Degradation Kinetics and Solvent Effects of Various Long-Chain Quaternary Ammonium Salts

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Abstract

Surfactants such as quaternary ammonium salts (QAS) have been in increasing demand, for emerging new applications. Recent attempts at process intensification of their production, have disclosed the need for a better understanding of QAS thermal stability. This work aims to determine degradation kinetics of various QASs, and the associated solvent effects.

Degradation kinetics of four methyl carbonate QASs were determined in various polar solvents in stainless steel batch autoclaves. ^{1}H NMR spectrometry was employed for offline analysis of the reaction mixtures. The kinetic parameters were then used to compare the thermal stability of the four compounds in the polar solvents. Water showed not degradation, and methanol (MeOH) was the solvent that provided the second-best stability. Water-MeOH mixtures may provide an overall optimum. More, and longer long-chain substituents increased the degradation rate.

Thermogravimetric Analysis was used to obtain the thermal stability in a solid-state, *i.e.* solventless environment. Isoconversional analysis showed that no reliable kinetic parameters could be determined. Nevertheless, the data did allow for a comparison of the thermal stability of 14 different QASs. Furthermore, the relative instability of the compounds in solid-state demonstrated the challenges of solventless QAS production.

Keywords: Degradation kinetics; Thermal stability; Thermogravimetric Analysis; Solvent effects.

1 Introduction

Surfactants serve a plethora of different use cases, in a continuously expanding market[1,2]. These compounds are predominately applied as detergents. Cationic surfactants such as quaternary ammonium salts (QAS), are employed in more speciality-focused application, as *e.g.* anti-microbials[3], and more recently in ion-exchange membranes[4,5]. These increasingly demanding appliances require highly stable compounds. Recent studies have therefore already focused on the elucidation of their thermal and alkaline stability[4,6].

QASs are conventionally produced in batch Menshutkin[7,8] reactions, but novel production methods with dimethyl carbonate (DMC) are also being explored[9]. Their production is kinetically limited, and there is a large potential for process intensification[8–11]. In current processes, the temperature is limited by consecutive degradation reactions of the products. This also highlights the importance of better quantification of the kinetics of this reaction for further optimisation of the process.

The scope of this research is to determine degradation kinetics of various QASs, with and without solvents. These kinetics are currently not available in literature, and they could disclose opportunities to further intensify QAS production through elevated temperature. Comparing the thermal stability in different solvents would also elucidate their relative eligibility. By also measuring the thermal stability in solid-state, the viability of solventless production can be assessed. Lastly, the effect of different number of long-chains, their length, and various anions will be investigated.

1.1 Degradation mechanisms

According to previous studies, at least two possible degradation mechanisms can occur for QASs at elevated temperatures. Hofmann elimination has been well-known since 1958 and is considered to be the main reaction pathway[12]. The mechanism proceeds via a nucleophilic attack of the anion on the β-hydrogen, relative to the nitrogen atom. Consequently, the long chain is eliminated from the nitrogen, resulting in an alkene, a tertiary amine and a protonated anion as is illustrated by Fig. 1. It is expected that the more substituted carbon can better accommodate a positive charge in its transition state, therefore, this elimination is expected to be more favourable than the elimination of a methyl group. This also implies that more long-chain substituents make it statically more likely for elimination to occur. However, in some cases, depending on the species, the protonated anion can perform a consecutive addition on the alkene double bond. Another proposed reaction mechanism is a nucleophilic substitution reaction on the carbon of the long-chain substituent[4]. Here, an alkane species is formed which contains the anion species of the original QAS, alongside a tertiary amine. This reaction pathway is also shown in Fig. 1. However, at most reaction conditions, it is presumed to have a less significant contribution to the degradation[4,6].

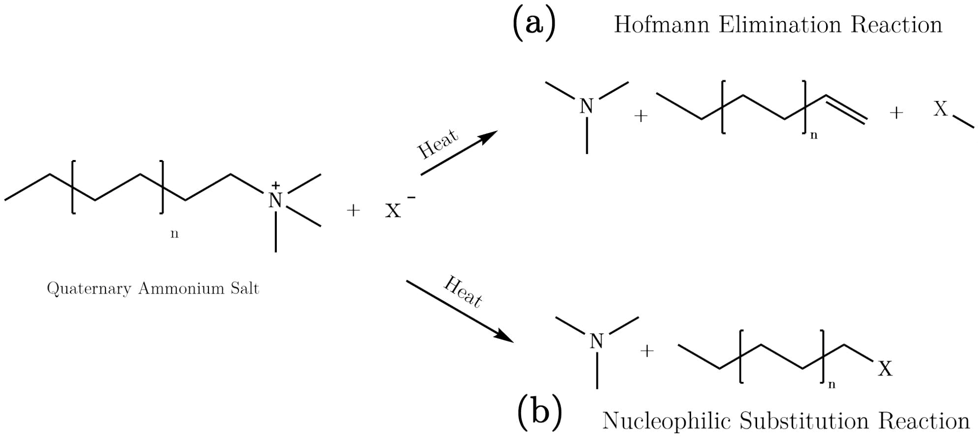


Figure 1: The main mechanisms for degradation (a) Hofmann elimination and (b) nucleophilic substitution[4,6,12].

