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C–H Activation

Highly Efficient and Selective C–H Activation in Gallium-Containing Molten-Salt Systems**

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Chloromethane has been found to react with Ga^0 suspended in an ionic liquid or molten salt medium with very high selectivities (up to 98 % of gaseous products) to form isobutane. During the reaction, hydrogen and anionic chlorogallate species of Ga^I and Ga^{III} are formed. The latter can be electrochemically reduced to Ga^0 in a subsequent step. The chlorine liberated in the regeneration of Ga^0 can be used for the synthesis of the chloromethane feedstock from methane, thus making this new reaction a potential key step in a fundamentally new process chain for increasing the value of methane in a closed chlorine/chloride cycle.

Rational and efficient conversion of methane to more useful higher hydrocarbons is a very important topic in natural gas utilization. Today, methane activation is mostly carried out indirectly by transformation of methane to syngas (a mixture of CO and hydrogen), which then is converted into higher hydrocarbons (olefins, gasoline, and waxes) by Fischer–Tropsch synthesis. Alternatively, syngas can be used to synthesize methanol, which later can be converted into hydrocarbons using methanol-to-olefins (MTO) or methanol-to-gasoline (MTG) catalysts.[1–4] In both routes, a great part of the overall cost stems from production of syngas.[5] Another problem of Fischer–Tropsch synthesis and methanol conversion processes is that it is not possible to produce a single product with high selectivity, as distributions of products with different chain lengths are obtained.

A true alternative for indirect methane conversion is the use of chloromethane as the activated intermediate. Chloromethane is obtained both from radical chlorination of methane and from oxyhydrochlorination[6] of methane. In 1988, Taylor and Noceti published a process for the production of gasoline from chloromethane in an MTG-like process.[7] The byproduct HCl of the MTG-like step can be recycled back to the production of chloromethane by oxyhydrochlorination, thus making the overall process attractive for technical use. In the following years, different types of zeolite catalysts were applied in this kind of chloromethane transformation, showing different performance with respect to catalytic activity, coke formation, and the distribution of hydrocarbons produced.[8–12] Recently, the application of SAPO-34-type molecular sieve catalysts was found to be promising (SAPO = silicon aluminum phosphates). With this type of catalyst, light alkenes (ethene, propene, butenes) can be produced at temperatures of 350–500 °C in 70–80 % selectivity in a temperature-dependent mix in which the maximum selectivity for one individual product hardly reaches 45 %.[13] Only minor amounts of light alkanes are obtained, while 15–20 % of the products are heavier than C_5.

Herein, we describe a new, highly efficient and selective C–H activation that may be the key reaction step in an alternative process to transform methane into higher hydrocarbons with unprecedented high selectivity. The new route involves the reaction of chloromethane with a Group III metal in a low oxidation state (in particular Ga^0) to form highly branched hydrocarbons, hydrogen, and chlorometalates. These chlorometalates dissolve in the molten salt or ionic liquid environment in which the reaction is carried out. The molten salt medium also acts as the electrolyte for the subsequent electrochemical reduction of the metal back to the reactive oxidation state M^0. The chlorine formed during this regeneration process can be used in the first step to produce chloromethane from methane. Because the products contain extremely low amounts of chlorinated hydrocarbons (below our detection limit of ca. 100 ppm), the overall process can be regarded as a closed cycle with respect to chlorine; methane and oxygen are converted into highly branched hydrocarbons, hydrogen, and water using electrical energy to overcome the thermodynamic limitations. Surprisingly, the selectivity for isobutane can be drastically enhanced by employing ionic liquid mixtures containing small amounts of benzyltrimethylammonium chloride. For such mixtures, a selectivity of the chloromethane conversion step for isobutane of more than 98 % has been shown (based on the analysis of gaseous reaction products).

The C–H activation reaction described herein is not catalytic. In contrast, we describe the combination of a stoichiometric reaction step with the electrochemical generation of highly reactive metal(0) suspended or emulsified in an ionic reaction medium. The step in which chloromethane

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reacts with a suspension of Al^0 needles or an emulsion of liquid Ga^0 in a LiCl/$AlCl_3$ molten salt is related to work by Sundermeyer and co-workers in which they describe the formation of methylaluminumdichloride by treating chloromethane in alkali melts with elemental Al.[14–16] However, this system has not been reported to liberate hydrocarbons in a selective manner.

