapse of microscopic bubbles in a liquid, leading to hot-spots. In the hot-spots, very high temperatures, pressures and heating and cooling rates can be obtained. These extreme conditions lead to the dissociation of chemical bonds and the formation of radicals [10–13]. The extent of radical formation is known to strongly depend on the cavity temperature attained upon collapse.

Many studies on ultrasound-induced chemistry, i.e. sonochemistry, involve liquid-phase reactions. Examples hereof include the free-radical polymerization of acrylates and styrene in aqueous solution and the non-selective oxidation of pollutants [14–16]. To achieve sufficiently high radical concentrations in the liquid, these studies aim for maximizing the temperature rise inside the cavity. Numerical simulations and sonoluminescence studies have indicated that the highest hot-spot temperatures are achieved with monoatomic gases, e.g., argon [17,18]. Accordingly, liquid-phase reactions are typically performed under saturated argon conditions.

The chlorination of methane is a reaction between two gaseous reactants and will proceed predominantly inside the collapsing cavities. Previous studies have demonstrated that such gas-phase reactions do not merely benefit from a high hot-spot temperature, but that it also has to be balanced with the reactant concentration inside the cavity [19,20]. Initially, the effect of gas feed composition on hydrogen formation rates from water have been studied

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in this work to gain more insight into gas-phase sonochemistry. Elaborating on these insights, the ultrasound-induced chlorination of methane in an aqueous environment under ambient conditions has been explored.

2. Experimental

2.1. Apparatus and analysis

Ultrasound with a frequency of 20 kHz was applied from the top of a glass reactor (300 mL) using an ultrasonic generator (Sonics and Materials, VC750). The piezoelectric transducer was coupled to the liquid with a 13 mm diameter full wave titanium alloy horn. The temperature inside the reactor was controlled externally using a thermostatic bath and a Pt-100 temperature sensor. Thermal mass flow meters (Bronkhorst High-Tech) were used to control the gas feed composition. For the chlorination experiments, the outgoing flow was scrubbed with two 0.1 M sodium hydroxide solutions and contacted with dry sodium hydroxide pellets to remove acid gases. The composition of the outgoing flow was analyzed using a gas chromatograph equipped with thermal conductivity detectors (Varian, Micro-GC CP4900). To separate and analyze the mixture two different columns were used: 10 m molsieve 5 Å column with 1 m Pora PLOT-Q precolumn (argon as carrier) and 10 m Pora PLOT-Q column with 1 m Pora PLOT-Q precolumn (helium as carrier).

2.2. General procedure

At the start of an experiment the reactor was filled with 250 mL of MilliQ filtered water (>18 MΩ cm^{-1}) and the temperature of the thermostat was set to 293 K. Prior to sonication the solution was saturated for at least 1 h with the desired gas mixture, containing the following gases or a mixture hereof: argon (grade 5.0, Hoek Loos), methane (grade 5.5, Hoek Loos), ethylene (grade 3.0, Hoek Loos), iso-butane (grade 2.5, Hoek Loos), and 10 v/v% chlorine in argon (Linde Gas). During ultrasound, the power input was maintained at 50 W and the total gas flow rate equalled 30 mL/min. At fixed time intervals a sample was taken from the outgoing flow for GC-analysis. Ultrasound was applied to the solution continuously until the measured concentrations reached steady state.

3. Results and discussion

During sonication of aqueous systems, the dissociation of water leads to the production of H- and OH-radicals, which predominantly recombine inside the cavity before entering the liquid [21,22]. Upon recombination, the main products formed are hydrogen and hydrogen peroxide and hence, hydrogen formation rates can provide valuable insights with respect to gas-phase sonochemistry [23]. Fig. 1 shows hydrogen formation rates for water saturated with a mixture of argon and either methane, ethylene or iso-butane.

As is evident from this figure, the extent of hydrogen gas formation strongly depends on the composition of the gas mixture. For water saturated with argon, hydrogen radicals can only arise from the dissociation of water molecules and hence, the experimentally determined rate of hydrogen gas formation is limited. The addition of a gaseous hydrocarbon leads to a higher concentration of hydrogen atoms in the cavity interior and as a result, the rate of hydrogen gas formation increases. However, polyatomic gases have a relatively high heat capacity and thereby suppress the temperature increase upon collapse. Accordingly, the hydrogen production decreases for higher methane fractions and approximates almost zero for a predominant methane feed. For a feed with a methane con-
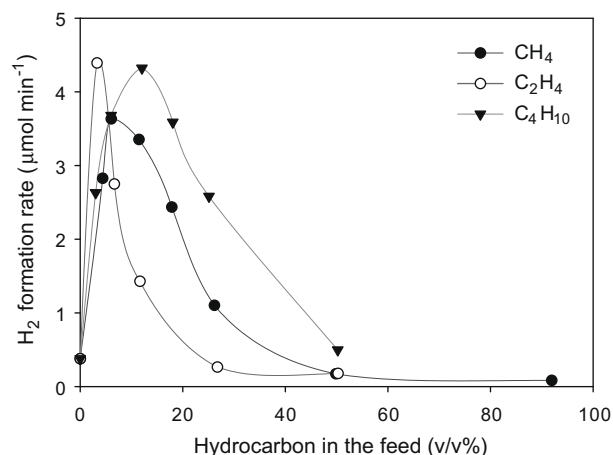

Fig. 1. Rate of hydrogen gas formation from water at 293 K using 20 kHz ultrasound with an intensity of 40 W/cm^2. Prior and during sonication a mixture of argon and hydrocarbon was sparged through the mixture.

centration of 8% these physical and chemicals effects are tuned in such a way that the highest hydrogen formation rate is observed. A similar dependence on gas feed composition has been found for the other hydrocarbons, i.e. ethylene and iso-butane (Fig. 1). Hence, performing gas-phase sonochemistry requires a subtle balancing of reactant concentration and heat capacity of the cavity content.

