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

Citation for published version (APA):

Kleijwegt, R. J. T., Winkenwerder, W., Baan, W., & van der Schaaf, J. (2022). Degradation Kinetics and Solvent Effects of Various Long-Chain Quaternary Ammonium Salts. *International Journal of Chemical Kinetics*, 54(1), 16-27. <https://doi.org/10.1002/kin.21537>

DOI:

[10.1002/kin.21537](https://doi.org/10.1002/kin.21537)

Document status and date:

Published: 01/01/2022

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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RESEARCH ARTICLE

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 the degradation kinetics of various QASs and the associated solvent effects. The degradation kinetics of four methyl carbonate QASs were determined in various polar solvents in stainless steel batch autoclaves. ¹H 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 no degradation, and methanol (MeOH) was the solvent that provided the second-best stability. Water–MeOH mixtures may provide an overall optimum. Moreover, and longer long-chain substituents increased the degradation rate. Thermogravimetric analysis was used to obtain the thermal stability in a solid state, that is, 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 the solid state demonstrated the challenges of solventless QAS production.

KEYWORDS

degradation kinetics, solvent effects, thermal stability, thermogravimetric analysis

1 | INTRODUCTION

Surfactants serve a plethora of different use cases in a continuously expanding market.^{1–4} These versatile compounds are predominately applied as detergents.⁵ Cationic surfactants, such as quaternary ammonium salts (QAS), are employed in more speciality-focused applications, as for example, antimicrobials^{5,6} and more recently in ion-exchange membranes.^{7–9} These increasingly demanding

applications require highly stable compounds. Recent studies have therefore already focused on the elucidation of their thermal and alkaline stability.^{7,10,11} Nevertheless, the amount of relevant attainable kinetic data of QAS degradation is still quite limited.

QASs are conventionally produced in batch Menshutkin^{12–14} reactions, but novel production methods with dimethyl carbonate (DMC) are also being explored.^{15,16} Their production is kinetically limited, and

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FIGURE 1 The main mechanisms for degradation (A) Hofmann elimination and (B) nucleophilic substitution^{7,10,19}

there is a large potential for process intensification.^{14,15,17,18} 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 optimization of the process.

The scope of this research is to determine the degradation kinetics of various QASs with and without solvents. These kinetics are currently not available in the literature, and they could disclose opportunities to further enhance 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 numbers 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. The Hofmann elimination has been well known since 1958 and is considered to be the main reaction pathway.^{19,20} With hydroxide present, different elimination and substitution mechanisms are possible.²¹ The Hofmann elimination 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 in Figure 1A.

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 favorable than the elimination of a methyl group. This also implies that more long-chain substituents make it statistically 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 α -carbon of the long-chain substituent.⁷ Here, an alkane species is formed which contains the anion species of the original QAS and a tertiary amine. This reaction pathway is also shown in Figure 1B. However, under most reaction conditions, it is presumed to have a less significant contribution to the degradation.^{7,10}

1.2 | Solvent effects

It is well known that solvents and their polarity greatly influence the rate of QAS production.^{18,22–25} It is expected that the degradation reaction is also sensitive to the solvent used and its polarity, as they can provide shielding to certain reactive sites.^{26,27} Higher polarity is expected to better shield the sensitive β -hydrogen site from potential elimination. Water, methanol (MeOH), and isopropanol (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, the 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 synthesized. All reactants and QASs, their source, and their purity are listed in Table 1. Besides these chemicals, all required solvents were obtained in technical grade from VWR Chemicals. The purity of MeOH and IPA was specified as 99.25% and 99.75%, respectively. 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 (PFR). The PFR has been thoroughly described in earlier work.¹⁸ The batch reactors were loaded with the respective reactants and MeOH as a solvent and placed in a preheated 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