In our study, the reaction of chloromethane in gallium-containing chloroaluminate molten salts was carried out using a Hastelloy C autoclave with a gas entrainment stirrer connected to a chloromethane supply with dosing by pressure drop (determination of V_{CH_3Cl} by gas measurement). Details of the setup and the experimental protocol are described in the Supporting Information.

In a typical experiment, a mixture of LiCl, $AlCl_3$, and the elemental Group III metal was filled into the reactor under inert conditions, and the mixture was heated to the reaction temperature. The reaction temperature was chosen high enough to form a suspension (for aluminum) or an emulsion (for gallium) of the metal in the liquid chloroaluminate.

In an initial experiment, we probed the reactivity of electrochemically generated Al^0 needles (see the Supporting Information for preparation details) suspended in acidic chloroaluminate ionic liquids towards chloromethane with the aim of observing ethane as the most likely product of an oxidative coupling reaction. Indeed, at 120 °C, 75 % of CH_3Cl conversion could be obtained in 34 min in an acidic chloroaluminate molten salt ($AlCl_3$/LiCl = 60:40) with ethane as the main product (Table 1, entry 1). We decided to continue further experiments with Ga^0 instead of Al^0 for two reasons. On the one hand, we expected easier application of Ga^0 because it is a liquid under the reaction conditions and during the electrochemical regeneration. On the other hand, we were interested to see whether the use of Ga^0 could reduce the large amount of methane formed with the Al^0 system.

Table 1: Reaction of CH_3Cl in an acidic lithium chloroaluminate molten salt in the presence of Al^0 or Ga^0.[a]

	1	2
reactive metal	Al^0	Ga^0
chloromethane conversion [%]	75	75
time to 75 % conversion [min]	34	91
methane (wt %)	39.1	69.1
ethane (wt %)	45.4	< 1.0
propane (wt %)	9.3	15.0
isobutane (wt %)	1.5	9.6
n-butane (wt %)	< 1.0	3.7
dimethylpropane (wt %)	4.5	< 1.0
methylbutane (wt %)	< 1.0	< 1.0
n-pentane (wt %)	< 1.0	< 1.0
hydrocarbons over C_5 (wt %)	< 1.0	< 1.0

[a] 55 g $AlCl_3$/LiCl = 60:40, 1.35 g CH_3Cl, 1.50 g Al^0 or 3.00 g Ga^0, T = 120 °C.

Chloromethane conversion in the presence of Ga^0 was quite different than the corresponding experiment with Al^0. While methane formation was much greater in the Ga^0 case, almost no ethane was formed. Surprisingly, a significantly greater amount of higher hydrocarbons was detected in the gas phase that could only originate from C–H activation steps occurring during the reaction. No chloromethane conversion was observed without the addition of metal(0).

To get a more detailed look at the melt's influence on this C–H activation process, the molten salt's acidity was varied (Table 2). The reaction temperature for this set of experiments was increased to 150 °C to ensure that the lithium chloroaluminate reaction medium was liquid in all cases under investigation.

Table 2: Reaction of CH_3Cl in lithium chloroaluminate molten salts of different acidities (modified by the $AlCl_3$/LiCl ratio) in the presence of Ga^0.[a]

	1	2	3	4
$AlCl_3$ (mol %)	50	51	55	60
LiCl (mol %)	50	49	45	40
time to 75 % conversion [min]	750	502	68	21
methane (wt %)	45.0	53.5	56.8	55.9
ethane (wt %)	< 1.0	< 1.0	< 1.0	< 1.0
propane (wt %)	2.5	1.0	12.4	26.9
isobutene (wt %)	44.5	35.2	17.8	10.1
n-butane (wt %)	1.1	< 1.0	3.3	5.1
dimethylpropane (wt %)	< 1.0	1.3	5.3	< 0.1
methylbutane (wt %)	6.5	6.2	3.0	< 1.0
n-pentane (wt %)	< 0.1	< 1.0	< 1.0	< 1.0
hydrocarbons > C5 (wt %)	< 0.1	< 1.0	< 1.0	< 1.0

[a] 55 g $AlCl_3$/LiCl, 35 g CH_3Cl, 3.00 g Ga^0, T = 150 °C.

