Chemical Structures of Thermal Stable Long-Chain n-Alkyl Amines Used in Corrosion Inhibiting Formulations in Water-Steam and Heating Water Systems in the Power Industry

Gerd Knupp¹, Peter Kusch¹, Marian Kozupa², and Maria Majchrzak²

¹ Department of Applied Natural Sciences
² Institute of Heavy Organic Synthesis “Blachownia”, ul. Energetyków 9, Pl-47-225 Kędzierzyn-Koźle, Poland

Gas chromatography with flame-ionization detection (FID) and gas chromatography-mass spectrometry (GC/MS) has been used for structure elucidation of long-chain primary n-alkyl amines after derivatization with trifluoroacetic anhydride (TFAA). Electron impact ionization- (EI) and positive chemical ionization- (PCI) mass spectra of trifluoroacetylated derivatives of the identified n-alkyl amines are presented. The corrosion inhibiting n-alkyl amines were applied in the investigation of a new anticorrosive and antifouling formulation for water-steam circuit of energy systems in the power industry. The presented results are part of an EU-funded international collaboration with partners from research institutes and industry from Poland, Lithuania, Romania, France and Germany (EUREKA project BOILTREAT E12426).

1 Introduction

Traditionally, the most common way to reduce corrosion is to add a corrosion inhibitor to a corrosive system to preserve metals. Corrosion inhibitors are chemical compounds or formulations which, when present in small amounts in an aggressive medium, inhibit corrosion by bringing about changes in the surface condition of the metal [1, 6-7, 17]. These should be low toxic, biodegradable and soluble in aqueous medium. One of the largest group of organic corrosion inhibitors is the class of organic amines. Aliphatic and aromatic amines, mono-, di-, or polyamines and their salts, all are used as corro-
sion inhibitors [2]. In agreement with the ideas of green chemistry, new types of corrosion inhibitors should result in reduced use of many of the more toxic aromatic amines/salts. The development and testing under industrial conditions of a new class of long-chain aliphatic mono-, di- or polyamines or their salts as replacement is one of the objectives of an international cooperation with partners from research institutes and industry from Poland, Lithuania, Romania, France and Germany (EUREKA project BOILTREAT E!2426) [3]. As a partner of this R&D-project our group is engaged with the analysis and the fate of these commercially available and patented corrosion inhibitors (e.g. Primene JM-T™, Armeen® HTD, Kotamina®), which are used in boiler water systems in the power industry. Neither the full structure nor details of the degradation of these compounds under vigorous conditions have been studied before.

In a previous paper [11] we have reported on a sensitive gas chromatographic method for the identification and quantitative determination of trifluoroacetylated derivatives of tert-octadecylamines Primene JM-T™-type. In the present work we report on the structure elucidation of long-chain primary n-alkyl amines of the Armeen® HTD-type (Fig. 1) by gas chromatography and gas chromatography-mass spectrometry. The EI- and PCI- mass spectra of trifluoroacetylated derivatives of these alkyl amines are reported and discussed. These results are part of the further investigation of a new class of anticorrosive and antifouling formulation for water-steam circuit of energy systems in the power industry [3, 9-10, 18]. They are important to understand the processes during its technical use and its ecological and economical impact.

2 Experimental

2.1 Chemicals

Armeen® HTD obtained from AKZO Nobel Surface Chemistry (Arnhem, The Netherlands) as well as 1-hexadecylamine (90 %) from ACROS ORGANICS (Geel, Belgium) were used in this investigation. n-Hexane for HPLC (Biosolve B.V., Valkenswaard, The Netherlands), tetrahydrofurane (THF) LiChrosolv for HPLC (Merck), trifluoroacetic anhydride (TFAA) from Macherey-Nagel (Düren, Germany) and 5 % dimethydichlorosilane (DMDCS) in toluene (Sylon CT) from Supelco (Bellefonte, PA, U.S.A.) were used. A mixture of C₆ – C₄₄ hydrocarbons in cyclohexane (ASTM D2887 Quantitative Calibration Mix) obtained from Supelco was used to calculate the retention index of each compound.

2.2 Derivatization

The derivatization procedure was the same as in our previous work [11].
Chemical Structures of Thermal Stable Long-Chain n-Alkyl Amines

Fig. 1. Chemical structures of selected investigated primary long-chain alkyl amines and their trifluoroacetylated (TFA) derivatives: a) 1-aminooctadecane; b) N-(1-octadecyl)-trifluoroacetamide.

2.3 Instrumentation

Gas chromatographic analyses were performed using an Clarus 500 gas chromatograph from PerkinElmer Instruments (Norwalk, CT, U.S.A.), equipped with two split/splitless and two flame-ionization detectors (FID). Chromatographic data were processed with TotalChrom Workstation version 6.3 software (PerkinElmer Instruments).

