HYDROLYSIS OF HALOACETONITRILES: LINEAR FREE
ENERGY RELATIONSHIP, KINETICS AND PRODUCTS

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Abstract—The hydrolysis rates of mono-, di- and trihaloacetonitriles were studied in aqueous bu/C128er sol-
solutions at di/C128erent pH. The stability of haloacetonitriles decreases and the hydrolysis rate increases with
increasing pH and number of halogen atoms in the molecule: The monochloroacetonitriles are the most
stable and are also less affected by pH-changes, while the trihaloacetonitriles are the least stable and
most sensitive to pH changes. The stability of haloacetonitriles also increases by substitution of chlorine
atoms with bromine atoms. The hydrolysis rates in different bu/C128er solutions follow first order kinetics
with a minimum hydrolysis rate at intermediate pH. Thus, haloacetonitriles have to be preserved in
weakly acid solutions between sampling and analysis. The corresponding haloacetamides are formed
during hydrolysis and in basic solutions they can hydrolyze further to give haloacetic acids. Linear free
energy relationship can be used for prediction of degradation of haloacetonitriles during hydrolysis in
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Key words—haloacetonitriles, hydrolysis, LFER, chlorination products

INTRODUCTION

Water chlorination yields halogenated byproducts due to the reaction of halogens with naturally
occurring organics, such as humic acids (Bellar and Lichtenberg, 1974; Rook, 1974; Johnson and
Randke, 1983; Oliver, 1983; Ami et al., 1990). The three most dominant families of chlorination by-
products, in order of abundance, are the trihalo-
methanes (THMs), halogenated acetic acids (HAAs)
and haloacetonitriles (HANs) (Bellar et al., 1974; U.S. EPA, 1979; Oliver and Shindler, 1980; Boyce
and Hornig, 1983; Urano et al., 1983; Coleman et
al., 1984; de Leer et al., 1985; Alouni and Seux,
1987; Singer et al., 1995). The latter is a product of
the chlorination of aminocides, proteins and other
nitrogen containing species. The toxicology of
HANs is less documented as compared to the more
abundant THMs and HAAs. For all HAN com-
pounds there are no data appropriate for develop-
ing acceptable limits for lifetime exposure to the
chemicals though in some cases mutagenic (dibro-
moacetonitrile and bromochloroacetonitrile
and dibromoacetonitrile in the periodic monitoring
requirements of the proposed United States’

HANs are less frequently studied compared to
THMs and HAAs and the occurrence of trihaloace-
tonitriles in water is rarely reported. The most
abundant HANs after water chlorination are
dichloroacetonitrile and its brominated analogs,
bromochloroacetonitrile and dibromoacetonitrile
(Oliver and Shindler, 1980; Coleman et al., 1984;
Reckhow and Singer, 1984; Trehy et al., 1986;
Reckhow et al., 1990; Peters et al., 1990a,b) and tri-
chloroacetonitrile (Coleman et al., 1984; Smith et
al., 1987; Koch et al., 1988; Singer et al., 1995).
Recently, Richardson et al. reported dibromochlor-
ocetonitrile in chlorine dioxide disinfected water,
though identification was based on mass spectral
match and was not confirmed by identification stan-
dards (Richardson et al., 1994, 1996).

Several factors complicate the investigation of the
HANs and particularly trisubstituted HANs in
chlorinated drinking water: (1) The HANs are in-
termediate compounds, susceptible to further conver-
sion to their corresponding haloacetic acids. (2)
Even in disinfectant-free water the HANs undergo
further hydrolysis and the hydrolysis rates of most
HANs are still not documented. (3) Some of the
HANs are still commercially unavailable, thus
quantification and identification require synthetic

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capabilities. In fact, the mass spectra of some HANs, like bromochloroacetonitrile, bromodichloroacetonitrile, dibromochloroacetonitrile and tribromoacetonitrile are not reported in the MS libraries.

This manuscript describes systematic studies of the hydrolysis products and the rate of the hydrolysis of all 9 possible HANs as a function of pH. We demonstrate that linear free energy relationships can be used to predict the hydrolysis and oxidation kinetics of the various HANs.