Remarkably, the tendency of the reaction to form higher hydrocarbons increases significantly with lower acidities of the lithium chloroaluminate medium. Apart from methane formation, which was above 45 wt % in all experiments, isobutane was found to form in quite high selectivity in the neutral chloroaluminate system (entry 1, Table 2). While reaction rates are clearly enhanced with higher melt acidities, increased propane selectivity was observed in the gaseous reaction products in more acidic melts at the expense of isobutane formation. In all experiments, only traces of ethane were detected.

In a related report, Power and Waggoner describe the reaction of trimethylaluminum and trimethylgallium with bulky primary amines.[17] In this very fundamental, crystallographic study, the authors conclude that, despite great structural similarity, the aminogallanes have a much greater tendency for methane elimination by C–H activation than for elimination by capture of N–H hydrogen. For example, although the reaction between $AlMe_3$ and H_2Ndipp (dipp = 2,6-$i$$Pr_2C_6H_3$) gave trimeric $(MeAlNdipp)_3$, the comparable reaction with $GaMe_3$ gave a compound in which the isopropyl methyl group on the aryl ring of the amine was bonded to gallium.

Inspired by this account of C–H activation in the presence of amines, we studied our molten salt system in the presence of ammonium salts. By replacing part of the LiCl by benzyltrimethylammonium chloride, we were able to lower the melting point of our reaction mixture below 100 °C (these melts fulfill the well-accepted definition of ionic liquids).

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Experiments were carried out at both 120 °C (for comparison with results without the ammonium salt) and 100 °C (to benefit from the melting point suppression), and the results are summarized in Table 3.

Table 3: Reaction of CH_3Cl in lithium chloroaluminate/benzyltrimethylammonium chloride ionic liquids in the presence of Ga^0.[a]

	1	2	3	4	5
$AlCl_3$ (mol %)	60	60	60	60	60
LiCl (mol %)	39	30	30	25	20
$[Me_3NCH_2C_6H_5]Cl$ (mol %)	1	10	10	15	20
reactive metal	Ga^0	Ga^0	Ga^0	Ga^0	Ga^0
temperature [°C]	120	120	120	100	100
time to 75 % conversion [min]	26	16	17	50	230
methane (wt %)	18.2	2.6	5.0	2.0	1.3
ethane (wt %)	<0.1	<0.1	<0.1	<0.1	<1.0
propane (wt %)	1.8	2.1	1.0	<1.0	<0.1
isobutane (wt %)	70.1	87.7	93.0	97.5	98.5
n-butane (wt %)	10.0	7.6	<1.0	<1.0	<0.1
dimethylpropane (wt %)	0.0	<0.1	<0.1	<0.1	<0.1
methylbutane (wt %)	<1.0	<0.1	<0.1	<0.1	<0.1
n-pentane (wt %)	<1.0	<0.1	<0.1	<0.1	<0.1
hydrocarbons $>$C5 (wt %)	<0.1	<0.1	<0.1	<0.1	<0.1

[a] 55 g $AlCl_3$/LiCl, 1.35 g CH_3Cl, 3.00 g Ga^0.

Surprisingly, the addition of only 1 mol % of the ammonium salt had a drastic effect on the reaction compared to the same experiment without the ammonium salt (entry 1, Table 3 vs. entry 2, Table 1). While the addition of small amounts of the ammonium salt had a rate-accelerating effect, the selectivity for methane decreased significantly while the selectivity for isobutane increased substantially. This effect became even more pronounced by adding 10 mol % of the ammonium salt, for which an isobutane selectivity of 87.7 % in the gaseous reaction products could be realized (Table 3, entry 3). By lowering the temperature to 100 °C, the selectivity for isobutane could even be increased to 98.5 % by increasing the amount of ammonium salt to a mixture with $AlCl_3/LiCl/[Me_3NCH_2C_6H_5]Cl = 60{:}20{:}20$ (entry 5, Table 3; for detailed conversion/yield and time/conversion plots, see the Supporting Information). However, reaction rates significantly decreased for ammonium salt contents above 10 mol %, probably because of a buffering effect of the ammonium salt on the melt's acidity at higher concentrations.

The formation of hydrogen could be confirmed by GC for these highly selective reactions, thus indicating the strongly C–H-activating nature of the reaction system. Moreover, product analysis with a chloride-sensitive GC method (see the Supporting Information) did not show any chlorinated hydrocarbons above our detection limit of 100 ppm. Furthermore, a control experiment at 120 °C, in which the ionic medium ($AlCl_3/LiCl/[Me_3NCH_2C_6H_5]Cl = 60{:}30{:}10$) was brought into contact with Ga^0 without adding chloromethane, did not reveal any detectable decomposition products of the ammonium salt.

