

# Hydrolytic removal of the chlorinated products from the oxidative free-radical-induced degradation of chloroethylenes: acid chlorides and chlorinated acetic acids

2 PERKIN

Lutz Prager,<sup>a</sup> Peter Dowideit,<sup>b</sup> Helmut Langguth,<sup>a</sup> Heinz-Peter Schuchmann<sup>b</sup> and Clemens von Sonntag<sup>b</sup>

<sup>a</sup> Institut für Oberflächenmodifizierung, Permoserstrasse 15, D-04318 Leipzig, Germany

<sup>b</sup> Max-Planck-Institut für Strahlenchemie, Stiftstrasse 34-36, P.O. Box 101365, D-45470 Mülheim an der Ruhr, Germany

Received (in Cambridge, UK) 20th February 2001, Accepted 28th March 2001

First published as an Advance Article on the web 25th April 2001

Progressive hydrolytic decomposition of acyl chlorides, among them the chlorinated acetyl chlorides, which are produced in the gas-phase oxidation of chlorinated ethylenes, permits the complete mineralization of organically bound chlorine to chloride anion. Hydrolysis rate constants (100% water) have been determined for the following acyl chlorides: acetyl ( $350\text{ s}^{-1}$ ), chloroacetyl ( $5.5\text{ s}^{-1}$ ), dichloroacetyl ( $300\text{ s}^{-1}$ ), trichloroacetyl ( $>350\text{ s}^{-1}$ ), and oxalyl dichloride ( $>350\text{ s}^{-1}$ ). The chlorinated acetyl chlorides thereby give rise to the chloroacetates whose decomposition has also been studied and the kinetic parameters determined. Mono- and dichloroacetate anion undergo hydrolytic dechlorination ( $k_{\text{obs}} = k_0 + k_{\text{OH}^-} \times [\text{OH}^-]$ ;  $\text{ClCH}_2\text{C}(\text{O})\text{O}^-$ :  $A_0$   $6.4 \times 10^{15}\text{ s}^{-1}$ ,  $E_0$   $148\text{ kJ mol}^{-1}$ ,  $A_{\text{OH}^-}$   $1.6 \times 10^9\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ,  $E_{\text{OH}^-}$   $86\text{ kJ mol}^{-1}$ .  $\text{Cl}_2\text{CHC}(\text{O})\text{O}^-$ :  $A_0$   $3.2 \times 10^{16}\text{ s}^{-1}$ ,  $E_0$   $156\text{ kJ mol}^{-1}$ ,  $A_{\text{OH}^-}$   $3.2 \times 10^{10}\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ,  $E_{\text{OH}^-}$   $104\text{ kJ mol}^{-1}$ ). Trichloroacetate anion decomposes by another mechanism, undergoing decarboxylation which is base-uncatalyzed:  $A_0$   $2.1 \times 10^{17}\text{ s}^{-1}$ ,  $E_0$   $146\text{ kJ mol}^{-1}$ . Procedures on a pilot-plant scale are pointed out that allow the elimination of these compounds upon oxidation of the strip-gas produced when contaminated water is freed from chlorinated ethylenes by air-stripping.

## Introduction

Some of the most widespread environmental contaminants, especially of ground-water, are found among the chlorinated ethylenes.<sup>1,2</sup> Air-stripping has proved to be an efficient method of ground-water remediation. The destruction of these compounds in the strip-gas is effected by electron-beam treatment<sup>3-5</sup> or UV-photolysis.<sup>6-8</sup> Under these conditions, part of the decomposition products consists of acyl chlorides such as mono-, di-, and trichloroacetyl chloride, phosgene, and formyl chloride.<sup>3-5</sup> These compounds can be removed from the air stream by alkaline washing and hydrolysis. Although the strip-gas contains water vapour, the hydrolysis must nevertheless be conducted in the liquid phase since the reaction of acid chlorides with water is slow in the gas phase.<sup>9</sup> Estimation of the rate of and optimization of the washing-out of these compounds from the air stream leaving the reactor require data on the mass transfer from the gas to the liquid phase. The rates of transfer of the acid chlorides and of the subsequent hydrolytic reactions are determining factors of this process and, therefore, important aspects of this paper.

The hydrolysis of the acid chlorides effects the removal of these contaminants from the strip-gas but does not necessarily achieve final detoxification. Chloroacetic acid chlorides are hydrolyzed to toxic chloroacetates, which must be further treated to achieve the transformation of the carbon-bound chlorine to chloride.<sup>7</sup>

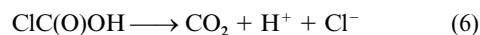
Dechlorination rate data concerning some of the acyl chlorides of interest here exist in the literature. Formyl chloride in aqueous solution mostly suffers non-hydrolytic HCl elimination [reaction (1),  $k = 10^4\text{ s}^{-1}$ ].<sup>10,11</sup> While near-neutrality reaction (2) contributes only a few percent, OH<sup>-</sup>-catalyzed



hydrolysis becomes competitive in strongly alkaline media [reaction (3),  $k = 2.5 \times 10^4\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ ]. These are fast processes from a technological point of view.



The hydrolysis of phosgene is a two-step process. The rate-determining step is the formation of carbonic acid monochloride, slow [reaction (4),  $k \approx 10\text{ s}^{-1}$ ]<sup>12,13</sup> at neutral pH, but fast in 1 M NaOH [reaction (5),  $k = 2.8 \times 10^4\text{ s}^{-1}$ ].<sup>13</sup> The subsequent decay of carbonic acid monochloride into carbon dioxide and hydrogen chloride is fast [reaction (6); expected:  $k \geq 10^5\text{ s}^{-1}$ , cf. refs. 10, 14–16].