### MATERIALS AND METHODS

**Equipment and instrumentation**

Hewlett-Packard GC-MS system using GC 5890 and 5971 Mass Selective Detector operated in EI (electron ionization) mode equipped with Altech Helixflex AT-1 capillary column (30 m long, 0.32 mm i.d., 0.25 μm film thickness) was used. The mass detector temperature was 280 °C; the injection port was operated at 180 °C, the GC temperature program was: initial temperature 35 °C, 9 min hold time; 2 °C/min ramp to 42 °C; a second ramp at 5 °C/min to 160 °C; third ramp at 30 °C/min to 220 °C and finally 4 min hold at 220 °C.

**Chemicals**

Analytical reagents were used unless otherwise specified. Commercial standards including chloroacetonitrile, bromoacetonitrile, dichloroacetonitrile, dibromoacetonitrile, trichloroacetonitrile and 2,2,2-trichloroacetoamide were purchased from Aldrich. Bromochloroacetonitrile, bromodichloroacetonitrile, dibromochloroacetonitrile and tribromoacetonitrile were synthesized by bromination of chloroacetonitrile and dichloroacetonitriles according to reported procedures (Hechenbleikner, 1946). Bromochloroacetonitrile and bromodichloroacetonitrile were isolated as individual compounds, purified by distillation under reduced pressure and used as standards. In the case of dibromochloroacetonitrile and tribromoacetonitrile rich fractions of these compounds were obtained by fractional distillation of the bromochloroacetonitrile synthesis product. Pure compounds could not be obtained and these compounds could only be used as reference materials but not for accurate quantitation. Quantitation of these compounds is reported in this article relative to trichloroacetonitrile MSD response.

**Chromatographic analysis**

Acetonitrile (Fluka) was used as solvent for the preparation of stock solutions instead of acetone that is traditionally the recommended solvent for HANs studies (U.S. EPA, 1988). Quenching of free chlorine with NH₄Cl additionally the recommended solvent for HANs studies (U.S. EPA, 1988). Quenching of free chlorine with NH₄Cl (U.S. EPA, 1988) was carried out at pH 5.4, 7.2, 8.7 and 0.1 M HCl solutions — pH 5.4, 7.2, 8.7 and 0.1 M HCl. The system includes sample acidification till pH 1, extraction with MTBE and further methylation with diazomethane. Acidification without methylation resulted in formation of the corresponding haloform by thermal decarboxylation in the injector. This was confirmed by injection of the extracts of model trichloro- and tribromoacetic acids under the same chromatographic conditions, which gave chloriform and bromiform artifact peaks, respectively.

### Table 1. GC retention times of haloacetonitriles

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviated name</th>
<th>Retention time (min)</th>
<th>Relative retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClCH₂CN</td>
<td>C1</td>
<td>4.47</td>
<td>0.23</td>
</tr>
<tr>
<td>Cl₂CN</td>
<td>C2</td>
<td>4.88</td>
<td>0.26</td>
</tr>
<tr>
<td>Cl₃CCN</td>
<td>C3</td>
<td>5.79</td>
<td>0.30</td>
</tr>
<tr>
<td>BrCH₂CN</td>
<td>Br1</td>
<td>8.05</td>
<td>0.42</td>
</tr>
<tr>
<td>Br₂CCN</td>
<td>Br2</td>
<td>10.69</td>
<td>0.56</td>
</tr>
<tr>
<td>Br₃CCN</td>
<td>Br3</td>
<td>11.59</td>
<td>0.64</td>
</tr>
<tr>
<td>Br₃CCN</td>
<td>Br3</td>
<td>18.01</td>
<td>0.95</td>
</tr>
<tr>
<td>Br₃CCN</td>
<td>Br3</td>
<td>23.26</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Hydrolysis of haloacetonitriles: application of linear free energy relationship (LFER).

Quantitative description of the influence of substituents in organic molecules on their reactivity was for first demonstrated by Hammet for the dissociation of substituted benzoic acids in 1937. Later, this approach was successfully developed for different classes of organic compounds and now it is well known as linear free energy relationship (LFER) (Taft, 1956; Lowry and Schueler Richardson, 1987; Hansen et al., 1991). LFER allows one to explain the influence of molecular structure on the thermodynamic and kinetic parameters of chemical reactions, to interpret IR-, UV-, NMR-spectra and also to predict the structure-activity relationships in medical chemistry and electrochemistry. The LFER approach penetrates slowly also into water and environmental chemistry (Schwarzenbach et al., 1993). LFER is manifested in the Hammet equation for aromatic compounds and in the tables below.