Fig. 1 also shows the strong variation of the optimal gas feed composition for the different reactants. The concentration at which the hydrogen production is maximal varies for the different hydrocarbons in the following order: $C_2H_4 < CH_4 < C_4H_{10}$. If the gas and liquid-phase compositions were to be in equilibrium, the optimal hydrocarbon concentration would shift to a lower value for gases with a higher specific heat capacity [24]. However, the order in optimum hydrocarbon concentration corresponds to the order in gas solubility [25]. This order suggests that the cavities are not in thermodynamic equilibrium with the surrounding liquid and that during cavity formation, gases with a relatively high solubility in water can accumulate in the cavity interior more readily, which results in a concentration exceeding that of the gas feed [23]. Numerical simulations have revealed that gas diffusion is relatively slow compared to the cavity dynamics [26]. Since 20 kHz sonication
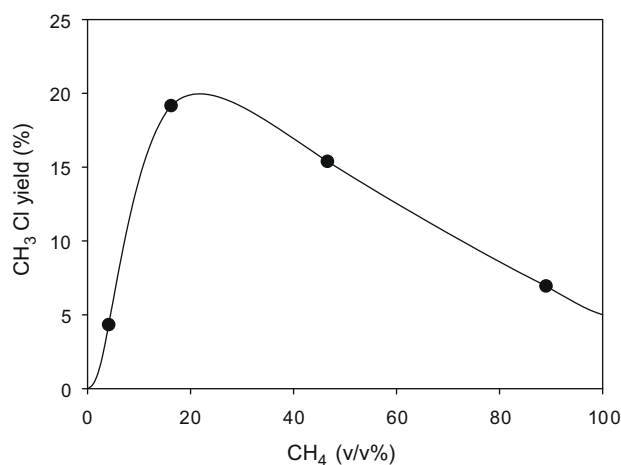

Fig. 2. Methyl chloride yield from water saturated with a mixture of methane, argon and chlorine. The chlorine supply consisted of a mixture of chlorine and argon (10 v/v%) for reasons of safety and hence, it was not possible to determine the methyl chloride yield in the absence of argon.

Table 1
Methyl chloride synthesis using ultrasound irradiation.

Gas feed composition (v%)			Time to steady state (min)	Methyl chloride yield
CH_4	Cl_2	Ar		
4.09	0.22	95.69	90	4
16.20	0.22	83.58	170	19
46.56	0.22	53.22	170	15
88.99	0.22	10.79	170	7

predominantly induces transient cavitation, the cavities have insufficient time to fully equilibrate with the surrounding liquid [27]. The aqueous solubilities of methane and argon are approximately equal at 293 K. As ethylene is more soluble in water than argon, a relatively large amount of ethylene is likely to be present inside the cavity when it forms. This would correspond with the observation that the hydrogen formation rate for ethylene has a maximum at a hydrocarbon concentration lower than in the case of methane. The same argument holds for a gas feed containing iso-butane.

Starting from the insights obtained by these hydrogen formation experiments, the feasibility of methane chlorination at ambient conditions has been explored. Relatively high concentrations of an inert monoatomic gas in the feed are required to assure a sufficient temperature rise upon collapse. Secondly, because the ratio of chlorine to methane in the cavity should be close to stoichiometric and the pronounced effect of gas solubility on the composition of the cavity interior, the difference in water solubility of the two reactants should be accounted for. During the experiments the concentration of chlorine in the gas feed was kept constant at a value of 0.22 v/v% and the ratio between methane and argon was varied. The steady state concentration of methyl chloride was measured by GC-analysis of the outgoing gas flow and from this the methyl chloride yield has been calculated. The results of these experiments are presented in Fig. 2 and Table 1.

The experiments have demonstrated that ultrasound enables the formation of methyl chloride under diluted and mild reaction conditions. By optimizing the ratio of argon to methane in the gas feed, methyl chloride yields as high as 19% have been observed. At lower methane concentrations the low reactant concentration inside the cavity limits the overall yield, whereas above the optimum concentration the decrease in hot-spot temperature results in lower conversions. In accordance with previous work, the highest product yield is obtained for a gas feed containing a higher fraction of methane as that corresponding to the maximum hydrogen formation rate from water [19]. This shift can be explained by the improved methane to chlorine ratio dissolved in the liquid. For a methane concentration in the feed of 50 v/v% this ratio equals approximately unity, leading to a more similar cavity concentration for both reactants. The head space contained no detectable amounts of dichloromethane, indicating that multiple chlorination of methane hardly occurred. This high selectivity in methyl chloride can probably be explained by the relatively low methyl chloride concentration in the reactor compared to the methane concentration. The acquired GC-spectra, however, suggested the formation of higher hydrocarbons [19].

4. Conclusions

This work has demonstrated that ultrasound irradiation allows for a more sustainable process towards methyl chloride as compared to the current industrial chlorination of methane. The extreme conditions inside the imploding cavities enable radical formation at ambient bulk conditions. Furthermore, this ultrasonic route is intrinsically safe as the reaction is performed under diluted conditions and the reaction stops when the ultrasounds source is switched off. Accurate control of the cavity contents is crucial for obtaining significant yields in such gas-phase reactions. Addition of a monoatomic gas is necessary to achieve the required temperature rise, whereas the reactant concentration inside the cavity is relevant for the chemical effect. When aiming at a particular reactant concentration inside the cavity, non-equilibrium thermodynamics have to be taken into account. Due to rapid cavity dynamics, the composition of the cavity interior does not equal the gas feed composition, yet strongly corresponds to the relative solubilities of the gases in the liquid.

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