1.2 Solvent effects

It is well-known that solvents, and their polarity greatly influence the rate of QAS production[11,13–15]. It is expected that the degradation reaction is also sensitive to the used solvent and its polarity, as they can provide shielding to certain reactive sites[16]. Higher polarity is expected to better shield the sensitive β-hydrogen site from potential elimination. Water, methanol (MeOH), and iso-propanol (IPA) were selected for this work based on their polarity and their relatively good ability to sufficiently dissolve all intended QASs. Moreover, DMC was selected in order to assess the viability of methyl carbonate QAS production, with excess DMC and no (additional) solvent present. Ultimately, confluence between the solvent's added stability and the solvent effects of QAS production, would magnify the potential for process intensification.

2 Experimental Procedure

2.1 Chemicals and Synthesis

The required chemicals were obtained from various vendors. Some QASs were not commercially available, and were synthesised. All used reactants and QASs, their source and their purity have been listed in Table 1. Besides these chemicals, all required solvents were obtained in Technical Grade from VWR Chemicals. Lastly, 1,4-Difluorobenzene (F_2Bz) was used as an internal standard and purchased from Sigma Aldrich with over 99% purity.

The synthesis of the QASs as shown in Table 1, was carried out in either 40 mL stainless steel batch autoclaves or a plug-flow reactor. The plug-flow reactor has been thoroughly described in earlier work[11]. The batch reactors were loaded with the respective reactants and MeOH as a solvent, and placed in a pre-heated oven. In order to ensure full conversion of the tertiary amine, all experiments were performed in excess MeI or DMC. The tertiary amine to MeI/DMC to MeOH molar ratio was 1:5:10. As BnCl is difficult to separate from the final mixture, this reactant was used in equimolar amounts compared to the tertiary amine. For all products, the method, reaction time, and temperature have been tabulated in Table 2.

To prevent consecutive degradation of the QAS, the reaction temperature was limited to a maximum of 120 °C. Note that this resulted in very long reaction times in some cases, as the reactivity of tertiary amines with an increasing amount of long-chain substituents severely diminishes. After the synthesis, all remaining excess reactant and MeOH was evaporated with a rotary evaporator or a vacuum oven. Thereafter, the purity was verified by means of ^{1}H NMR spectroscopy (Table 1).

Table 1: All used chemicals, their source, and their purity. [a]These QASs were synthesised, and their purity was measured with ^{1}H NMR.

Chemical	Source	Purity
Reactants		
N,N-dimethyldecylamine (DMDA)	TCI	$\geq$ 95%
N-Methyldidecylamine (MDDA)	Sigma Aldrich	$\geq$ 95%
Tri-N-decylamine (TDA)	TCI	$\geq$ 97%
Tri-N-butylamine (TBA)	TCI	$\geq$ 95%
Dimethyl carbonate (DMC)	Sigma Aldrich	$\geq$ 99%
Benzyl chloride (BnCl)	Sigma Aldrich	$\geq$ 99%
Methyl iodide (MeI)	Sigma Aldrich	$\geq$ 99%
QASs		
N,N,N-tridecyl-N-methylammonium methylcarbonate (TDMA-MC)	Synthesis	$\geq$ 95% [a]
N,N,N-tributyl-N-methylammonium methylcarbonate (TBMA-MC)	Synthesis	$\geq$ 96% [a]
N,N,N-tridodecyl-N-methylammonium nitrate (TD(12)MA-NO3)	Sigma Aldrich	$\geq$ 99%
N,N,N-tridodecyl-N-methylammonium chloride (TD(12)MA-Cl)	Sigma Aldrich	$\geq$ 98%
N,N,N-tridodecyl-N-methylammonium iodide (TD(12)MA-I)	Sigma Aldrich	$\geq$ 97%
N,N-didecyl-N,N-dimethylammonium methylcarbonate (DDMA-MC)	Synthesis	$\geq$ 98% [a]
N,N-didecyl-N,N-dimethylammonium chloride (DDMA-Cl)	Sigma Aldrich	$\geq$ 98%
N,N-didecyl-N,N-dimethylammonium bromide (DDMA-Br)	Sigma Aldrich	$\geq$ 98%
N-benzyl-N-decyl-N,N-dimethylammonium chloride (BzDDMA-Cl)	Synthesis	$\geq$ 97% [a]
N-decyl-N,N,N-trimethylammonium methylcarbonate (DTMA-MC)	Synthesis	$\geq$ 98% [a]
N-octyl-N,N,N-trimethylammonium bromide (OTMA-Br)	Alfa Aesar	$\geq$ 98%
N-decyl-N,N,N-trimethylammonium chloride (DTMA-Cl)	Sigma Aldrich	$\geq$ 97%
N-decyl-N,N,N-trimethylammonium bromide (DTMA-Br)	Sigma Aldrich	$\geq$ 98%
N-decyl-N,N,N-trimethylammonium iodide (DTMA-I)	Synthesis	$\geq$ 99% [a]

Table 2: Synthesis method and the operating conditions. The molar ratio is expressed as tertiary amine:BnCl/MeI/DMC:MeOH.