In view of these interesting results, we used ^{71}Ga and ^{1}H NMR spectroscopy measurements to investigate the reaction mechanism (for details of sample preparation and spectra, see the Supporting Information). The measurements were carried out at 150 °C to ensure that all samples were in a liquid state. We first investigated molten salt media without ammonium salts. Depending on the amount of Ga^0 added to the reaction, the ^{71}Ga NMR spectrum shows signals in the typical ranges for Ga^I and Ga^{III} species (for low initial Ga^0/chloromethane ratios) or only signals in the typical range for Ga^I species (for high initial Ga^0/chloromethane ratios). However, ^{71}Ga NMR spectra of Ga^I are known to be much sharper than those of Ga^{III},[18–20] so that some Ga^{III} might also have been formed in the latter case. Moreover, the acidity of the melt had a pronounced influence on the detection of the different Ga species, with Ga^{III} appearing much more pronounced in neutral melts. These results confirmed our mechanistic expectations that some kind of oxidative addition process of chloromethane to Ga^0 is the starting point of the reaction, with subsequent formation of Ga^{III}. The NMR spectroscopic investigation of the ionic liquids containing benzyltrimethylammonium chloride revealed that no major decomposition or aromatic alkylation of the ammonium cation takes place during the reaction (the sample was taken after experiment entry 2, Table 3). Apart from the unchanged ammonium cation, the ^{1}H NMR spectrum shows only a small number of signals in the alkyl range representing reaction intermediates still dissolved in the melt.

However, the true role of the ammonium salt is not yet fully understood. The ^{71}Ga NMR spectrum of the ionic liquid obtained from entry 2, Table 3 showed only one clear signal in the typical Ga^I range. It is not clear whether the ammonium cation takes part in the reaction directly (e.g. as a ligand precursor) or whether it allows for lower reaction temperatures and modulates the melt's acidity to suppress detrimental cracking. Preliminary experiments with other ammonium salts revealed an important role for the aromatic ring of the ammonium cation, as non-aromatic ammonium cations led to much less selective C–H activation.

Apart from the chain-growth step, we also investigated the electrochemical reduction of the metal(III) species formed during the reaction. For the chloroaluminate system both without organic additives and with benzyltrimethylammonium chloride, the electrochemical regeneration of the reactive metal (Al^0 or Ga^0) could be achieved in a simple electrochemical chamber. Al^0 grows as needles on the cathode and can be removed from the electrode surface either by mechanical abrasion or by reversion of polarity. As Ga^0 is a liquid under the reaction and electrolysis conditions (m.p. = 29.8 °C), it deposits on the corresponding electrode as small, immiscible droplets that can be collected easily at the bottom of the electrolysis chamber and pumped back into the chain-growth reactor (see the Supporting Information for details).

A particularly attractive use of the reaction/regeneration cycle would be the direct use of methane. In the first step of such a scheme, the methane is converted into chloromethane. On the basis of the stoichiometry of the overall process, we propose a combination of oxyhydrochlorination and radical chlorination according to Equations (1) and (2), resulting in Equation (3) for the overall chlorination of methane:

$$2\,CH_4 + O_2 + 2\,HCl \rightarrow 2\,CH_3Cl + 2\,H_2O \tag{1}$$

$$2\,CH_4 + 2\,Cl_2 \rightarrow 2\,CH_3Cl + 2\,HCl \tag{2}$$

$$4\,CH_4 + O_2 + 2\,Cl_2 \rightarrow 4\,CH_3Cl + 2\,H_2O \tag{3}$$

Assuming that Ga^{III} is indeed the final oxidation state of gallium during its reaction with chloromethane in the chloroaluminate ionic liquid, Equation (4) represents the selective formation of isobutane and hydrogen:

$$12\,CH_3Cl + 4\,LiCl + 4\,Ga^0 \rightarrow 3\,i\text{-}C_4H_{10} + 4\,Li[GaCl_4] + 3\,H_2 \tag{4}$$

The final step involves the reduction of the chlorogallate anion back to the high energetic level of Ga^0 [Eq. (5)]. The reduction is carried out electrochemically, and the chlorine formed in this step is recycled into the chlorination step shown in Equation (2).