TABLE 1 All used chemicals, their source, and their purity

Chemical	Source	Purity
<i>Reactants</i>		
<i>N,N</i> -Dimethyldodecylamine (DMDA)	TCI	≥95%
<i>N</i> -Methyldodecylamine (MDDA)	Sigma Aldrich	≥ 95%
Tri- <i>N</i> -decylamine (TDA)	TCI	≥97%
Tri- <i>N</i> -butylamine (TBA)	TCI	≥95%
Dimethyl carbonate (DMC)	Sigma Aldrich	≥99%
Benzyl chloride (BnCl)	Sigma Aldrich	≥99%
Methyl iodide (MeI)	Sigma Aldrich	≥99%
<i>QASs</i>		
<i>N,N,N</i> -Tridecyl- <i>N</i> -methylammonium methylcarbonate (TDMA-MC)	Synthesis	≥95% ^a
<i>N,N,N</i> -Tributyl- <i>N</i> -methylammonium methylcarbonate (TBMA-MC)	Synthesis	≥96% ^a
<i>N,N,N</i> -Tridodecyl- <i>N</i> -methylammonium nitrate (TD(12)MA-NO ₃)	Sigma Aldrich	≥99%
<i>N,N,N</i> -Tridodecyl- <i>N</i> -methylammonium chloride (TD(12)MA-Cl)	Sigma Aldrich	≥98%
<i>N,N,N</i> -Tridodecyl- <i>N</i> -methylammonium iodide (TD(12)MA-I)	Sigma Aldrich	≥97%
<i>N,N</i> -Didecyl- <i>N,N</i> -dimethylammonium methylcarbonate (DDMA-MC)	Synthesis	≥98% ^a
<i>N,N</i> -Didecyl- <i>N,N</i> -dimethylammonium chloride (DDMA-Cl)	Sigma Aldrich	≥98%
<i>N,N</i> -Didecyl- <i>N,N</i> -dimethylammonium bromide (DDMA-Br)	Sigma Aldrich	≥98%
<i>N</i> -Benzyl- <i>N</i> -decyl- <i>N,N</i> -dimethylammonium chloride (BzDDMA-Cl)	Synthesis	≥97% ^a
<i>N</i> -Decyl- <i>N,N,N</i> -trimethylammonium methylcarbonate (DTMA-MC)	Synthesis	≥98% ^a
<i>N</i> -Octyl- <i>N,N,N</i> -trimethylammonium bromide (OTMA-Br)	Alfa Aesar	≥98%
<i>N</i> -Decyl- <i>N,N,N</i> -trimethylammonium chloride (DTMA-Cl)	Sigma Aldrich	≥97%
<i>N</i> -Decyl- <i>N,N,N</i> -trimethylammonium bromide (DTMA-Br)	Sigma Aldrich	≥98%
<i>N</i> -Decyl- <i>N,N,N</i> -trimethylammonium iodide (DTMA-I)	Synthesis	≥99% ^a

^aThese QASs were synthesized, and their purity was measured with ¹H NMR.

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

QAS	Method	Molar ratio	<i>T</i> (°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 days
TBMA-MC	Autoclave	1:5:10	120	3 days
BzDDMA-Cl	Autoclave	1:1:10	120	4 h
DTMA-I	Autoclave	1:5:10	20	2 h

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 are presented 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 number of long-chain substituents severely diminishes. After the synthesis, all remaining reactants and MeOH were

evaporated with a rotary evaporator or a vacuum oven. Thereafter, the purity was verified by means of ¹H NMR spectroscopy (Table 1).

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) 316 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 a small amount of chemicals was required. The required parts to build the reactors were obtained from Swagelok and are listed below (including their corresponding catalogue numbers):

1. 1/4" tubing (SS-T4-S-035-20)
2. 1/4" nuts (female tube fitting: SS-402-1)
3. 1/4" caps (male tube fitting: SS-400-C)

FIGURE 2 Exemplary ^1H NMR spectrum with peak justification of DTMA-MC and its degradation products

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 vapor 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 preheated oil bath. One by one they were later removed at regular, predetermined time intervals and immediately quenched in an ice bath to ensure the reaction was stopped immediately.