QAS	Method	Molar ratio	T [°C]	Reaction time
DTMA-MC	PFR	1:5:10	120	4 h
DDMA-MC	PFR	1:5:10	120	24 h
TDMA-MC	Autoclave	1:5:10	120	6 d
TBMA-MC	Autoclave	1:5:10	120	3 d
BzDDMA-Cl	Autoclave	1:1:10	120	4 h
DTMA-I	Autoclave	1:5:10	20	2 h

2.2 Reaction Kinetics in a Batch Autoclave

The degradation reaction required relatively high temperatures of around 200 °C, for reaction times of no more than a single workday. Small volume (2.5 mL) Swagelok stainless steel autoclaves were devised to perform the kinetic experiments. These self-made reactors were low-cost, allowed for elevated temperatures and pressures, and were convenient to make in numbers. Moreover, their small volume meant that not a large amount of chemicals was required.

For each experiment, a new stock solution was made. This solution consisted of the concerning solvent, 0.2 M of QAS, and a known amount of F_2Bz as an internal standard. The 0.2 M was the maximum concentration that would dissolve for all solvent-QAS combinations. The internal standard was added to account for potential solvent evaporation. The reactors were flushed with the solvent, the stock solution, and then filled with the stock solution. A minimum amount of headspace was ensured, to limit the formation of a vapour phase. Thereafter, the autoclaves were locked, airtight. For each solvent-QAS combination, a time series was measured at five different temperatures. One time series consisted of five samples, taken after different reaction times, and the stock solution. At $t = 0$, five autoclaves were placed in a pre-heated oil bath. One-by-one they were later removed at regular, pre-determined time intervals, and immediately quenched in an ice bath.

All QASs from Table 1 were initially supposed to be analysed according to this method. However, upon testing, only the four methyl carbonate QASs showed sufficient degradation. The other compounds were too stable at temperatures up to ca. 250 °C, and these were thus excluded from this part of the experiments.

2.3 ^{1}H NMR Spectroscopy

After the reaction mixtures were quenched, a sample was added to a NMR tube, and a small amount of deuterated chloroform was added. If any signs of immiscibility were observed, further addition of the respective solvent ensured a single phase. The vials were analysed in a Bruker-400 400 MH NMR spectrometer, programmed to take 32 scans with a recycle delay of 2 s.

Fig. 2 represents a typical ^{1}H NMR sprectrum. The solvent's protons and peaks could change, as well as the number of longer chains and their protons. However, one peak remained a clear and distinguishable indicator the reaction progression, which was located around 1.7 ppm (C). By integrating the area under that peak, and comparing with the area of the internal standard, the concentration could be computed. Evidently, correcting for the amount of respective protons was also required. The internal standard confirmed that the protons at the end of the long chain (A) could also serve as a reference. This confluence between the results of the two reference peaks reaffirmed the results.

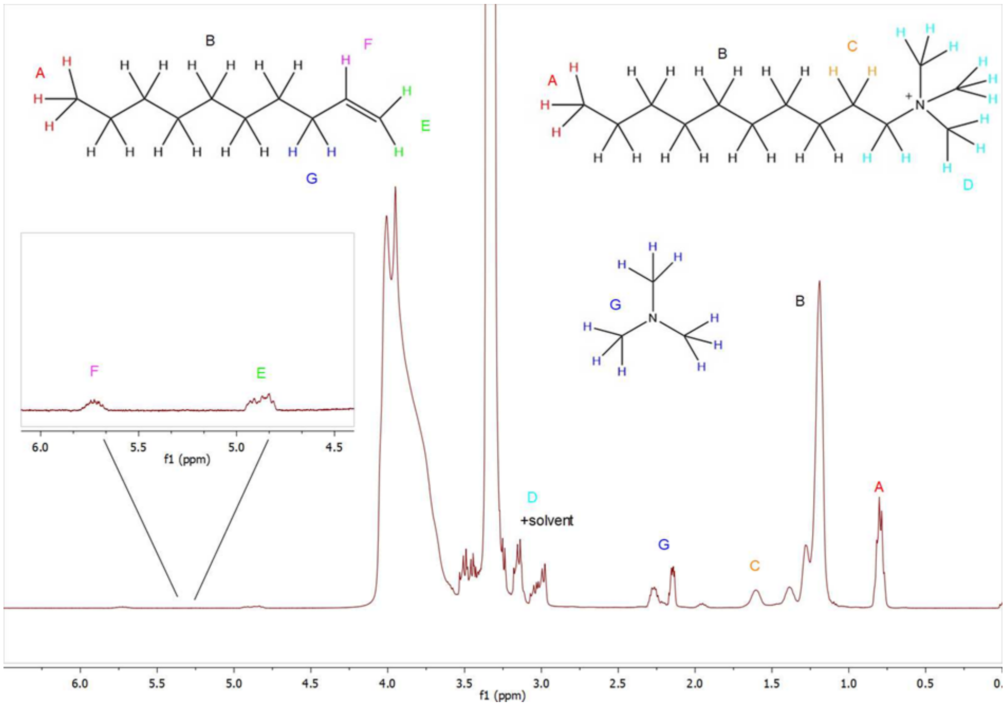


Figure 2: Examplary ^{1}H NMR sprectrum with peak justification of DTMA-MC and its degradation products.

It should be noted that all reactions that were performed in DMC caused some additional complexity, as DMC can re-alkylate the formed tertiary amine. This results in two different QASs. In the case of DTMA-MC, for example, the re-alkylated QAS would be tetramethylammonium methyl carbonate. Fortunately, in this case the degradation could still successfully be accounted for by the decrease in the peak at 1.7 ppm (C). However, for DDMA-MC, the re-alkylated QAS would be DTMA-MC, which in turn, could also degrade again. This second degradation reaction is indistinguishable from the first degradation on the ^{1}H NMR sprectrum. This means that the second degradation reaction would result in an overestimation of the actual reaction rate. Similarly for TDMA-MC and TBMA-MC, in which the second and third potential degradation reaction would result in an overestimation. Nevertheless, it is expected that these second and third degradation reaction rates are significantly lower the the first. This assumption, and its implications will be further discussed in Section 4.1.