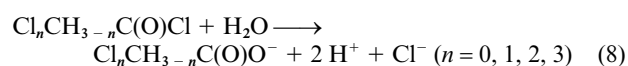


Recent publications have been concerned with the study of the uptake of haloacetyl and carbonyl halides with the aim of modelling cloud/atmosphere hydrolysis processes,<sup>17-21</sup> whose principles are very briefly gone into here. The net flux  $J$  of gaseous molecules into the aqueous phase is quantitatively characterized [expression (7)] by the mass uptake coefficient  $\gamma$ ,

$$J = n_g u \gamma / 4 \quad (7)$$

the concentration  $n_g$  in molecules per unit volume, and the mean molecular velocity  $u$ . The factor of  $1/4$  reflects the fact that only half of the molecules approach the interface, and in a more or less slanted direction. The quantity  $\gamma$  (*cf.* ref. 20) increases with (i) the mass accommodation coefficient  $a$ , which is defined as the fraction of sticky collisions relative to the total, (ii) the solubility (which for these compounds *decreases* with increasing ionic strength), and (iii) the rate of hydrolysis. Details are discussed in refs. 17 and 20. A relatively low rate of hydrolysis may lead to the saturation of the boundary layer which impedes mass transfer. Such a situation is reflected, for instance, in the data obtained for phosgene uptake,<sup>12</sup> with  $\gamma < 1.5 \times 10^{-6}$  for water but, at  $8 \times 10^{-5}$ , more than 40 times larger for 1 M NaOH.<sup>17</sup> In the case of trichloroacetyl chloride, the mass uptake coefficient is about ten times larger than for phosgene, as can be derived from the data given in refs. 21 and 22. Based on the knowledge of the quantities in expression (7) and bearing in mind that the amount of mass transferred depends on the contact time of the gas (which is inversely proportional to the strip-gas flow rate), a scrubber can be designed with the dimensions such that it achieves the desired scrubbing ratio  $c_{\text{gas,final}}/c_{\text{gas,initial}}$ .

In the present paper, rate determinations are reported regarding the hydrolysis of acetyl chloride and halogenated acetyl chlorides [reaction (8)] in aqueous mixed-solvent systems. In

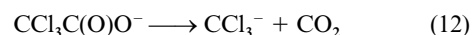
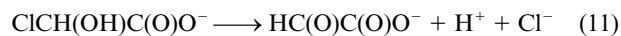
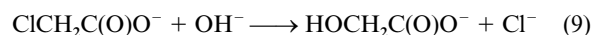


100% water, the hydrolysis of aliphatic acyl chlorides is usually so fast that its rate cannot be followed by slow conventional techniques. To reduce the rate, but also to elucidate the hydrolysis mechanism with respect to the order of the kinetics as a function of the water concentration, organic cosolvents and low temperatures have often been used,<sup>23-27</sup> but such data do not readily allow an extrapolation to the neat-water situation at room temperature. Thus, fast kinetics techniques must be applied. There are some past examples of this. The rate of the hydrolysis of acetyl chloride in water-rich solvent systems has been studied kinetically by a stopped-flow method.<sup>28</sup> The hydrolysis of phosgene has been studied by shooting a water jet through a phosgene atmosphere; from the HCl taken up, the rate of phosgene hydrolysis was estimated by applying non-equilibrium absorption theory.<sup>12</sup> Phosgene has been generated *in situ* using the pulse radiolysis technique, and its hydrolysis followed by fast conductometry.<sup>13</sup> This has allowed the study of a wider temperature range and has yielded values for the rate constants in a straightforward way as no additional assumptions are needed in this case since the system is monophasic. Succinic dichloride<sup>15</sup> and formyl chloride<sup>10</sup> can be similarly generated *in situ*. A study of the hydrolysis of trichloroacetyl chloride reports rate constants in the order of between  $10^2$  and  $10^3 \text{ s}^{-1}$ , using the stopped-flow and the droplet-train techniques.<sup>22</sup> For comparison, our own result is that this rate constant is considerably in excess of  $350 \text{ s}^{-1}$  (see below).

From the foregoing discussion it can be assumed that these acid chlorides should, in principle, be easily hydrolyzed, especially by the use of alkaline washing liquids, once they have penetrated into the aqueous phase. The rate of acid-chloride transfer from the gas to the aqueous phase must be kept in mind; a pilot-plant packed-column absorber has been used<sup>29</sup> to determine the overall acid-chloride removal efficiency (see below).

Harsher conditions must be employed for the transformation of the chloroacetates into innocuous end products. The alkaline hydrolysis of monochloroacetate into glycolate<sup>30</sup> and of dichloroacetate into glyoxylate<sup>31</sup> [reactions (9) and (10), (11)] shows second-order kinetics {the first step being rate-determining while the hydrolysis of the chlorohydroxyacetate [reaction (11)], a geminal chlorohydrin, is fast}. In contrast,

trichloroacetate decomposes by a unimolecular pathway whereby chloroform is released [reactions (12) and (13)].<sup>31</sup> In the latter case, the mineralization of the organic chlorine requires the subsequent hydrolysis of the chloroform [reactions (14), (15) and (1)].



The alkali-catalyzed rate of hydrolysis of chloroform<sup>32</sup> is faster than that of monochloroacetate and dichloroacetate under the same conditions (at lesser alkalinities it may be slower than the decomposition of trichloroacetate [reaction (12)] which is not alkali-catalyzed). Thus, if the decomposition of the chloroacetates is carried out in strongly alkaline solution chloroform will not accumulate. Dichloromethanol promptly eliminates HCl [reaction (15)]<sup>10</sup> producing formyl chloride, which decays very quickly under these conditions [reactions (1) and (2)].<sup>10,11</sup>

It is thus seen that complete mineralization of organic chlorine in these systems is feasible. In the present work, further kinetic studies of the hydrolysis of these compounds are undertaken with a view to developing an optimized procedure that operates on a pilot-plant scale.<sup>29</sup>

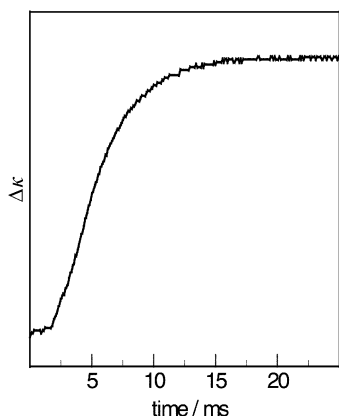
## Experimental

### Stopped-flow experiments

All acyl chlorides were of the highest purity commercially available and used without further purification. 1,4-Dioxane, the organic component of the mixed-solvent systems, was dried over sodium wire and redistilled. The Milli-Q-filtered (Millipore) water had a background resistivity of  $18 \text{ M}\Omega \text{ cm}^{-1}$ .