All QASs from Table 1 were initially supposed to be analyzed according to this method. However, upon testing, only the four methyl carbonate QASs showed sufficient degradation. The other compounds were too stable at tem-

peratures up to ca. 250°C , and these were thus excluded from this part of the experiments.

2.3 | ^1H NMR spectroscopy

After the reaction mixtures were quenched, a sample was added to an 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 analyzed in a Bruker-400 400 MHz NMR spectrometer, programmed to take 32 scans with a recycle delay of 2 s.

Figure 2 represents a typical ^1H NMR spectrum of DTMA-MC and its degradation products. Depending on the QAS (its number of long alkyl chains) and solvent used during the experiment, protons and their peak positions could change. However, peak C in Figure 2 remained a clear and distinguishable indicator for the reaction progression. By integrating the area under that peak, and comparing it 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. The peak was unaffected by the reaction, as expected. This confluence between the results of the two reference peaks reaffirmed the results.

It should be noted that all reactions that were performed in DMC caused some additional complexity, as DMC can realkylate the formed tertiary amine. This results in two different QASs. In the case of DTMA-MC, for example, the realkylated 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 realkylated QAS would be DTMA-MC, which in turn, could also degrade again. This second degradation reactions is indistinguishable from the first degradation on the ^1H NMR spectrum. 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 reactions would result in an overestimation. Nevertheless, it is expected that these second and third degradation reaction rates are significantly lower than 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 the 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 a dissolved state. This concerns all nonmethyl 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 the pure QAS sample. In the TGA, the sample was equilibrated at 30°C for 30 min and then subjected to a temperature gradient ranging from 30 to 300°C at heating rates of 2, 5, 10, and $20^\circ\text{C min}^{-1}$ under a nitrogen atmosphere. 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 the first-order kinetics. The Hofmann elimination is known to be a second-order reaction, yet it is stated in

the literature that its conversion is independent of the initial concentration.⁷ The assumption will later be validated. The QAS concentrations that were computed from the ^1H NMR spectral data were thus fitted in accordance with Equations (1) and (2). A linear plot of $-\ln(C) - \ln(C_0)$ versus t (Equation 2) would confirm the first-order assumption and allow for fitting k as its slope.

$$\frac{dC}{dt} = -kC, \quad (1)$$

$$kt = -\ln(C) - \ln(C_0). \quad (2)$$

3.2 | Isoconversional method

The isoconversional method enables the ability to gain insights regarding 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 (α) (Equation 3). The conversion is computed from the TGA data according to Equation (5), where m_0 is the initial mass and m is the mass at time, t .

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

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

$$\alpha = \frac{m_0 - m}{m_0}. \quad (5)$$

At a constant conversion, Equation (3) takes a more explicit form in Equation (4), where t and temperature (T) are correlated through the fixed heating rate (applied by the TGA), that is, β . The differential or the integrated form could be used, each having its advantages and disadvantages. The Kissinger–Akahira–Sunose method (Equation 6) was selected because it is reported to have superior accuracy for determining activation energies.^{28,29} For each (discretized) value of α , ranging from 0.05 to 0.95, Equation (6) was used to fit the respective β and T_{α} to acquire E_{α} .

$$\ln \left(\frac{\beta_i}{T_{\alpha,i}^{1.92}} \right) = \text{constant} - 1.0008 \left(\frac{E_{\alpha}}{RT_{\alpha}} \right). \quad (6)$$

Analysis of the behavior of E_{α} versus α can provide information about the complexity of the degradation mechanism. Activation energy independent of conversion (where

(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 versus reaction time, for all measured temperatures

E_α is not changing) indicates a single-step mechanism. Such a process could be modeled with Arrhenius correlations, for example, first order (Equation 7). A varying E_α as conversion proceeds indicates a multistep process where the rate-determining step, and thus also E_α , is changing during the process.²⁸

$$\ln\left(-\frac{1}{m} \frac{dm}{dt}\right) = \ln k_0 - \frac{E_A}{RT}. \quad (7)$$

4 | RESULTS AND DISCUSSION

4.1 | Degradation kinetics

Analysis of the ^1H 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 Figure 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 (Figure 3B). This is in accordance with the literature.⁷ Further validation of the assumption of the 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 the first-order behavior. 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 slight curvature in the plot, no apparent consequences were recognized. No substantial amount of solvent evaporation was observed in any of the experiments.