$$4\,Li[GaCl_4] \xrightarrow{\text{electrolysis}} 4\,LiCl + 4\,Ga^0 + 6\,Cl_2 \tag{5}$$

Independent on the final oxidation state of the reactive metal, the overall reaction is shown in Equation (6).

$$4\,CH_4 + O_2 \xrightarrow{\text{electric energy}} i\text{-}C_4H_{10} + 2\,H_2O + H_2 \tag{6}$$

In conclusion, we have described a new and highly selective, albeit noncatalytic, method for C–H activation in molten salt or ionic liquid media. In a slightly acidic $AlCl_3$/$LiCl$/$[Me_3NCH_2C_6H_5]Cl$ mixture, chloromethane reacts to isobutane and hydrogen with up to 98.5% selectivity (based on analysis of gaseous products). The new reaction may be the key step of a new process to convert methane into higher hydrocarbons. The thermodynamic limitation of the direct reaction is overcome by introducing electric energy into the reaction via highly reactive metal(0) species.

From an industrial perspective the described reaction sequence could open up a highly attractive alternative to increase the value of stranded gas in remote areas, since the process can be carried out from methane as the only feedstock (the electrical energy for the electrolysis can also be generated from methane). The inventory of molten salt and elemental metal would be constantly recycled in a continuous process. Furthermore, the process does not form any byproducts that must be disposed of. In particular, no chlorinated hydrocarbons are formed in detectable amounts. Besides the main hydrocarbon, the only products are hydrogen, water, and CO_2 (from the power plant if it is hydrocarbon-based). The hydrogen (from the growth step and from isobutane dehydrogenation) could be used on-site to regain a small portion of the required energy.

From the perspective of ionic liquid chemistry, the reaction demonstrates the potential of ionic reaction media to allow new and highly attractive combinations of electrochemical and reaction steps in closed cycles. Obviously, highly reactive metal intermediates can be formed electrochemically in ionic liquid media that provide quite unique reactivity patterns. This observation could well be relevant beyond the case of selective C–H activation described herin.

Experimental Section

All chemicals where handled using standard Schlenk techniques.

Conversion of CH_3Cl: Before starting an experiment, the equipment was dried in an oven overnight at 70 °C. To prepare the molten salt medium, the chemicals for the chloroaluminate system were mixed under argon in the desired ratio, keeping a constant mass of 55 g for all compositions. The components of the melt were filled into a Hastelloy C autoclave (see Figure S-1 in the Supporting Information); for melts containing benzyltrimethylammonium chloride, ice cooling was necessary to avoid hotspots owing to the highly exothermic formation of the ionic liquid. The reactive metal (1.50 g Al^0 as needles or 3.00 g Ga^0 in small pieces) was then added.

After closing the autoclave, the whole system was flushed with argon for 20 min. Then the reactor was pressurized with He (10 bar). If the pressure in the reactor kept constant for 30 min, the He was discharged and the autoclave was heated to the desired temperature (100–150 °C) with slow stirring (100 rpm). The reaction temperature was kept constant for at least one hour to ensure complete melting of all chemicals. Then the reactor was filled with 600 mL_N (1.35 g) of chloromethane by pressure drop. The amount of chloromethane was measured by a volume flow indicator.

The reaction was carried out with a continuous stirring rate of 1000 rpm. During the reaction, gas samples were taken for GC analysis. After conversion of more than 95%, the reaction was deliberately stopped.

Electrochemical regeneration of Ga^0: For electrolysis of Ga-containing melts, the same setup as for production of Al^0 needles was used (see the Supporting Information). The electrochemical regeneration of Ga^0 was carried out in a melt consisting of $AlCl_3$ (60 mol%), LiCl (30 mol%), and benzyltrimethylammonium chloride (10 mol%). In order to avoid crystallization, the flask was heated to slightly above melting temperature of the system (105 °C) and stirred with a magnetic stirrer.

For the deposition of Ga^0, 1.0–2.5 V were applied to the tungsten electrodes. During the electrolytic regeneration Ga^0, droplets formed on the cathode and fell off. These droplets formed a visible liquid phase at the bottom of the flask from which they could be pumped back into the reactor.

Details of GC analytic and NMR spectroscopic investigations are given in the Supporting Information, which also includes diagrams with detailed results of selectivity and conversions and some NMR spectra.

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