GC/MS measurements were made using an ThermoQuest Trace 2000 gas chromatograph (ThermoQuest CE Instruments, Milan, Italy) interfaced to a ThermoQuest/Finnigan Voyager quadrupole mass spectrometer (ThermoQuest/Finnigan MassLab Group, Manchester UK) operated in electron impact ionization (EI) mode and positive chemical ionization (PCI) mode. A Combi-PAL autosampler (CTC Analytics AG, Zwingen, Switzerland) was used for sampling. Recording, processing and analysing of data was done by use of the ThermoQuest Xcalibur data system with NIST 02 mass spectra library. The detailed analytical conditions for GC and GC/MS measurements were described in our previous work [12].

3 Results and Discussion

Amines are generally known to be very difficult to analyze by gas chromatography due to their basic character [4, 11]. In addition to the basic character, the amino group introduces a large dipole in the molecule. The dipole is responsible for strong interaction with silanol groups and siloxane bridges in the structure of the stationary phase of the GC capillary column. This often results in nonlinear adsorption effects and can be seen as strong tailing peaks in the chromatogram. Most critical are the primary alkyl amines and alkyl diamines [5]. The best way to prevent interaction of the strong dipole and to improve the chromatographic separation and the detection sensitivity is a prior derivatization step. Good results from our previous work [11] with acylation of alkyl amines with trifluoroacetic anhydride (TFAA) stimulated us to proceed our work with derivatization of the investigated long-chain alkyl amines (Fig. 1) with the same derivatizing reagent (TFAA) [8, 11] (equation 1):
Fig. 2. GC/FID chromatogram of trifluoroacetylated (TFA) derivative of Armeen® HTD (hydrogenated tallow amine) in THF. Fused silica capillary column: DB-17ms, 60 m x 0.25 mm I.D., film thickness 0.25 µm. Column temperature programmed from 150°C (1 min hold) at 3°C min⁻¹ to 280°C (hold 50 min). Split/splitless injector: 290°C. Helium constant pressure 120 kPa, split flow 20 cm³ min⁻¹. FID 320°C. For retention data and peak identification, see Table 1.

\[
\text{R-NH}_2 + (\text{CF}_3\text{CO})_2\text{O} \rightarrow \text{R-NH-C(O)CF}_3 + \text{CF}_3\text{COOH}
\]  

Fig. 2 shows the GC/FID chromatogram of trifluoroacetylated derivative of Armeen® HTD (hydrogenated tallow amine [15]) in THF obtained by using moderately polar DB-17ms fused silica capillary column. The identification of compounds was carried out by calculation of increments of retention indices and interpretation of the recorded mass spectra of trifluoroacetylated derivatives of Armeen® HTD and 1-hexadecyloamine (standard substance). As can be seen from Table 1, the increments of retention indices of compounds differ for both non-polar and moderately polar capillary columns by average 97 index units. According to basis of the retention index system itself, the theoretical value is equal to 100 index units, while the members of a homologous series differ by 100 index units per methylene group [16]. The mass spectra formed by the electron-impact ionization (EI) of the trifluoroacetylated \( n \)-alkyl amines (C\(_{14} \) – C\(_{20} \)) identified in Armeen® HTD are presented in Fig. 3. The characteristic fragments at \( m/z \) 240, 254, 268, 282, 296, 310 and 324 in the mass spectra (Fig. 3: A – G) are formed by the loss of the \( \text{CF}_3 \)-radical of 1-amino-
Chemical Structures of Thermal Stable Long-Chain n-Alkyl Amines

Fig. 3. Electron impact ionization (EI) mass spectra of \( n \)-alkylamines identified in hydrogenated tallow amine Armeen<sup>®</sup> HTD. Mass spectra identification: (A) 1-aminotetradecane-TFA; (B) 1-aminopentadecane-TFA; (C) 1-aminohexadecane-TFA; (D) 1-aminheptadecane-TFA; (E) 1-aminoctadecane-TFA; (F) 1-aminononadecane; (G) 1-aminoeicosane-TFA.

tetradecane-TFA, 1-aminopentadecane-TFA, 1-aminohexadecane-TFA, 1-aminheptadecane-TFA, 1-aminoctadecane-TFA, 1-aminononadecane-TFA and 1-aminoeicosane-TFA ions, respectively (equation 2):

\[
[RCH_2N(H)C(O)CF_3]^+ \rightarrow [RCH_2N(H)CO]^+ + CF_3
\]  
(2)

\[
[M – 69]^+
\]

where \( R = C_{13}H_{27} \div C_{19}H_{39}. \)

The peaks at \( m/z \) 241, 255, 269, 283, 297, 311 and 325 (Fig. 3: A – G) are probably due to the suitable \([M + H – CF_3]^+\) ions. The peak at \( m/z \) 69 represents the \([CF_3]^+\) ion. The mass spectra (Fig. 3: A, C and E) exhibits also a series of fragments at \( m/z \) 126, 140, 154, 168, 182, 196, 210, 224, 238, 252, 266, 280 and 294. They are formed in the alkyl cleavage mechanism of 1-aminotetradecane-TFA, 1-aminohexadecane-TFA and 1-aminoctadecane-TFA, respectively with a ring formation reaction, producing a series of \([(H_2C)_nNHC(O)CF_3]^+\)
fragments (n = 2–13) with the positively charged nitrogen, and abstracting an alkyl radical. The fragment at m/z 126 corresponds to the [(H$_2$C)NHC(O)CF$_3$]$^+$ ion from the β-cleave of the TFA derivatives of the alkylamines (equation 3):

\[
[RCH_2N(H)C(O)CF_3]^+ \rightarrow [CH_2N(H)C(O)CF_3]^+ + \cdot R
\]

\(m/z\) 126

where \(R = C_{13}H_{27} \div C_{19}H_{39}\).