Application of linear free energy relationship (LFER) for hydrolysis of HANs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviated name</th>
<th>Retention time (min)</th>
<th>Relative retention time</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClCH₂CN</td>
<td>C1</td>
<td>77(23), 73(100), 50(22), 48(67), 47(10), 40(25)</td>
<td></td>
</tr>
<tr>
<td>BrCH₂CN</td>
<td>Br1</td>
<td>12(97), 110(100), 94(11), 81(50), 79(24), 49(75)</td>
<td></td>
</tr>
<tr>
<td>Cl₂CHCN</td>
<td>Cl2</td>
<td>84(44), 82(65), 76(33), 74(100), 48(9), 47(25)</td>
<td></td>
</tr>
<tr>
<td>Br₂CHCN</td>
<td>Br2</td>
<td>155(27), 153(21), 81(12), 79(12), 76(33), 74(100)</td>
<td></td>
</tr>
<tr>
<td>Cl₃CCN</td>
<td>Cl3</td>
<td>201(23), 196(68), 197(26), 120(100), 118(100), 81(22)</td>
<td></td>
</tr>
<tr>
<td>Br₃CCN</td>
<td>Br3</td>
<td>112(11), 110(68), 108(100), 82(11), 73(14), 47(15)</td>
<td></td>
</tr>
<tr>
<td>ClBrCCN</td>
<td>ClBr</td>
<td>154(26), 152(21), 112(11), 110(68), 108(100), 73(17)</td>
<td></td>
</tr>
<tr>
<td>Br₂CCN</td>
<td>Br2</td>
<td>190(10), 156(22), 154(100), 153(76), 81(10), 79(12)</td>
<td></td>
</tr>
<tr>
<td>Br₃CCN</td>
<td>Br3</td>
<td>205(48), 198(100), 196(52), 119(11), 117(12), 79(12)</td>
<td></td>
</tr>
</tbody>
</table>

Italic values were used for SIM analysis.

Values in brackets represent relative abundance.
Taft equation for aliphatic compounds. The Taft equation divides the substituent effects to polar and steric components. In this work Taft equation is used to describe the hydrolysis rate of HANs according to equation 1:

\[ R \cdot CN + H_2O \rightarrow R \cdot CONH_2 \]  
(1)

where \( R = X_1, X_2, X_3 \) and \( X_1, X_2, X_3 \) are chlorine, bromine, or hydrogen atoms.

The Taft’s polar (\( \sigma^* \)) and steric (\( \xi \)) substituent constants can be used to predict the rate constants of hydrolysis reaction (equation 1) according to equation 2:

\[ \log(k_b/k_0) = \rho \sigma^* + \delta \xi \]  
(2)

where \( k_0 \) is the hydrolysis rate constant for unsubstituted compound (in this case acetoneitrile); \( k_b \) the hydrolysis rate constant for compound with substituent \( R \); \( \sigma^* \) and \( \xi \) are, respectively, Taft polar and steric constants; and \( \rho \) and \( \delta \) are empirical parameters representing the sensitivity of the hydrolysis rate to the polar and steric factors.

The Taft polar constants (\( \sigma^* \)) for CHCl₂, CH₂Cl₂, CCl₃ and BrCH₂ substituents have been reported by Taft (1956) and Hansch et al. (1991). These constants for mixed bromochlorosubstituents and di- and tri-bromosubstituents were not available, but they could be evaluated based on correlations describing the relationship between the inductive component of the Hammett constant, \( \sigma_r \), and Taft polar constant, \( \sigma^* \).

Thus, the Taft polar constant for CH₂X substituent can be calculated by equation 3 (Lowry and Schueller Richardson, 1987; Hansch et al., 1991).

\[ \sigma^*_{(CH_2X)} = \sigma_{(CH_2)}/0.45 \]  
(3)

where \( \sigma_{(CH_2)} \) is the inductive component of the Hammett constant and 0.45 is an empirical constant.