In the course of our studies on the reaction of ozone with chlorinated olefins,<sup>33</sup> a fast small-volume conductometric detection system was constructed from glass tubing (the cell volume, containing the two mutually opposite glassy-carbon electrodes of 1 mm diameter, was only  $30 \mu\text{l}$ ),<sup>11</sup> and fitted to a stopped-flow set-up (Biologic SFM-3), which allowed the measurement of conductance changes with a time resolution of 2 ms, *i.e.* within times very close to the mixing time, corresponding to rate constants of up to  $350 \text{ s}^{-1}$ . This arrangement is about five times faster than that of a similar conductometric set-up.<sup>34</sup> The conductance change was measured with a Wheatstone-bridge arrangement adapted from a pulse radiolysis detection system<sup>35</sup> against a reference cell filled with a fully reacted sample from a preceding run (for details see ref. 11). With the help of this set-up the rate constants for a series of acyl chlorides were determined in 1,4-dioxane-water mixtures, where the acyl chlorides were dissolved in dry 1,4-dioxane and mixed with aqueous dioxane of the required water content. It was possible to extend the experiments to such low 1,4-dioxane concentrations that a meaningful extrapolation to the neat-water situation was considered feasible.

The fast progress of the hydrolysis of acetyl chloride is shown in Fig. 1. The acidification of the solutions in the course of the hydrolysis does not interfere with the kinetics since acid catalysis is practically absent in this class of compounds (see below).



**Fig. 1** Kinetic trace (conductivity vs. time) of the hydrolysis of acetyl chloride ( $[\text{H}_2\text{O}] = 35 \text{ mol dm}^{-3}$  in 1,4-dioxane). The initial period of the mixing event with its concomitant noisy signal has been omitted.

### Hydrolytic absorber for the acyl chlorides

Simulated oxidized strip-gas, *i.e.* air loaded with the acid chloride to be studied [the acid chlorides were produced from trichloro-, tetrachloro-, or (*E*)-1,2-dichloroethylene by UV (222 nm) photooxidation] at a flow rate in the order of  $10^2 \text{ m}^3 \text{ h}^{-1}$  enters a pilot-plant-scale scrubber with one or two (optional in series) packed columns (supplier: Dr Günther, Engineering, Wittenberg, Germany), packed volume  $1.25 \times 0.33 \text{ m}$ , filled with Pall™ rings, specific surface  $220 \text{ m}^2 \text{ m}^{-3}$  (supplier Vereinigte Füllkörper-Fabriken, Ransbach-Baumbach, Germany). 0.5–1.5 M NaOH ( $0.35 \text{ m}^3$ , circulated through the absorber at a flow rate of  $0.5\text{--}2.3 \text{ m}^3 \text{ h}^{-1}$ ) is sprayed in at the top. The set-up has previously been described in detail.<sup>29</sup> These experiments take into account the fact that the rate of mass transfer from the gas to the aqueous phase is an important parameter in the removal of the acid chlorides from the strip-gas. The disappearance of the acid chlorides was followed on-line by FTIR (Fourier-transform infrared) spectroscopy (Bruker Vector 22; windows NaCl, optical path length 0.2 m, detection limit for the acid chlorides about 1 ppm).<sup>29</sup>

### Alkaline hydrolysis of chloroacetates

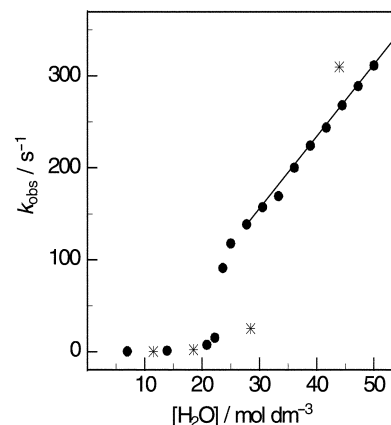
Batch-type, bench-scale experiments were carried out to determine the degradation rate constants of mono-, di-, and trichloroacetates as a function of NaOH concentration (up to 1 M) and temperature (range from 80 to 120 °C). The samples of chloroacetate concentrations in the millimolar range were hydrolyzed in closed glass or PTFE vessels capable of sustaining the pressure that builds up when the aqueous solution is heated to above 100 °C, or of resisting attack by highly alkaline solutions.<sup>29</sup> The samples were kept in a heated oil bath for the desired time, chilled after the run, diluted with distilled water, and analyzed for the remaining chloroacetate and for the ionic products by ion chromatography (Dionex, column AS12A 4 mm, eluent 50 mM sodium hydroxide).

Experiments to determine the conditions needed to achieve degradation of the chloroacetates so as to conform to the maximum statutory limit for disposal in the municipal sewage system were carried out in a pilot-plant-scale flow-reactor, which was run at temperatures of up to 210 °C. Details regarding its construction and operation have already been reported.<sup>29</sup>

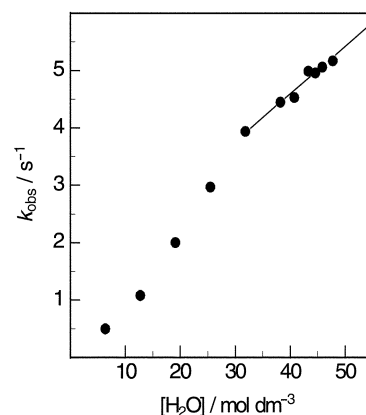
## Results and discussion

### Acyl-chloride hydrolysis rate constants

The rate of hydrolysis of some aliphatic acyl chlorides has been determined by the stopped-flow technique with conductometric detection. The upper detection limit of this setup is  $350 \text{ s}^{-1}$  (equivalent to a mixing-time of 2 ms). The acyl chlorides were



**Fig. 2** Rate of hydrolysis of acetyl chloride in 1,4-dioxane–water mixtures. Data from ref. 28 (\*) are also included.