2.4 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed to assess the thermal stability of the QASs in solid-state. This would mimic the conditions of a solventless production process. Also, the TGA allowed for measuring the compounds that had proven to be too stable in dissolved state. This concerns all non methyl carbonate QASs. The TGA measurements were carried out in a TA Instruments Q500. Inert and empty, platinum pans were tared by the TGA. Subsequently, the pans loaded on a 0.1 mg accuracy balance with approximately 15 ±1 mg of pure QAS sample. In the TGA, the sample was subjected to temperature gradient ranging from 30 °C to 300 °C at heating rates of 2, 5, 10, 20 °C min^{-1} under an inert nitrogen atmosphere. Prior to the temperature ramp, a half hour isothermal step at 30 °C was programmed. This reaffirmed the purity of the sample, as any water that it may have been attracted due to its hygroscopic nature, will be removed by the nitrogen purge. After that, every 0.25 s the temperature and mass of the sample were recorded.

3 Methods

3.1 Fitting the Batch Kinetics

The batch reactions were assumed to occur according to first-order kinetics. Hofmann elimination is known to be a second-order reaction, yet it is stated in literature that its conversion is independent of the initial concentration[4]. The assumption will later be validated. The QAS concentrations that were computed from the ^{1}H NMR spectral data were thus fitted in accordance with Eq. 1 and 2. A linear plot of $-ln(C) - ln(C_0)$ vs. t (Eq. 2) would confirm the first-order assumption, and allow for fitting k as its slope.

$$\frac{dC}{dt} = -kC \tag{1}$$

$$kt = -ln(C) - ln(C_0) \tag{2}$$

3.2 Isoconversional Method

The isoconverional method enables the ability to ascertain the mechanisms of the reaction, without making prior assumptions about a model. In this model, the reaction rate is represented by a temperature dependent part and a conversion dependent part (Eq. 3).

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{3}$$

$$\left[\frac{\partial \ln \frac{d\alpha}{dt}}{\partial T^{-1}}\right]_{\alpha} = -\frac{E_{\alpha}}{R} \tag{4}$$

At a constant conversion, the equation can be rewritten to obtain Eq. 4. As the remaining variables, t and T, are correlated through a fixed heating rate applied by the TGA, *i.e.* β. Resulting isoconversional methods can be either differential or integral, each with its advantages and disadvantages. In this study, the Kissinger-Akahira-Sunose method was selected, as depicted in Eq. 5[17]. Compared to other methods, this method has shown to have superior accuracy for determining activation energies[18].

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = constant - 1.0008\left(\frac{E_\alpha}{RT_\alpha}\right) \tag{5}$$

Analysis of the behaviour of E_α vs. α can then provide information about the actual degradation mechanism and the relating model. Significant variation of this relation would imply a complex process, with potentially multiple kinetic or physical steps involved[17]. In contrast, relative independence of these variables indicates a more straightforward reaction. Such reaction could be modelled with general Arrhenius correlations, *e.g.* for first order shown in Eq. 6.

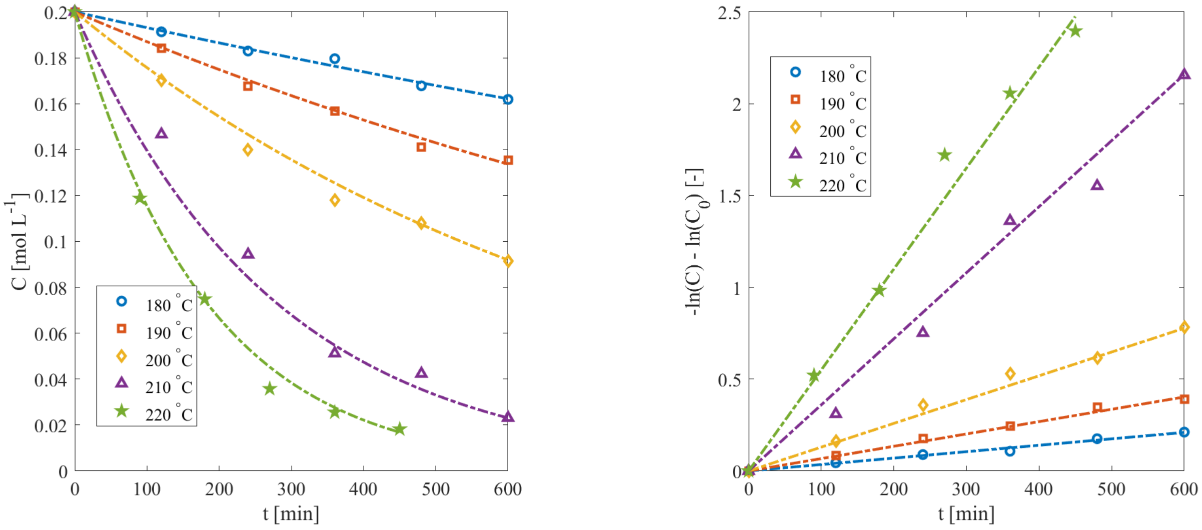
$$\ln\left(-\frac{1}{m}\frac{dm}{dt}\right) = \ln k_0 - \frac{E_A}{RT} \tag{6}$$