\( \sigma_{(CH_2)} \) of bromine and chlorine atoms were reported to be 0.47 and 0.45, respectively. Thus, using this approach \( \sigma^*_{(CH_2Cl)} = 1.0 \) and \( \sigma^*_{(CH_2Br)} = 1.05 \) which coincide with the published value of \( \sigma^* \) (Lowry and Schueller Richardson, 1987; Schwarzenbach et al., 1993). Extrapolation of this approach can be used to extend equation 3 to multsubsitu- 

where \( \sigma_{(CH_2Cl)} \) and \( \sigma_{(CH_2Br)} \) were the least stable and the most sensitive to pH changes. Under basic conditions decrease of trihaloacetonicnitriles can be observed already after 1 h, while in acidic media there was no significant change in trihaloacetonitriles concentration even after 24 h. Figure 2 compares the relative stability of the HANs at the various pH levels.

The percent of each of the HANs that remain after 96 h hydrolysis is described as a function of pH. For most compounds optimal stability of the trihaloacetonicnitriles is obtained at pH 5.4. Much faster hydrolysis occurs at higher pH with exception for chloroacetonicnitrile which remains in high concentration also after 96 h. Comparison of hydrolysis rates at pH 5.4 and pH 1 shows that the differences in degradation rate vs. pH are less pronounced in acidic media as compared to basic solutions. Generally the stability of HANs is on the same level or even slightly improved at pH 5.4, except for trichloroacetonicnitrile which was more stable in 0.1 N HCl. Mono- and di-substituted HANs are very stable in acidic media and only after 48 h some
A decrease in their concentrations could be observed, while the stability of the trisubstituted compounds was much inferior. The nature of the halogen atom in substituent influences also the HANs hydrolysis rate. Subsequent substitution of chlorine with bromine atoms in trichloroacetoneitrile increases HANs stability. The influence increases for the series Cl₃CCN–BrCl₂CCN–Br₂ClCCN–Br₃CCN.

Hydrolytic pathways of trihaloacetonitriles

Under all pH conditions, the decrease in concentration of trihaloacetonitriles is accompanied by appearance of new chromatographic peaks. These

Fig. 1. Hydrolysis of haloacetonitriles at pH 8.7 (a) and at pH 5.4 (b).
were identified as the corresponding trihaloacetamides. The commercial standard of trichloroacetamide was available and the compound was identified both by matching chromatographic retention time and by spectral matching. For other trihaloacetamides the library mass-spectra were not available and they were identified based on their MS-spectra fragmentation. In the case of dibromo-chloroacetamide the following peaks correspond to the EI fragments, their relevant chemical structure is given in brackets: 249 (0.7%), 251 (2.1%), 253 (2.1%)/M+; 205 (1.4%), 207 (2.8%), 209 (1.8%)/CBr2Cl+; 170 (2.0%), 172 (3.5%), 174 (1.0%)/CBr2+; 154 (1.1%), 156 (1.4%), 158 (0.2%)/CBrCl+; 142 (2.5%), 144 (3.5%), 146 (0.7%)/CBrClCO+; 126 (5.0%), 128 (6.7%), 130 (1.0%)/CBrCl+; 91(2.8%), 93 (2.8%)/CBr+; 79 (3.5%), 81 (3.9%)/Br+; 47 (3.5%), 49 (1.1%)/CCI+; 44 (100%)/CONH2+.

Small relative abundances of all mass-spectra peaks in comparison with the base peak, 44 corresponding to the ion /CONH2/+ was typical also for trichloroacetamide.

Fig. 2. The influence of pH on stability of haloacetonitriles. Remaining percentage after 96 h.

Fig. 3. Products formation by the hydrolysis of trichloroacetonitrile at pH 8.7: (1) trichloroacetonitrile, (2) trichloroacetamide, (3) trichloroacetic acid (detected in ester form) and (4) sum of 1 + 2 + 3.
Hydrolysis of the HANs under basic conditions yielded also the corresponding haloacetic acids as demonstrated for trichloroacetonitrile (Fig. 3). The haloacetic acids were determined as the corresponding methylester by MTBE extraction in acidic solution and subsequent methylation with diazomethane. The chromatographic retention times for all trihaloacetonitriles hydrolysis products are presented in Table 4. In basic solution, the molar sum of haloacetonitrile + haloacetamides + haloacetic acids was time invariant (Fig. 3). In acid and neutral solutions the sum of haloacetamide and haloacetonitrile was conserved demonstrating that these are indeed the only, or at least the dominant hydrolysis products.