Although the 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. Other studies have shown that methyl carbonate can react with water to form methanol and bicarbonate.^{20,30} This change in anion could result in a more stable QAS, which would explain the profound stabilizing effect that water facilitates.

These reaction rate constants were thereafter subjected to Arrhenius fitting. For all compounds, reasonably linear fits were observed. Figure 4 shows two exemplary comparisons: first the comparison of DTMA-MC in MeOH, IPA, and DMC (Figure 4A) and second a comparison DTMA-MC, DDMA-MC, TDMA-MC, and TBMA-MC in MeOH (Figure 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 are compiled in Table 3. The coefficients of the

(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

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

determination indicate reasonably good fits were acquired with values ranging from 0.9345 to 0.9852.

The Arrhenius parameters were used to interpolate and extrapolate reaction rate constants at 120 and 200 °C, respectively (Figure 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 as generally used in industry. 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 water (with no observable degradation), followed by MeOH. Overall, IPA provides more stability than DMC, with the

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

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 the synthesis of these compounds. Moreover, solventless production with excess DMC poses a significant drawback, as the product's stability is greatly diminished. Figure 5 also shows that more long-chain substituents cause a relative increase in 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 1990.³¹ 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.

As noted in Section 2.3, the measurements in DMC posed the additional intricacy of secondary (with DDMA-MC, TDMA-MC, and TBMA-MC) and tertiary (with TDMA-MC and TBMA-MC) degradation reactions, which were expected to be slower. This is supported by Figure 5, where in all cases less long-chain substituents result in a lower degradation rate. Moreover, these additional degradation reactions can only occur after the initial degradation and the consecutive realkylation have transpired. This will lead to lower concentrations of secondary QASs and even lower concentrations of tertiary QASs, which can be considered to be negligible altogether. Overall, these unaccounted (additional) degradation reaction rates will be profoundly slower. Therefore, the measured rate constants shown in Figure 5 provide a reasonable comparison. Here the increased degradation rate by about a factor of two for each step in the progression DTMA-MC to DDMA-MC to TDMA-MC seems reasonable. However, for TBMA-MC in DMC it seems that the measured reaction rate may be an overestimate since shorter chain amines alkylate faster.

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 stabilizing effect in a recent paper.³² It is generally known that polar (protic) solvents, such as water, MeOH, and IPA can provide shielding to certain reactive sites.²⁶ 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.²³ Water's relatively 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 hydrolyzed in water-based systems to form carbon dioxide and MeOH.³³ Water caused immiscibility 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 (composed of five samples each) are presented in Figure 6. Calculated conversions in the pure

FIGURE 6 Conversion of four QASs in pure MeOH and IPA, as well as in 10:1 and 5:1 MeOH/IPA:H₂O mixtures. Reaction time was 7 h at 200°C

solvents, based on the reaction rate constants at 200°C, were added for reference.

The addition of some water to MeOH has a significant stabilizing effect. Ratios of 5:1 and 10:1 in MeOH: H₂O show only slight differences. It would be interesting to explore ratios with less water to see if there is a transition trend. The effect of adding water to IPA was statistically insignificant for the ratios tested. It may require higher concentrations of water to impart a stabilizing effect for IPA solutions. This remarkable observation may be caused by trace amounts of water that are already present in the solvents. While higher proportions of water may contribute further, in these amounts the effect was considered negligible. The effect of water on 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 versus temperature for all 14 QASs. In Figure 7, two typical plots are shown that have been recorded between 30 and 300°C at 2, 5, 10, and 20 K min⁻¹. BzDDMA-Cl (Figure 7A)