4 Results and Discussion

4.1 Degradation Kinetics

Analysis of the ^{1}H NMR data that was collected from the degradation reaction experiments, resulted in concentration profiles for all methyl carbonate QASs. DTMA-MC represented a typical profile as depicted in Fig. 3a. First-order kinetics were assumed for the subsequent fits. The required linearity that clearly followed, confirmed this assumption and the reaction rate constants were computed (Fig. 3b). This is in accordance with literature[4]. Further validation of the assumption of first-order was achieved by comparing the conversion for different initial concentrations (duplicates of 0.2, 0.4, and 0.6 M), and a reaction time of 1 h at 220 °C. This experiment led to identical conversions for all samples, also indicating first-order behaviour. It should be noted that for DTMA-MC and DDMA-MC in DMC, some instances of bad solubility were noticed after the reaction. It is unclear at which point in the reaction this demixing occurred, so its effect cannot be quantified. However, besides some lesser fits, no apparent consequences were recognised.

Although water was part of the four selected solvents, it remarkably prevented all MC QASs from degrading at all. Even after subjecting the water-dissolved samples for 8 h at an increased temperature of 250 °C, no observable conversion was noticed. Evidently, this rendered kinetic experiments in water infeasible. Only the other three solvents (MeOH, IPA, and DMC) were therefore further explored.



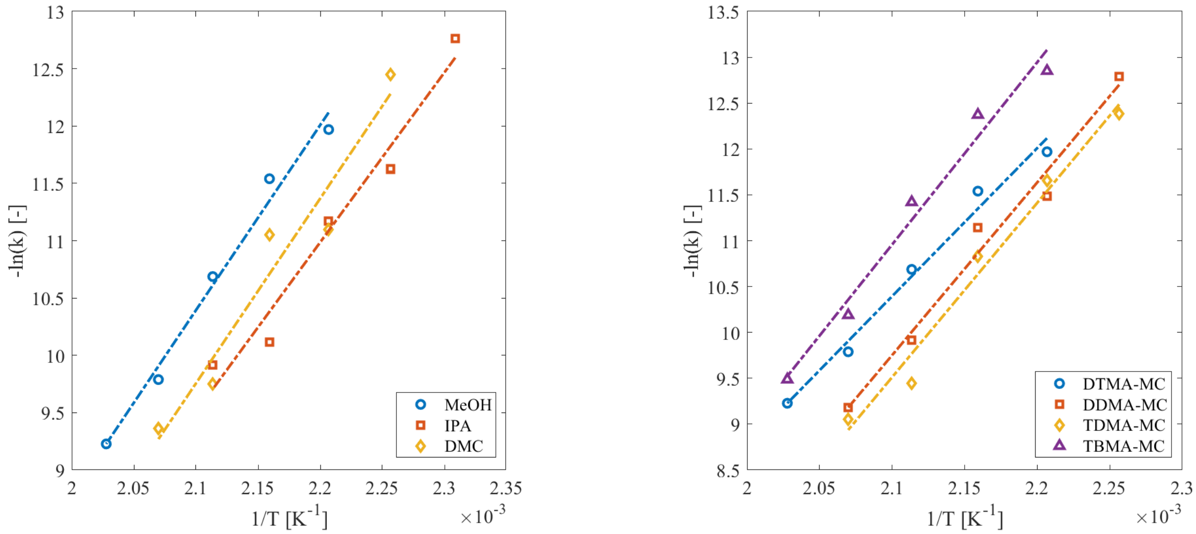
(a) Concentration profiles per temperature.

(b) First-order kinetic fits.

Figure 3: DTMA-MC concentration and first-order fitting $(-ln(C) - ln(C_0))$ plotted vs. reaction time, for all measured temperatures.

These reaction rate constants were thereafter subjected to Arrhenius fitting. For all compounds, linearity and comparable fits were observed. Fig. 4 shows two exemplary comparisons: first the comparison of DTMA-MC in MeOH, IPA, and DMC (Fig. 4a), and second a comparison DTMA-MC, DDMA-MC, TDMA-MC, and TBMA-MC in MeOH (Fig. 4b). This distinctly illustrates their relative degradation rates, and their inversely correlated thermal stability. The Arrhenius fits allowed for the determination of all first-order kinetic parameters. These values, along with the concerning 95% confidence intervals, and the R^2_{adj}

values have been compiled in Table 3. The coefficients of determination indicate reasonably well fits were acquired, with values ranging from 0.9345 to 0.9852.



(a) DMTA-MC in MeOH, IPA, and DMC.

(b) DTMA-MC, DDMA-MC, TDMA-MC, and TBMA-MC in MeOH.

Figure 4: Comparison of all Arrhenius plots for DTMA-MC and MeOH, respectively.

The Arrhenius parameters were used to interpolate and extrapolate reaction rate constants at 120 and 200 °C, respectively (Fig. 5). These values allow for a comparison of the QASs' thermal stability at a more or less average investigated temperature, as well as at a more conventional synthesis temperature. The relative degradation rates at 200 °C are particularly useful for identifying process intensification opportunities.