**Table 4. Retention time of the hydrolysis products of trihaloacetonitriles**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₃CCOOCH₃</td>
<td>19.71</td>
</tr>
<tr>
<td>BrCl₂CCOOCH₃</td>
<td>23.70</td>
</tr>
<tr>
<td>Br₂ClCCOOCH₃</td>
<td>27.21</td>
</tr>
<tr>
<td>Cl₃CCONH₂</td>
<td>29.10</td>
</tr>
<tr>
<td>BrCl₂CCONH₂</td>
<td>32.29</td>
</tr>
<tr>
<td>Br₂ClCCONH₂</td>
<td>35.02</td>
</tr>
<tr>
<td>Br₃CCONH₂</td>
<td>37.10</td>
</tr>
</tbody>
</table>

In basic solution, the molar sum of haloacetonitrile + haloacetamides + haloacetic acids was time invariant (Fig. 3). In acid and neutral solutions the sum of haloacetamide and haloacetonitrile was conserved demonstrating that these are indeed the only, or at least the dominant hydrolysis products.

**Taft equation for haloacetonitriles hydrolysis**

The hydrolysis of the trihaloacetonitriles obeyed first order kinetics as demonstrated for the hydrolysis of trichloroacetonitrile. The kinetic coefficient can be obtained from the linear \( \ln(C) \) vs. \( t \) dependence (Fig. 4). The \( C \) and \( 1/C \) vs. \( t \) dependencies were not linear showing that zero order and second order kinetics can be ruled out. The hydrolysis rate constants of the trihaloacetonitrile compounds at different pH-values are presented in Table 5. The qualitative conclusions that were derived earlier based on Figs 1 and 2, that rate constants \((k)\) increase with pH and depend on the nature of the substituents can now be confirmed based on the quantitative kinetic data of Table 5. For the trihaloacetonitrile molecules, consecutive substitution of bromine atoms by chlorine increases the stability of the trihaloacetonitriles.

Table 3 also depicts the values of the hydrolysis rate constants of the HANs at pH 8.7. The hydrolysis rate constants depend on the number of halogen atoms in the HAN molecule. The trihaloacetonitriles are less stable than mono- and di-substituted compounds. Thus, the expected quantitative dependence between the chemical structure and the reactivity of the HAN molecules can be described by linear free energy relationship (LFER), demonstrating the influence of structural changes in the organic molecule on its chemical characteristics, using the constants of Table 3.

For pH 8.7 the LFER equation is best fitted by equation 6:

\[
\log k_R = -8.44 \pm 0.26 + (2.91 \pm 0.50)\sigma^* + (1.36 \pm 0.40)E_S. \tag{6}
\]

The standard deviations of the coefficients are given in the regular brackets in equation 6. The linear correlation coefficient was \( r = 0.97 \) and the number of degrees of freedom was \( n = 6 \). Graphic presentations of equation 6 are given in Fig. 5(a), (b) for \( E_S \) and \( \sigma^* \) parameters, respectively. Comparison of

![Fig. 4. ln(C) vs. time dependence for the hydrolysis of trichloroacetonitrile at pH 8.7 (correlation coefficient, \( R = 0.99 \), degrees of freedom, \( n = 5 \)).](image)
Taft’s sensitivity constants $\rho$ and $\delta$ in equation 6 shows that the hydrolysis rate is more sensitive to the polar than to the steric constant. These constants have opposite signs and influence the log $k$-values in opposite directions. Increasing the polar constant $\sigma^*$ increases the hydrolysis rate constants, while increasing the absolute value of the steric constant, $E_s$, decreases the hydrolysis rate constant. Thus, the increase of amount of halogen atoms in a HAN molecule increases log $k$ due to larger $\rho \sigma^*$ contribution which is more significant than the change in $\delta E_s$. Inside a group of the same number of halogen atoms the substitution of chlorine by bromine atoms decreases the hydrolysis rate because the polar constant, $\sigma^*$ decreases and the absolute values of the steric constant, $E_s$, increases.