**Fig. 3** Rate of hydrolysis of chloroacetyl chloride in 1,4-dioxane–water mixtures.

dissolved in dry 1,4-dioxane, which is fully miscible with water. The rate of hydrolysis was observed to increase with increasing water concentration, but not in a linear fashion over the full concentration range studied. Examples are shown in Figs. 2 and 3. In the case of acetyl chloride (Fig. 2) three domains may be distinguished: in the dioxane-rich region the rate of hydrolysis remains low up to about  $22 \text{ mol dm}^{-3}$  water after which the rate increases steeply; between about 25 and  $50 \text{ mol dm}^{-3}$  water the rate increases linearly with the water content. It is expected that this linear part of the rate vs.  $[\text{H}_2\text{O}]$  relationship may be extrapolated to 100% water, *i.e.* that no further discontinuity occurs in the range between 90 and 100% water content. The uneven trend of these results is in contradiction to that reported in the literature<sup>28</sup> for the same solvent system where the rate constant rises in an almost exponential manner with the water concentration (symbols \* in Fig. 2). If one accepts the results obtained in the present work, the extrapolation leads to a hydrolysis rate constant of  $350 \text{ s}^{-1}$  for acetyl chloride in 100% water. This extrapolation seems justified since the gap between the last point measured (90% water) and the dioxane-free system is small, and one might expect a continuation of the linear change of the variable in question with the molar fraction of water (provided that the interaction of a 1,4-dioxane molecule with the acetyl chloride molecule is relatively weak, which is probably the case).

Extrapolation of the results reported by Hudson and Moss in ref. 28 (their<sup>28</sup> Fig. 3 and taking the Grunwald–Winstein parameter<sup>36</sup>  $Y(100\% \text{ H}_2\text{O})$  equal to 3.6,<sup>36</sup> together with their<sup>28</sup> Table 3) leads to a rate constant of  $1200 \text{ s}^{-1}$ .

While the rate of hydrolysis of chloroacetyl chloride in the higher water-concentration range is much lower, the overall picture at the higher molar fractions of water is qualitatively the same (Fig. 3). Extrapolation leads to a hydrolysis rate constant

**Table 1** Rate of hydrolysis of some aliphatic acyl chlorides at 20 °C (100% water)

Acyl chloride	$k_{\text{hydrolysis}}$	Ref.
Phosgene	$6 \text{ s}^{-1}$	12
	$9 \text{ s}^{-1}$	13
	$[\text{OH}^-] \times 2.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	13
Formyl chloride	$(10^4 \text{ s}^{-1})^a$	10
	$\sim 400 \text{ s}^{-1}$	10, 37
	$[\text{OH}^-] \times 2.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	10
Acetyl chloride	$350 \text{ s}^{-1}$	This work
Chloroacetyl chloride	$5.5 \text{ s}^{-1}$	This work
Dichloroacetyl chloride	$300 \text{ s}^{-1}$	This work
Trichloroacetyl chloride	$>350 \text{ s}^{-1}$	This work
	$150\text{--}500 \text{ s}^{-1}$	22
Oxalyl dichloride	$>350 \text{ s}^{-1}$	This work
Succinyl dichloride	$6 \text{ s}^{-1}$	15

<sup>a</sup> Mainly decarbonylation [reaction (1)].

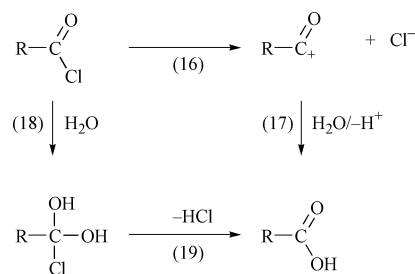
of  $5.5 \text{ s}^{-1}$  for chloroacetyl chloride in 100% water. Rate constants for the hydrolysis of these and several other aliphatic acyl chlorides also measured in the present study are compiled in Table 1, together with some additional data from the literature.

In the series of aliphatic acyl chlorides its first member, formyl chloride, decomposes relatively rapidly into CO and HCl [reaction (1)], such that the competing hydrolysis into formic acid and HCl [reaction (2)] is difficult to assess with accuracy,<sup>10</sup> but from our earlier<sup>10</sup> and more recent<sup>37</sup> data a value close to  $400 \text{ s}^{-1}$  seems to be reasonable. While acetyl chloride in 100% water hydrolyzes with a rate constant of  $350 \text{ s}^{-1}$ , substitution with one chlorine reduces the rate to  $5.5 \text{ s}^{-1}$ ; further chlorine substitution however re-enhances the rate, to  $300 \text{ s}^{-1}$ . The rate of hydrolysis of trichloroacetyl chloride is so fast that it exceeds the detection limit ( $350 \text{ s}^{-1}$ ) of the present set-up. Similarly, a study of the hydrolysis of trichloroacetyl chloride under atmospheric/cloud conditions reports rate constants in the order of between  $k = 150 \text{ s}^{-1}$  (pH 4.8–5.8) using the stopped-flow technique and  $k = 500 \text{ s}^{-1}$  (below pH 3.4) with the droplet-train technique.<sup>22</sup> The discontinuity observed on going from acetyl chloride to monochloroacetyl chloride clearly indicates a change in the mechanism of hydrolysis.

### Mechanistic aspects

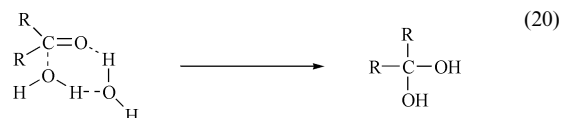
The present work is focused on hydrolysis rates in purely aqueous systems; the dioxane–water system used here provides the basis for extrapolation to the 100%-water situation where the rate may be too fast to measure in our set-up. Compared with purely aqueous solutions, mixed-solvent systems usually have the additional complexity of hydrophobic binding of the organic component with the substrate molecule. This implies, for instance, that the dependence of the rate of hydrolysis on the water content reflects variations of accessibility of the water molecules to the substrate molecule as well as a possible shift (with higher water content) toward the  $\text{S}_{\text{N}}1$  pathway, or the consequences of molecularity ( $[\text{H}_2\text{O}]^n$ ).