All QASs have clearly proven to be most stable in MeOH. Overall, IPA provides more stability than DMC, with the noteworthy exception of DTMA-MC. The slight demixing that was described earlier may have somewhat suppressed the reaction. Generally, these observations illustrate that MeOH would be most eligible as a solvent for synthesis of these compounds. Moreover, solventless production with excess DMC poses a significant drawback, as the product's stability is greatly diminished. Fig. 5 also shows that more long-chain side-chains cause a relative increase of the degradation rate. This is a well-known effect, as it provides more β-hydrogen sites where a potential Hofmann elimination can occur.

Finally, comparing the reaction rates of TDMA-MC and TBMA-MC demonstrates the overall increased stability that shorter chains provide. This is in line with findings by Friedli *et al.* in 1990[19]. The described trends apply both at 120 and 200 °C. It is peculiar that the effect of chain length (TDMA-MC vs. TBMA-MC) seems to be reversed at 200 °C in DMC. No viable explanation was found for this remarkable observation.

Table 3: Arrhenius parameters, confidence intervals, and coefficients of determination for all four methyl carbonate QASs.

	Solvent	E_a [kJ mol^{-1}]	$ln(k_0)$ [-]	R^2_{adj} [-]
DTMA-MC	MeOH	134.2 ±0.6328	23.51 ±0.1610	0.9852
	IPA	123.1 ±0.8991	21.60 ±0.2389	0.9653
	DMC	134.0 ±1.280	24.10 ±0.3330	0.9421
DDMA-MC	MeOH	156.5 ±0.8971	29.79 ±0.2333	0.9784
	IPA	152.7 ±1.012	29.23 ±0.2690	0.9712
	DMC	152.7 ±0.9116	25.77 ±0.2423	0.9707
TDMA-MC	MeOH	158.0 ±0.9259	30.40 ±0.2407	0.9774
	IPA	157.8 ±1.105	31.01 ±0.2938	0.9680
	DMC	139.2 ±0.8029	27.08 ±0.2182	0.9781
TBMA-MC	MeOH	165.2 ±0.9526	30.77 ±0.2424	0.9788
	IPA	166.3 ±1.286	32.32 ±0.3346	0.9612
	DMC	172.4 ±1.758	36.18 ±0.4780	0.9345

As mentioned in Section 2.3, the measurements in DMC posed the additional intricacy of secondary (DDMA-MC), and tertiary (TDMA-MC and TBMA-MC) degradation reactions. It was the expectation that these were slower, which is confirmed by Fig. 5. In all cases, less long-chain substituents results in a lower degradation rate. Moreover, the additional degradation reactions can only occur after the initial degradation and the consecutive re-alkylation have occurred. This will result in lower concentrations of secondary QASs and even lower concentrations of tertiary QASs. Overall, these unaccounted resulting reaction rates will be profoundly slower. The progression from DTMA-MC to DDMA-MC to TDMA-MC, with around a factor 2 increase in degradation rate seems plausible. Still, a slight overestimation the DDMA-MC and TDMA-MC degradation rate in DMC can not be precluded. For TBMA-MC in DMC, it seems that the reaction rate is probably overestimated.

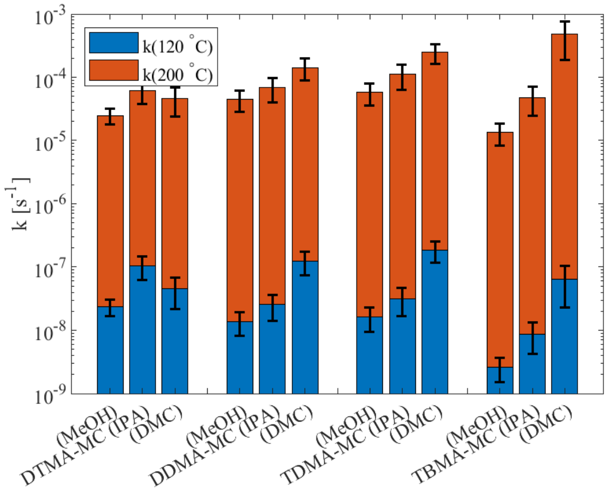


Figure 5: Computed reaction rate constants and their 95% confidence interval at 120 and 200 °C.

4.2 Solvent Effects

The remarkable observation of water's elimination of the degradation reaction inspired further investigation. Dekel *et al.* have also described water's profound stabilising effect[20]. It is generally known that polar (protic) solvents, such as water, MeOH, and IPA can provide shielding to certain reactive sites[16]. The fact water transcends MeOH and IPA in this regard is perhaps due to its higher dielectric constant. The dielectric constants for water, MeOH, and IPA at 25 °C are 79, 33, and 11, respectively[14]. Water's smaller molecular size may also contribute, as it could allow the molecule to better shield the concerning site.

Water was now added to the earlier investigated mixtures in small amounts to form binary solvent mixtures. DMC was excluded from these measurements, as it can be hydrolysed in water-based systems to form carbon dioxide and MeOH[21]. Water caused too many miscibility complications for TDMA-MC and TBMA-MC, so these QASs were also not included. For MeOH and IPA, mixtures with water in 10:1 and 5:1 ratio were measured after 7 h at 200 °C. The resulting conversions (comprised of five samples each) have been presented in Fig. 6. Calculated conversions in the pure solvents, based on the reaction rate constants at 200 °C, were added for reference.