The hydrolysis rate constants also depend on the pH of the media — lowering the pH diminishes the

<table>
<thead>
<tr>
<th></th>
<th>pH 5.4</th>
<th>pH 7.2</th>
<th>pH 8.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_3$CCN</td>
<td>$2.0 \times 10^{-6}$</td>
<td>$1.5 \times 10^{-5}$</td>
<td>$3.9 \times 10^{-6}$</td>
</tr>
<tr>
<td>BrCl$_2$CCN</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.2 \times 10^{-5}$</td>
<td>$2.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Br$_2$ClCCN</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$0.9 \times 10^{-5}$</td>
<td>$0.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>Br$_3$CCN</td>
<td>$0.7 \times 10^{-5}$</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$0.4 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Fig. 5. Projections of the linear free energy relationship for haloacetonitriles hydrolysis at pH 8.7:
(a) Dependence of Taft steric constants $E_s$, (b) Dependence of Taft polar constants $\sigma^*$. 

Table 5. Hydrolysis rate constants ($s^{-1}$) of trihaloacetonitriles
hydrolysis rates (Fig. 2) and decreases the value of the coefficients in equation 2. This is demonstrated
for pH 7.2 (equation 7) and pH 5.4 (equation 8):
\[
\log k_R = -8.65 \pm 0.28 + (2.73 \pm 0.53)\sigma^* + (1.31 \pm 0.41)E_S,
\]
\(r = 0.97, n = 6\),

\[
\log k_R = -8.47 \pm 0.14 + (1.70 \pm 0.27)\sigma^* + (0.81 \pm 0.21)E_S,
\]
\(r = 0.97, n = 6\).

Comparison of equations 6)–(8) suggests that the \(\log k_R\) values be twice more sensitive to substi-
tuent’s polar constants as compared to the steric
constants.

**Mechanism of trihaloacetonitrile hydrolysis**

The hydrolysis of trihaloacetonitriles can be either acid or base catalyzed (Schaefer, 1970). The
mechanism of basic hydrolysis involves nucleophilic addition of \(\text{OH}^–\) (Schaefer, 1970):

\[
\text{RCN} + \text{OH}^– \rightarrow \text{RC(OH)}\text{N}^– \rightarrow \text{RC(OH)}\text{NH} \rightarrow \text{RCONH}_2,
\]

where \(R = \text{CH}_3\chi_nX_n\), \(n = 1,2,3\) and \(X = \text{Cl, Br or their combination}\).

The main products of this process are the acetamides and further basic hydrolysis of these forms
the corresponding carboxylic acids. The acid-cata-
yzed process starts with protonation of the nitro-
gen atom in the nitrile group (Schaefer, 1970) and
is slower than in basic media. The differences
between pH 1 and pH 5 can be explained by
increase of hydrolysis rate in more acidic media.

The general scheme of haloacetonitriles hydrolysis
followed by determination of the corresponding
esters after methylation by diazomethane can be
presented by equation 10:

\[
\text{R-CN} + \text{H}_2\text{O} \rightarrow \text{R-CO}_2\text{H} \quad \text{RCONH}_2 + \text{H}_2\text{O} \rightarrow \text{RCOO}^- + \text{NH}_4^+
\]

The hydrolysis of haloacetonitrile compounds
under basic conditions yields the corresponding
acetamides, which in basic media can be further
hydrolyzed to the corresponding acid. During the
extraction with MTBE the trihaloacetic acid anions
remain in the aqueous phase and can not be identi-
ified by GC-MS analysis, whereas acidification
yields the acidic form, which can be extracted to
the organic phase and further methylated. The hy-
drolysis of trihaloacetamides is a much slower pro-
cess as compared to the hydrolysis of the starting
compound (see Fig. 3) and it is carried out only
under basic solutions. In acid solutions the hydroly-
sis process is terminated by formation acetamides
which are stable under acidic conditions. Based on
these observations it can be concluded that preser-
vation of HAN samples between sampling and
analysis, can be best accomplished by adjusting the
pH to weakly.