For the non-catalyzed hydrolysis of acyl chlorides, mainly two mechanisms have been considered, *i.e.*  $\text{S}_{\text{N}}1$  [reactions (16) and (17)], and  $\text{S}_{\text{N}}2$ , which may proceed *via* a hydrate [reactions (18) and (19)],<sup>38–41</sup> while solvent–acyl chloride charge-transfer complexes have often been considered as well. Arguments in favour of the relative importance of these different pathways have been reviewed.<sup>42–46</sup> The rate-limiting steps will be reactions (16) and (18), since the lifetimes of carbocations in water, even when stabilized by electron-donating substituents, are at the most a few  $\mu\text{s}$ ,<sup>47–49</sup> and the decomposition of geminal chlorohydrins in water is also very fast (in the order of  $10^6 \text{ s}^{-1}$ ).<sup>14–16</sup> The existence of acetyl chloride hydrate as an intermediate has



been inferred by IR spectroscopy in dioxane solutions of low water content.<sup>26</sup>

Hydration [reaction (18)] is perhaps a concerted process that involves more than one water molecule, as exemplified in reaction (20) whose transition-state might include two molecules of water.

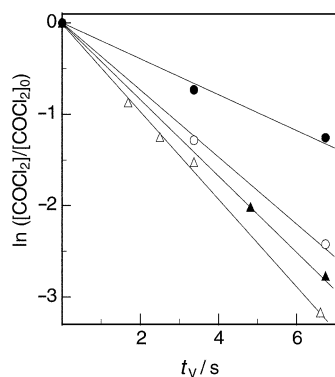


Reactions that occur in aqueous solutions are often facilitated by the co-operation of a cluster of water molecules even though they might not be hydrolytic. A case in point is the very rapid decomposition of formyl chloride which occurs in water many orders of magnitude faster than in the gas phase.<sup>10</sup> The termination of formaldehyde radical anion appears to be another example of the involvement of more than one water molecule in the reaction.<sup>50</sup>

Assuming that acetyl chloride decomposes according to an  $\text{S}_{\text{N}}1$  mechanism in media of sufficiently high ionizing power, electron-drawing substituents which disfavour the release of a chloride ion are thus expected to hamper the  $\text{S}_{\text{N}}1$  reaction. In agreement with this expectation the hydrolysis rate of chloroacetyl chloride is about two orders of magnitude slower than that of the unsubstituted compound. However, with the dichloro compound, the rate is found to be greater again which might indicate a change of mechanism, and further substitution with chlorine increases the rate of hydrolysis even more (Table 1). It might be argued that this can be attributed to an increase, from the mono- to the trichloroacetyl chloride, in the rate of hydrate formation. An analogy suggests itself: one recalls that while acetaldehyde and its hydrate are present in water at about equal concentrations, its trichloro derivative is almost exclusively hydrated (“chloral hydrate”). The irregular trend of the rate constants as regards the 100%-aqueous solutions is in contrast with the systems of low water content where the rate rises regularly with the degree of chlorine substitution (*cf.* Figs. 2 and 3, and ref. 25).

Regarding the catalysis of hydrolysis reactions in acyl halides, the nucleophilic pathway ( $\text{OH}^-$ ) is more effective than the electrophilic one (*e.g.*,  $\text{H}^+$ ). In the case of acetyl chloride, the catalytic effect of acid is apparently nil,<sup>51</sup> while it is observable in trichloroacetyl chloride at pH below about 5.<sup>22</sup> There is also a catalytic effect in the case of acyl fluorides where the proton appears to attach to the fluorine halide which is then removed as hydrogen fluoride.<sup>42,45</sup>  $\text{OH}^-$  reacts by addition at the carbonyl carbon, followed by release of the halide ion.

The rate constants of the  $\text{OH}^-$ -induced hydrolysis of phosgene<sup>13</sup> and formyl chloride<sup>10</sup> and the  $\text{OH}^-$ -induced hydration of acetaldehyde<sup>52</sup> are in the order of  $10^4\text{--}10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , *i.e.* slow compared to the deprotonation at a heteroatom (*e.g.* at O–H) which are close to diffusion controlled.<sup>53</sup> Assuming a maximum rate of  $\text{OH}^-$ -addition of  $10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , this sets the limit for a contribution of  $\text{OH}^-$  at pH 7 at  $10^{-2} \text{ s}^{-1}$ . All of the rates measured in the present study are well above this value, and even in the slowest ones the kinetics do not change as the pH drops in the course of the reaction. As mentioned above,



**Fig. 4** Absorption of phosgene from an air stream containing products from the photooxidation of chlorinated ethylenes as a function of absorber-column contact time and absorber pH.  $[\text{C}(\text{O})\text{Cl}_2]_0 \sim 50$  ppm. pH 13.26 (●), 13.61 (○), 13.80 (▲), 13.90 (△).

any  $\text{H}^+$ -catalyzed hydration as a prelude to hydrolysis can be disregarded. Thus, it is justified to discuss the observed rates on the basis of the reactions (16)–(19).

#### Pilot-plant-scale acyl chloride hydrolysis

Trichloroethylene, tetrachloroethylene, and (*E*)-dichloroethylene were photooxidized and the concentrations of the products dichloroacetyl chloride, trichloroacetyl chloride, phosgene, and formyl chloride, as well as carbon dioxide and carbon monoxide, obtained at different alkalinities and gas flow rates, were determined by FTIR spectroscopy in front, between, and behind the two absorber columns of the set-up used.<sup>29</sup> The results for phosgene are shown in Fig. 4.