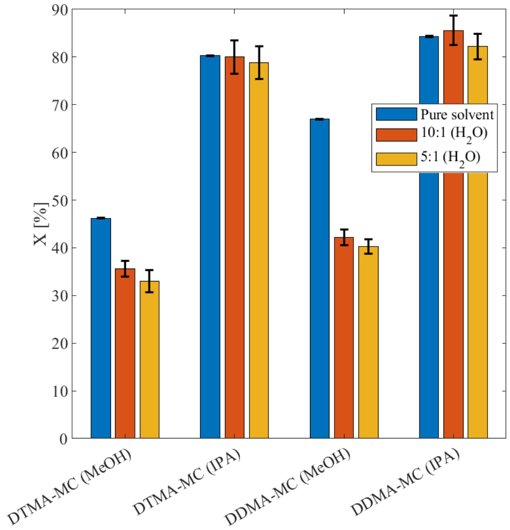


Figure 6: Conversion of four QASs in pure MeOH and IPA, as well as in 10:1 and 5:1 MeOH/IPA:H_2O mixtures. Reaction time was 7 h, at 200 °C.

In MeOH there appears to be a distinct effect of the addition of water, in increasing amount. In IPA the effect is certainly less pronounced, and in DDMA the 10:1 ratio caused higher conversions even. While higher proportions of water may contribute further, in these amounts the effect was considered negligible. The effect of water in MeOH definitely shows potential for further increased thermal stability of QASs. Further research could also unveil if the effect persists for more QASs and similar compounds. There may be an optimum ratio involved (varying per QAS), depending on the solubility and the influence on the formation reaction rate.

4.3 Thermogravimetric Analysis and Isoconversional Plots

The TGA experiments resulted in mass loss profiles vs. temperature for all 14 QASs. In Fig. 7 a typical plot is shown of BzDDMA-Cl for 2, 5, 10, and 20 K min^{-1}. Most compounds followed a similar trajectory, although some showed some slight slope transitions, indicating more complex (kinetic) behaviour.

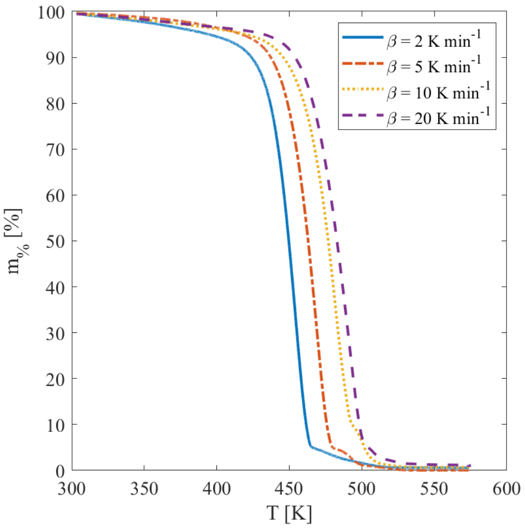
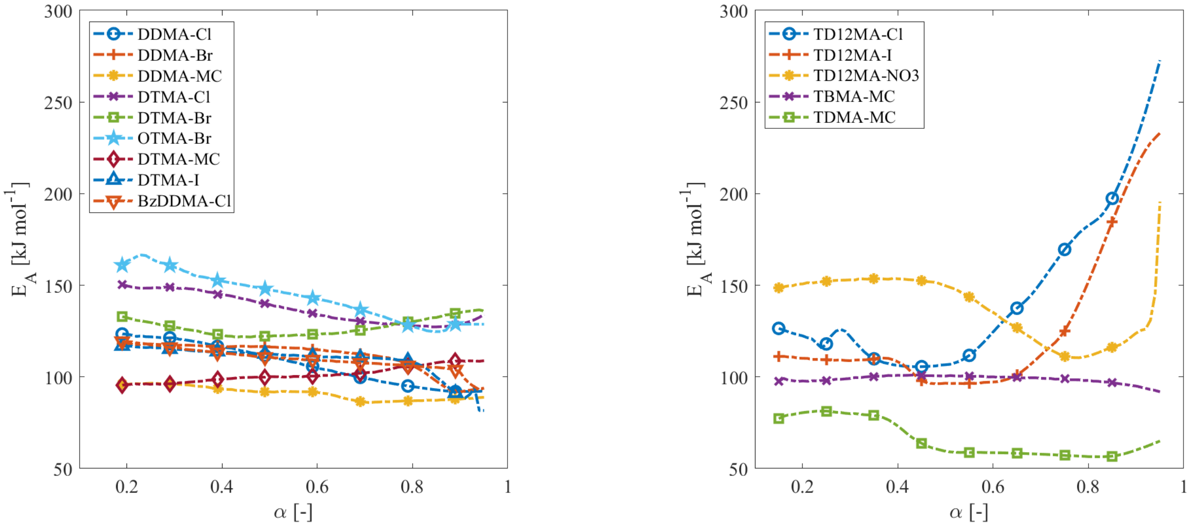


Figure 7: Relative mass loss of BzDDMA-Cl vs. temperature ranging from 30 to 300 °C for 2, 5, 10, and 20 K min^{-1} recorded by with TGA.