**Chlorination of haloacetonitriles**

The mechanism of HANs chlorination was sug-
uggested by Peters et al. (1990b), equation 11. It
may followed either direct chlorination by HOCl,
forming the corresponding N-chloroamides (route A)
or an indirect route through hypochlorite catal-
yzed hydrolysis of the cyano group producing an
amide that reacts with HOCl to give the corre-
sponding N-chloramide (route B). The proposed
mechanisms of HAN chlorination are analogous to
HAN hydrolysis, which allows use of the LFER
approach also for this case.

\[
\text{R-CN} + \text{HOCI} \rightarrow \text{R-C(ON)}\text{N} \rightarrow \text{R-C(OH)}\text{N} \rightarrow \text{R-C(OH)}\text{NH} \rightarrow \text{R-C(OH)}\text{NH}_2
\]

\[
\text{R-CN} + \text{HOCI} \rightarrow \text{R-C(OH)}\text{NCl} \rightarrow \text{R-C(OH)}\text{NHCl}
\]

\(\quad (11)\)
Degradation of the HANs by chlorination is much faster compared to their hydrolysis. For example, at pH 7.2 only 2 of the 4 starting trihaloacetonitriles remained in solution after 1 h (Fig. 6) and after 24 h only the monohaloacetonitriles remained undegraded. The stability ranking observed for the hydrolysis step was preserved for the chlorination reaction as well. The stability increases with increasing number of bromine atoms in the molecule.

The successful application of LFER in describing the hydrolysis of the HANs stimulated the application of the LFER and the Taft’s parameters to describe the chlorination of the HANs as well. This is of course relevant as an end in itself and as a
further supports for the linear approach taken to derive the missing Taft’s constants, though unlike hydrolysis chlorination is a second order process:

\[
\log k = -1.69 \pm 0.16 + (1.05 \pm 0.47)\sigma^* + (0.48 \pm 0.33)E_S, \tag{12}
\]

\(r = 0.93\).

Equation 12 describes the best fit second order reaction kinetic coefficient of chlorination at pH 7.2.

The comparison of equation 12 and equation 7, describing the kinetic coefficients of hydrolysis under the same pH, reveal that the independent constant is much larger for chlorination as compared to hydrolysis while the steric and polar dependencies are somewhat less significant for chlorination as compared to the hydrolysis. Thus, the overall stability of unsubstituted acetonitrile is 6 orders of magnitude larger for hydrolysis as compared to its stability in the presence of the specified chlorination conditions. Interestingly, the polar constant was found to be twice larger than the steric constants for all the hydrolysis and chlorination test cases. This again point on the mechanistic similarity of hydrolysis and chlorination.

**Termination of the chlorination reaction by chloramination**

Nieminski *et al.* (1993) demonstrated that termination of the chlorination step can be best achieved by addition of ammonium chloride which captures effectively the active chlorine. Unlike sulfite, thiosulfate and hexacyanoferrate, ammonium ions do not reduce the HAN compounds concentration.

It was, therefore, interesting to verify the stability sequence of HANs in the presence of monochloramine. These tests were conducted in the presence of chloramine (NaClO was added in the presence of NH4Cl) at pH 7.2. The rate of disappearance of HANs under these conditions was best fitted by equation 13:

\[
\log k = -7.90 \pm 0.29 + (2.38 \pm 0.55)\sigma^* + (1.15 \pm 0.44)E_S, \tag{13}
\]

\(r = 0.94, n = 6\).

The rate of disappearance of haloacetonitriles in the presence of chloramine is slightly higher when compared to nonchlorinated media (equation 7) and (Fig. 7), but it is still much smaller as compared to the degradation in the presence of hypochlorite (equation 12).

**Concluding Remarks**

The disappearance of haloacetonitriles (hydrolysis under different pH conditions and by chlorination) can be adequately described by LFER approach. The stability of haloacetonitriles for both hydrolysis and chlorination reactions decreased for larger number of halogen substituents and increased upon replacing chlorine with bromine. Under acid conditions the hydrolysis of haloacetonitriles gave haloacetamides and in basic media further hydrolysis to the corresponding trihaloacetic acid was observed.

A practical conclusion that arise from the studies is that HAN samples are best preserved (between sampling and analysis) under weak acid conditions due to their superior stability under such conditions. Weak acid conditions are also optimal for preservation of chlorinated samples after ammonium chloride quenching of the oxidant.

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**References**