FIGURE 7 Relative mass loss versus temperature ranging from 30 to 300°C for 2, 5, 10, and 20 K min⁻¹ recorded with TGA

FIGURE 8 Isoconversional plots of all 14 measured QASs. The E_{α} versus α relation indicates possible reaction mechanisms

represents a typical trajectory that was observed with most compounds. Conversely, Figure 7B (of DTMA-MC) indicates more complex (kinetic) behavior. The transitions in the slope were observed with TD12MA-Cl, TD12MA-I, and TD12MA-NO₃ as well, and they imply a multistep process. It is presumed that a physical process (evaporation) mainly occurs after the first bend in the graph (leading to a more shallow slope).

Subsequently, the TGA data were used to perform the isoconversional analysis. The resulting E_{α} versus α plots provided further insight into the degradation mechanism, and they are shown in Figure 8. They have been divided into di- and trimethyl QASs (Figure 8A) and monomethyl

QASs (Figure 8B). Stable (i.e., independent) activation energies with an increase in conversion would signal simple first-order kinetics. A deviation of up to 10% from low to high can be still be considered independent.²⁸ 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 not boiling at these temperatures, and its evaporation is gradual rather than instantaneous. At a certain progression in the reaction, its evaporation limits the

TABLE 4 Average E_α values and average temperatures at which 50% of the compound had degraded ($T_{50\%}$) in solid state

	QAS	Average E_α (kJ mol ⁻¹)	$T_{50\%}$ (K)
	TDMA-MC	65.69	483.0
	TBMA-MC	94.55	463.4
Monomethyl	TD(12)MA-NO ₃ ^a	138.6	529.6
	TD(12)MA-Cl ^a	142.6	542.4
	TD(12)MA-I ^a	123.7	524.3
	DDMA-MC	93.37	468.5
Dimethyl	DDMA-Cl	110.5	483.9
	DDMA-Br	110.2	506.4
	BzDDMA-Cl	109.3	468.0
	DTMA-MC	96.52	460.6
	OTMA-Br	134.4	528.8
Trimethyl	DTMA-Cl	117.2	529.9
	DTMA-Br	128.7	533.0
	DTMA-I	132.0	514.4

^aThese QASs showed clear signs of evaporation limitation, resulting in a probable overestimation of both their computed values.

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 isoconversional 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.^{28,34,35} However, this is beyond the scope of this work.

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 provide insight into the (relative) thermal stability of the measured compounds. In Table 4, the average E_α 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 were demonstrated to be more stable than the dimethyl compounds. This

was expected, as more long-chain substituents 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 species with a boiling point exceeding the TGA temperature, 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⁻ > NO₃⁻ > 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 demonstrate the profound impact of solvents on 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.

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 terms 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 stabilizing the methyl carbonate QASs during their production and that an optimum MeOH: water ratio could be beneficial to explore further.

In solid state, 14 QASs were evaluated. Isoconversional analysis proved that their kinetic and physical behavior was too complex to determine Arrhenius parameters. Nevertheless, the isoconversional method did provide average, model-less E_α 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 parameters provided a comparison of the relative thermal stability of the compounds. This showed that different anions provided various degrees of stability (Br⁻ > Cl⁻ > NO₃⁻ > I⁻ > MC⁻).

In accordance with the findings in the dissolved state, solid-state thermal analysis showed stability decreased with increasing chain length and with increasing number

of longer chains attached to the quaternary nitrogen. Finally, degradation rates have proven to be orders of magnitude faster in the absence of a solvent.

ACKNOWLEDGMENTS

This research was carried out within the HighSinc Program – a joint research initiative between Nouryon and the Department of Chemical Engineering and Chemistry at the Eindhoven University of Technology.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author, upon reasonable request.

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How to cite this article: Kleijwegt RT, Winkenwerder W, Baan W, van der Schaaf J. Degradation kinetics and solvent effects of various long-chain quaternary ammonium salts. *Int J Chem Kinet.* 2022;54:16–27. <https://doi.org/10.1002/kin.21537>