Subsequently, the TGA data was used to perform the isoconversional analysis. The resulting E_a vs. α plots provided further insight into the degradation mechanism, and they are shown in Fig. 8. They have been divided into di- and trimethyl QASs (Fig. 8a) and monomethyl QASs (Fig. 8b). Stable (*i.e.* independent) activation energies with an increase in conversion would signal simple first-order kinetics. A generally accepted deviation of up to 10% from low to high can be still be considered independent[17]. Only TBMA-MC appears to suffice with ca. 6%. DDMA-MC, DTMA-Cl, and DTMA-Br seem to come close with 16%, 18%, and 11% respectively. All other compounds far exceed these numbers, with TD(12)MA-Cl, TD(12)MA-I, and TD(12)MA-NO3 showing clear signs of complex kinetic or physical mechanisms. It is expected that one of their degradation products is involatile, and that at a certain progression in the reaction its evaporation limits the measured weight loss. In other words, from a certain α, evaporation was measured, rather than degradation. This appears as a resistance, and translates to a runaway of the activation energies.

Based on these observations, it is concluded that the QASs are generally prone to complex degradation mechanisms. The expected first-order kinetic fitting is therefore not possible here. Further kinetic analysis is required to obtain the desired kinetic parameters. Differential Thermal Analysis plots, deconvolution, and Master Plots are two approaches that could provide the required insight[17,22,23]. However, this is beyond the scope of this work.



(a) Di- and trimethyl QASs

(b) Monomethyl QASs

Figure 8: Isoconversional plots of all 14 measured QASs. The E_a vs. α relation indicates possible reaction mechanisms.

4.4 Solid-State Thermal Stability

In the previous section it was concluded that no reliable kinetic constants could be computed. Still, the thermogravimetric data does provide insight into the (relative) thermal stability of the measured compounds. In Table 4, the average E_a values based on the isoconversional analysis and (an average over the four different heating rates) $T_{50\%}$, the temperature at which 50% of the compound had degraded, are presented. As explained earlier, the activation energies are model-less, and they are only shown for reference and comparison purposes. For both parameters, higher values correspond with a higher degree of thermal stability.

In general, the trimethyl compounds demonstrate to be more stable than the dimethyl compounds. This was expected, as more long-chain sustituents increase the probability of a Hofmann elimination. This perception should also extend from the dimethyl to monomethyl QASs. However, due to the aforementioned formation of involatile species, the values of the monomethyl compounds are magnified. Based on the analysis thermal stability provided by various anions can also be compared. Overall, their thermal stability appears to relate according to the following sequence: $Br^- > Cl^- > NO_3^- > I^- > MC^-$. With respect to the halides' relative basicity, one would expect I^- ensure the most stable QAS-anion combination though. No explanation was found for this remarkable observation.

The thermogravimetric data also demonstrates the profound impact of solvents on the thermal stability. DDMA-MC in MeOH, for example, will reach 50% conversion at 200 °C after ca. 200 h. In contrast, in solid-state, the same compound reaches 50% degradation at an average of 130 °C after ca. 18 min. Methyl carbonate QASs are therefore already excluded from production at high temperatures without a solvent.

Table 4: Average E_a values and average temperatures at which 50% of the compound had degraded ($T_{50\%}$) in solid-state. [a]These QASs showed clear signs of evaporation limitation, resulting in a probable overestimation of both their computed values.

	QAS	Average E_a [kJ mol^{-1}]	$T_{50\%}$ [K]
Monomethyl	TDMA-MC	65.69	483.0
	TBMA-MC	94.55	463.4
	TD(12)MA-NO3[a]	138.6	529.6
	TD(12)MA-Cl[a]	142.6	542.4
	TD(12)MA-I[a]	123.7	524.3
Dimethyl	DDMA-MC	93.37	468.5
	DDMA-Cl	110.5	483.9
	DDMA-Br	110.2	506.4
	BzDDMA-Cl	109.3	468.0
Trimethyl	DTMA-MC	96.52	460.6
	OTMA-Br	134.4	528.8
	DTMA-Cl	117.2	529.9
	DTMA-Br	128.7	533.0
	DTMA-I	132.0	514.4

5 Conclusions

The degradation reaction's kinetic parameters have been successfully determined for four methyl carbonate QASs in MeOH, IPA, and DMC. Water showed no observable degradation, and in term of thermal stability it was found that MeOH > IPA > DMC. As expected, more long-chain substituents and longer chains resulted in lower thermal stability. Binary solvent mixtures were also investigated, and small additions of water to MeOH (10:1 and 5:1 ratio) further enhanced the QAS stability. This effect was not observed in IPA. It can be concluded that MeOH is most suitable for stabilising the methyl carbonate QASs during their production, and that an optimum MeOH:water ratio could be beneficial to further explore.

In solid-state, 14 QASs were evaluated. Isoconversional analysis proved that their kinetic and physical behaviour was too complex to determine Arrhenius parameters. Nevertheless, the isoconversional method did provide average, model-less E_a values. Furthermore, the thermogravimetric data allowed for the computation of average $T_{50\%}$ values, which indicated at which temperature 50% of the compound had degraded. Together, these to parameters provided a comparison of the relative thermal stability of the compounds. This showed that different anions provided various degrees of stability ($\mathrm{Br}^- > \mathrm{Cl}^- > \mathrm{NO}_3^- > \mathrm{I}^- > \mathrm{MC}^-$). In accordance with the findings in dissolved state, solid-state thermal stability showed to decrease with more, and longer long-chain substituents. Finally, degradation rates have proven to be orders of magnitude faster in absence of a solvent.

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