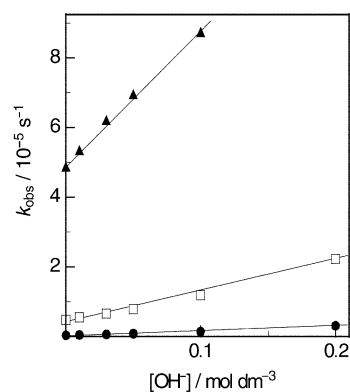
The logarithm of the ratio of exit to entry concentrations is seen to decrease linearly with the contact time (*i.e.* a dependence of the time constant of phosgene removal on its initial concentration was not observed). It is pH-sensitive in the (strongly alkaline) pH range investigated (Fig. 4). Under the conditions that apply in the experiments referred to in Fig. 4, the absorption of phosgene is incomplete. Here, the criterion for “completeness” is a  $c_{\text{gas,final}}$  of 0.2 ppm, *i.e.* about one fifth of the statutory (in Germany) emission limit of  $1 \text{ mg m}^{-3}$ . In contrast, for the chlorinated acetyl chlorides whose mass uptake coefficients  $\gamma$  are larger by about an order of magnitude (see above), *no* column overflow was observed (detection limit,  $c_{\text{gas,final}}/c_{\text{gas,initial}} < 0.02$ ). This is in agreement with rough calculations based on the mass uptake coefficients  $\gamma$  (see above) and data characterizing the reaction conditions in the scrubber such as the gas–liquid interfacial area, residence time, and gas flow rate.

Thus, in technical applications, phosgene absorption provides the limiting factor in the design of a gas scrubber.

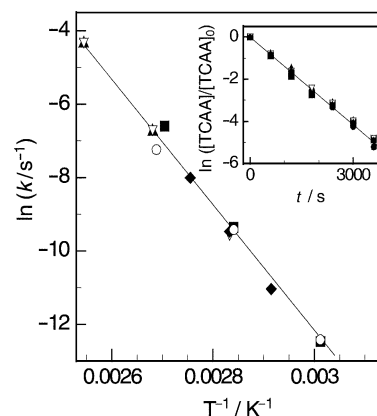
#### Alkaline degradation of chloroacetates

The complete hydrolytic dechlorination of chloroacetic acids, the products of the hydrolysis of the chlorinated acetyl chlorides, requires harsher conditions (temperatures beyond the boiling point of water up to  $200^\circ\text{C}$ ) than the hydrolysis of the corresponding acid chlorides.<sup>7</sup> Kinetic studies have been done on monochloroacetate ( $\text{S}_{\text{N}}2$  kinetics),<sup>30</sup> dichloroacetate ( $\text{S}_{\text{N}}2$  kinetics),<sup>30,31</sup> and trichloroacetate (decarboxylation).<sup>31</sup> Fig. 5 shows, by way of example, some kinetic results of the batch hydrolysis experiments of dichloroacetate.

In the cases of the mono- and dichloroacetates the rate constant is made up of two terms, *i.e.*  $k_{\text{obs}} = k_0 + k_{\text{OH}^-} \times [\text{OH}^-]$ . For monochloroacetate, the temperature dependence of the intercept gives  $\ln k_0 = 36.4 - 17800/T$ , corresponding to an activation energy of  $148 \text{ J mol}^{-1}$  (*cf.* Table 2; diagram not shown). The Arrhenius plot of the second-order rate constant  $k_{\text{OH}^-}$  gives  $\ln k_{\text{OH}^-} = 21.2 - 10300/T$  ( $E_a$   $85.7 \text{ kJ mol}^{-1}$ ). The



**Fig. 5** Kinetics of the hydrolysis of dichloroacetate at  $80^\circ\text{C}$  (●),  $100^\circ\text{C}$  (□) and  $120^\circ\text{C}$  (▲) as a function of the  $\text{OH}^-$  concentration.



**Fig. 6** Arrhenius plot of the degradation of trichloroacetate (○, water; ▽, water, vessel silanised; ■, 5 M NaOH; ▲, 1.5 M NaOH, vessel silanised; ◆, ref. 31). Inset: kinetics of the degradation of trichloroacetate at  $100^\circ\text{C}$ ;  $\ln k_{\text{obs}}$  as a function of time at varying  $\text{OH}^-$  concentrations (●,  $5 \times 10^{-3} \text{ mol dm}^{-3}$  NaOH; ■,  $1 \times 10^{-2} \text{ mol dm}^{-3}$  NaOH; ▽,  $0.1 \text{ mol dm}^{-3}$  NaOH; ◆,  $0.5 \times 10^{-3} \text{ mol dm}^{-3}$  NaOH).

products chloride ion and glycolic acid give an essentially complete material balance.<sup>29</sup>

The degradation rate constants of dichloroacetate and trichloroacetate were obtained in a like manner (for data see ref. 29). In the case of dichloroacetate as in the monochloro compound, the rate constant consists of two terms, with  $\ln k_0 = 38.0 - 18800/T$  ( $E_a$   $156 \text{ kJ mol}^{-1}$ ) and  $\ln k_{\text{OH}^-} = 24.2 - 12500/T$  ( $E_a$   $103.7 \text{ kJ mol}^{-1}$ , in good agreement with the literature<sup>31</sup>). Wall effects appear to play some role in  $k_0$ .<sup>29</sup> The degradation essentially furnishes chloride and glyoxylic acid. A decarboxylation reaction analogous to reaction (12) is unimportant here (below 1%). The presence of glycolic and oxalic acids is ascribed to the Cannizzaro reaction of glyoxylic acid under these strongly alkaline conditions.

In contrast to the mono- and dichloroacetates, trichloroacetate decays by decarboxylation, owing to the strongly electron-drawing trichloromethyl group, essentially uncatalyzed by  $\text{OH}^-$ . An Arrhenius plot is presented in Fig. 6 which shows that the kinetics is not influenced by alkali or the nature of the vessel walls.