Fig. 4. Proposed EI-MS fragmentation pattern for \(N\)-(1-ocadecyl)-trifluoroacetamide.

a) cleavage mechanism, b) McLafferty rearrangement. For mass spectra, see Fig. 3.
Fig. 5. Positive chemical ionization (PCI) mass spectra of \( n \)-alkylamines identified in hydrogenated tallow amine Armeen® HTD. Mass spectra identification: (A) 1-amino-tetradecane-TFA; (B) 1-amino-pentadecane-TFA; (C) 1-amino-hexadecane-TFA; (D) 1-amino-heptadecane-TFA; (E) 1-amino-octadecane-TFA; (F) 1-amino-nonadecane; (G) 1-amino-eicosane-TFA.

Other characteristic fragments in Fig. 3: \([C_4H_7]^+\) (m/z 55), \([C_5H_9]^+\) (m/z 69), \([C_6H_{11}]^+\) (m/z 83), \([C_7H_{13}]^+\) (m/z 97) and \([C_8H_{15}]^+\) (m/z 111) are formed in the McLafferty type-reaction of alkene elimination from the \( N \)-(alkylo)-trifluoroacetamide ions. The McLafferty rearrangement is common for carbonyl compounds such as ketones, carboxylic acids and esters or amides [14]. The peak at m/z = 114 is due to the \([F_3CC(OH)NH_2]^+\) ion. The proposed EI-MS fragmentation pattern for \( N \)-(1-octadecyl)-trifluoroacetamide is shown in Fig. 4.

Fig. 5 shows the mass spectra obtained by the positive chemical ionization (PCI) of the trifluoroacetylated \( n \)-alkyl amines (C\(_{14} \) – C\(_{20} \)) identified in Armeen® HTD. The quasimolecular ions \([M + H]^+\) (m/z 310, 324, 338, 352, 366, 380 and 394) in Fig. 5 (A – G) corresponds to 1-aminotetradecane-TFA, 1-amino-pentadecane-TFA, 1-amino-hexadecane-TFA, 1-amino-heptadecane-TFA, 1-amino-octadecane-TFA, 1-amino-nonadecane-TFA and 1-amino-eicosane-TFA, respectively. The characteristic fragments at m/z 240, 254, 268, 282, 296, 310 and 324 in the mass spectra (Fig. 5: A – G) are formed, as in the case of electron-impact ionization of Armeen® HTD, by the loss of the \( CF_3 \)-radical of
Table 1. Retention data of trifluoroacetylated (TFA) derivative of Armeen® HTD (hydrogenated tallow amine) (Fig. 2)

<table>
<thead>
<tr>
<th>Peak</th>
<th>Capillary column</th>
<th>Proposed chemical structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DB-5ms</td>
<td>DB-17ms</td>
</tr>
<tr>
<td></td>
<td>$t_R^*$ [min]</td>
<td>$I_p^{**}$</td>
</tr>
<tr>
<td>A</td>
<td>29.70</td>
<td>1843</td>
</tr>
<tr>
<td>B</td>
<td>33.14</td>
<td>1941</td>
</tr>
<tr>
<td>C</td>
<td>36.78</td>
<td>2046</td>
</tr>
<tr>
<td>D</td>
<td>39.94</td>
<td>2139</td>
</tr>
<tr>
<td>E</td>
<td>43.54</td>
<td>2245</td>
</tr>
<tr>
<td>F</td>
<td>46.48</td>
<td>2331</td>
</tr>
<tr>
<td>G</td>
<td>49.92</td>
<td>2424</td>
</tr>
</tbody>
</table>

$t_R^*$: retention time; $I_p^{**}$: retention index in temperature programmed GLC [13, 19];
$\Delta I_p^{***}$: increment of retention indices $I_p(n+1) - I_p(n)$

1-aminotetradecane-TFA, 1-aminopentadecane-TFA, 1-aminohexadecane-TFA, 1-aminheptadecane-TFA, 1-aminoctadecane-TFA, 1-aminononadecane-TFA and 1-aminoeicosane-TFA, respectively. The proposed chemical structures of the investigated $n$-alkyl amines are summarized in Table 1.

4 Conclusions

Gas chromatography with flame-ionization detection and gas chromatography-mass spectrometry were successfully used for separation and identification of commercially available long-chain primary alkyl amines of the Armeen® HTD-type. The identified corrosion inhibiting alkyl amines were applied in the investigation of a new anticorrosive and antifouling formulation for water-steam circuit of energy systems in the power industry [3].

Acknowledgment

This work was done under the Eureka-research project E!2426 BOILTREAT: New technology for boiler water chemical treatment in the energy industry, 01.01.2001 – 29.08.2006, [3].
References