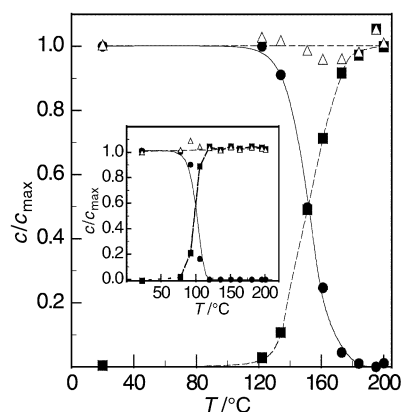
The kinetics is described by  $\ln k_0 = 39.9 - 17400/T$  ( $E_a$   $144.6 \text{ kJ mol}^{-1}$ , in good agreement with the literature<sup>31</sup>). While the presence of strong base is irrelevant for the degradation of the trichloroacetate, it ensures the subsequent decomposition of the chloroform resulting from the decarboxylation reaction [*cf.* reactions (12) and (13)] according to an  $\text{S}_{\text{N}}2$  mechanism [*cf.* reactions (14) and (15)].

Some comments can be made regarding the quantities in Table 2, columns 2 and 5. The frequency factors in column 2, in particular the bottom one, appear to be quite large. High frequency factors may be associated with reactions in which more

**Table 2** Activation parameters of the dechlorination/degradation of chlorinated acetates

Chlorinated acetate	H <sub>2</sub> O-induced <i>A</i> /s <sup>-1</sup>	H <sub>2</sub> O-induced <i>E<sub>a</sub></i> /kJ mol <sup>-1</sup>	OH <sup>-</sup> -induced <i>A</i> /dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>	OH <sup>-</sup> -induced <i>E<sub>a</sub></i> /kJ mol <sup>-1</sup>
Chloroacetate	6.4 × 10 <sup>15</sup>	148	1.6 × 10 <sup>9</sup>	86
Dichloroacetate	3.2 × 10 <sup>16</sup>	156	3.2 × 10 <sup>10</sup>	104
Trichloroacetate	2.1 × 10 <sup>17a</sup>	146 <sup>a</sup>	—	—

<sup>a</sup> First-order but not H<sub>2</sub>O-induced.



**Fig. 7** Degree of degradation  $c_{\text{measured}}/c_{\text{max}}$  of dichloroacetate (●) without alkali; liberated chloride (■); sum (Δ) of 2 × dichloroacetate and liberated chloride; contact time in the hydrothermal flow reactor, 480 s. Inset: trichloroacetate (●), liberated chloride (■), sum (Δ) of 3 × trichloroacetate and liberated chloride; contact time, 450 s.

than one bond is ruptured simultaneously, as well as certain dissociation reactions where a bond is broken that links two groups of atoms.<sup>54</sup> The hydrolytic removal of chloride in the mono- and dichloroacetates can be viewed as an example of the first class, e.g. reaction (21), with a C–Cl and an O–H bond



being cleaved as a water molecule attaches to the chlorine-bearing carbon atom. On the other hand, the decomposition of trichloroacetate seems akin, for instance, to the homolysis of alkanes [e.g.  $\text{C}(\text{CH}_3)_4 \rightarrow \cdot\text{CH}_3 + \cdot\text{C}(\text{CH}_3)_3$  has  $A \sim 10^{17} \text{ s}^{-1}$ ].<sup>54</sup>

The activation energy of the OH<sup>-</sup>-catalyzed dechlorination is seen to increase on going from the mono- to the dichloroacetate (Table 2, column 5). This is in agreement with the idea that as the partial charge on the chloromethyl group increases, the barrier for the entry of OH<sup>-</sup> also increases, so that finally in the case of the trichloroacetate the hydrolytic pathway is practically blocked, relative to decarboxylation. It is, moreover, reasonable to assume that OH<sup>-</sup> attack is at the chloromethyl group not at the carbonyl group, which in fact has lost its usual characteristics owing to carboxylate mesomerism.

#### Hydrothermal flow reactor

The results of some systematic decomposition studies with a hydrothermal flow reactor<sup>29</sup> (in which the disappearance of the reactant and the appearance of products were followed as functions of temperature and alkalinity) conform to expectation based on the foregoing rate constants. This technique has been applied to chloroacetates before.<sup>7</sup> Practically complete dechlorination (a typical example is shown in Fig. 7) of these compounds is achievable within a time span in the order of 10<sup>2</sup> s at temperatures well below 200 °C.

In 1 M NaOH as the medium, the half-way point of the dichloroacetate degradation is shifted to lower temperatures by about 22 °C, i.e. to below 130 °C (data not shown). Thus, complete dechlorination of dichloroacetate is achieved after 8 min

in 1 M NaOH at 150 °C, or in water at 180 °C, i.e. there is a trade-off between the operation of the process at relatively low overpressures but in a relatively corrosive reaction medium, and *vice versa*.

#### Acknowledgements

Partial financial support by the German Federal Ministry of Education and Research (Project No. 02WT9656/57) and the Stadtwerke Düsseldorf AG (Project No. 230/45083468) is gratefully acknowledged.

#### References

- R. Koppmann, F. J. Johnen, C. Plass-Dülmer and J. Rudolph, *J. Geophys. Res.*, 1993, **98**, 20517.
- A. McCulloch and P. M. Midgley, *Atmos. Environ.*, 1996, **40**, 601.
- L. Prager, R. Mehnert, A. Sobottka, H. Langguth, W. Baumann, W. Mätzing, H.-R. Paur, J. Schubert, R. Rashid, K. M. Taba, H.-P. Schuchmann and C. von Sonntag, *J. Adv. Oxid. Technol.*, 1998, **3**, 87.
- T. Mill, M. G. Su, C. C. D. Yao, S. M. Matthews and F. T. S. Wang, *Radiat. Phys. Chem.*, 1997, **50**, 283.
- T. Hakoda, S. Hashimoto, J. Fujiyama and A. Mizuno, *J. Phys. Chem. A*, 2000, **104**, 59.
- E. Sanhueza, I. C. Hisatsune and J. Heicklen, *Chem. Rev.*, 1976, **76**, 801.
- W. R. Haag, M. D. Johnson and R. Scofield, *Environ. Sci. Technol.*, 1996, **30**, 414.
- L. Prager and E. Hartmann, *J. Photochem. Photobiol. A*, 2001, **138**, 177.
- R. Butler and A. Snelson, *J. Air Pollut. Control Assoc.*, 1979, **29**, 833.
- P. Dowideit, R. Mertens and C. von Sonntag, *J. Am. Chem. Soc.*, 1996, **118**, 11288.
- P. Dowideit, Doctoral thesis, Ruhr-Universität Bochum, 1996.
- W. H. Manogue and R. L. Pigford, *AIChE J.*, 1960, **6**, 494.
- R. Mertens, C. von Sonntag, J. Lind and G. Merényi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1259.
- R. Köster and K.-D. Asmus, *Z. Naturforsch., B. Anorg. Chem. Org. Chem.*, 1971, **26**, 1108.
- R. Mertens and C. von Sonntag, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2181.
- N. Latif, P. O'Neill, D. Schulte-Frohlinde and S. Steenzen, *Ber. Bunsen-Ges. Phys. Chem.*, 1978, **82**, 468.
- W. J. De Bruin, S. X. Duan, X. Q. Shi, P. Davidovits, D. R. Worsnop, M. S. Zahniser and C. E. Kolb, *Geophys. Res. Lett.*, 1992, **19**, 1939.
- P. Davidovits, J. H. Hu, D. R. Worsnop, M. S. Zahniser and C. E. Kolb, *Faraday Discuss.*, 1995, **100**, 65.
- G. M. Nathanson, P. Davidovits, D. R. Worsnop and C. E. Kolb, *J. Phys. Chem.*, 1996, **100**, 13007.
- C. E. Kolb, J. T. Jayne, D. R. Worsnop and P. Davidovits, *Pure Appl. Chem.*, 1997, **69**, 959.
- W. J. De Bruyn, J. A. Shorter, P. Davidovits, D. R. Worsnop, M. S. Zahniser and C. E. Kolb, *Environ. Sci. Technol.*, 1995, **29**, 1179.
- C. George, J. Lagrange, P. Lagrange, P. Mirabel, C. Pallares and J. L. Ponche, *J. Geophys. Res.*, 1998, **99**, 1255.
- T. W. Bentley, G. Llewellyn and J. A. McAlister, *J. Org. Chem.*, 1996, **61**, 7927.
- V. Gold and J. Hilton, *J. Chem. Soc.*, 1955, 3303.
- I. Ugi and F. Beck, *Chem. Ber.*, 1960, **94**, 1839.
- V. A. Terentev and V. V. Varfolomeeva, *Russ. J. Gen. Chem.*, 1996, **66**, 1954.
- E. J. Cairns and J. M. Prausnitz, *J. Chem. Phys.*, 1960, **32**, 169.
- R. F. Hudson and G. E. Moss, *J. Chem. Soc.*, 1962, 5157.

- 29 L. Prager, Doctoral thesis, Leipzig University, Leipzig, Germany, 2000.
- 30 H. Dautzenberg and B. Philipp, *Z. Phys. Chem. (Leipzig)*, 1979, **260**, 289.
- 31 H. Dautzenberg and B. Philipp, *Z. Phys. Chem. (Leipzig)*, 1979, **260**, 298.
- 32 P. M. Jeffers, L. M. Ward, L. M. Woytowitch and N. L. Wolfe, *Environ. Sci. Technol.*, 1989, **23**, 965.
- 33 P. Dowideit and C. von Sonntag, *Environ. Sci. Technol.*, 1998, **32**, 1112.
- 34 H. Strehlow, *Rapid Reactions in Solution*, VCH, Weinheim, 1992.
- 35 E. Bothe and E. Janata, *Radiat. Phys. Chem.*, 1994, **44**, 455.
- 36 E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.
- 37 A. Leitzke, R. Flyunt and C. von Sonntag, in preparation.
- 38 D. A. Brown and R. F. Hudson, *J. Chem. Soc.*, 1953, 3352.
- 39 V. Gold, J. Hilton and E. G. Jefferson, *J. Chem. Soc.*, 1954, 2756.
- 40 V. Gold and J. Hilton, *J. Chem. Soc.*, 1955, 3303.
- 41 E. W. Crunden and R. F. Hudson, *J. Chem. Soc.*, 1956, 501.
- 42 R. J. E. Talbot, in *Ester Formation and Hydrolysis and Related Reactions*, ed. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1972, p. 209.
- 43 A. Kivinen, *Acta Chem. Scand.*, 1965, **19**, 845.
- 44 H. Minato, *Bull. Chem. Soc. Jpn.*, 1964, **37**, 316.
- 45 A. Kivinen, in *The Chemistry of Acyl Halides*, ed. S. Patai, Wiley Interscience, London, 1972, p. 177.
- 46 D. P. N. Satchell and R. S. Satchell, in *Supplement B. The Chemistry of Acid Derivatives, Vol. 2*, ed. S. Patai, Wiley, New York, 1992, p. 747.
- 47 S. Steenken, J. Buschek and R. A. McClelland, *J. Am. Chem. Soc.*, 1986, **108**, 2808.
- 48 S. Steenken and R. A. McClelland, *J. Am. Chem. Soc.*, 1989, **111**, 4967.
- 49 D. J. Deeble, M. N. Schuchmann, S. Steenken and C. von Sonntag, *J. Phys. Chem.*, 1990, **94**, 8186.
- 50 W.-F. Wang, M. N. Schuchmann, V. Bachler, H.-P. Schuchmann and C. von Sonntag, *J. Phys. Chem.*, 1996, **100**, 15843.
- 51 V. Gold and J. Hilton, *J. Chem. Soc.*, 1955, 838.
- 52 J. L. Kurz and J. I. Coburn, *J. Am. Chem. Soc.*, 1967, **89**, 3528.
- 53 M. Eigen, W. Kruse, G. Maass and L. De Maeyer, *Prog. React. Kinet.*, 1964, **2**, 285.
- 54 C. Steel and K. J. Laidler, *J. Chem. Phys.*, 1961, **34**, 1827.