11288 *J. Am. Chem. Soc.* **1996,** *118,* 11288−11292

Non-Hydrolytic Decay of Formyl Chloride into CO and HCl in Aqueous Solution

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Received July 24, 1996⊗

Abstract: Formyl chloride has been generated in aqueous solution (i) by stopped-flow ozonation of vinyl chloride and (ii) by reacting dichloromethyl radicals with OH radicals using the pulse radiolysis technique. Vinyl chloride reacts in water with ozone ($k = 1.7 \times 10^4$ dm^3 mol^{-1} s^{-1}, as determined by stopped-flow) yielding as final products (mol per mol of ozone) chloride ions (1.05), CO (1.01), and formate ions (0.06). Hydroxymethyl hydroperoxide (formaldehyde plus H_2O_2; 1.08) is also formed. HCl and formic acid are formed in less than 2 ms (the detection limit of the stopped-flow setup). At high pH the CO yield decreases (at pH 13.6 by 50%). It is concluded that the precursor of CO, HCl, and formic acid is formyl chloride. It predominantly decays into CO and HCl, and only at very high pH can hydrolysis to formic acid and HCl compete successfully. Using the pulse radiolysis technique dichloromethyl radicals are generated in Ar-saturated solutions from chloroform by reacting it with the solvated electron (originating from the radiolysis of water). The OH radicals (also from the radiolysis of water) partially react with the dichloromethyl radicals yielding dichloromethanol. Alternatively, dichloromethanol is generated in N_2O-saturated solutions from dichloromethane, where some of the OH radicals are allowed to abstract an H atom from dichloromethane and another fraction to add to the dichloromethyl radicals. The observed conductivity changes are attributed to a very rapid decay ($t_{1/2} < 20$ μs) of dichloromethanol into formyl chloride and HCl followed by the decay of formyl chloride into CO and HCl ($k = 10^4$ s^{-1}). From these data and the decrease of the CO yield at high pH (ozonation of vinyl chloride) it is estimated that the OH$^-$-induced hydrolysis of formyl chloride occurs with a rate constant of ca. 2.5×10^4 dm^3 mol^{-1} s^{-1}.

Introduction

Formyl chloride (HC(O)Cl) was first prepared[1] by photolysing a mixture of formaldehyde and chlorine at low temperatures. A product was obtained which subsequently decomposed into CO and HCl (reaction 1) preventing the purification and full characterization of this unstable product. In aqueous solutions, formyl chloride again decomposed into CO and HCl and only traces of formic acid, the product of hydrolysis (reaction 2), were found.[1]

$$HC(O)Cl \rightarrow CO + HCl \qquad (1)$$

$$HC(O)Cl + H_2O \rightarrow HCOOH + HCl \qquad (2)$$

Formyl chloride was later characterized by its gas-phase infrared absorption spectrum[2] and found to be an intermediate in the atmospheric degradation of several chlorinated hydrocarbons. Quantum mechanical calculations indicate that the activation energy and energy difference between formyl chloride and the products resulting from its unimolecular decomposition, CO and HCl, are 43.95 kcal mol^{-1} and -1.16 kcal mol^{-1}, respectively.[3] Such a high activation energy should result in a lifetime at room temperature in the order of 10^{13} years. However, its measured gas-phase lifetime is much shorter and seems to depend on the size of the reaction vessel: in a 0.1-dm^3 vessel its lifetime was only about 10 min,[2] while in a 480-dm^3 vessel it increased to between 28 and 190 min.[4] This strongly points to wall effects, whereby traces of water could play an important role in its decomposition.

Our interest in the reactions of formyl chloride in aqueous solutions resulted from our studies on the UV-, ozone-, and OH-radical-induced degradation of chlorinated hydrocarbons.[5−11] These compounds have become frequent pollutants of drinking-water resources. Remediation is sought by the so-called Advanced Oxidation Processes (*e.g.* UV/hydrogen peroxide, UV/ozone, ozone/hydrogen peroxide, and electron beam irradiation).[12] They all have in common that they generate the highly reactive OH radical (for rate constants see reference 13). The more reactive pollutants may also be destroyed with ozone (for rate constants see reference 14). The kinetics of the OH-radical-induced degradation of chlorinated hydrocarbons can be studied readily by pulse radiolysis, while ozone reactions can

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⊗ Abstract published in *Advance ACS Abstracts,* October 15, 1996.

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be followed by stopped-flow techniques. In both cases, the method of conductometric detection[15-18] is used advantageously, since the liberation of chloride ions (and concomitantly protons) in the course of the oxidative degradation cascade is accompanied by a conductance change.

In order to assign a kinetic component of a sequence of conductance changes to a given elementary step in such an ozone- or OH-radical-induced oxidation, the kinetic parameters of the reaction must be determined independently. This has recently been done for phosgene,[9] but the kinetics of the decomposition of formyl chloride in water has so far remained unknown.

In order to generate formyl chloride in water *in situ* two approaches have been followed in the present study: the ozonation of vinyl chloride (overall reaction 3) and the reaction of the dichloromethyl radical with an OH radical (reactions 4 and 5).

$$CH_2{=}CHCl + O_3 + H_2O \rightarrow HOCH_2OOH + HC(O)Cl \quad (3)$$

$$^{\bullet}CHCl_2 + {}^{\bullet}OH \rightarrow HOCHCl_2 \quad (4)$$

$$HOCHCl_2 \rightarrow HC(O)Cl + HCl \quad (5)$$

It will be shown that in water formyl chloride decays very rapidly into CO and HCl, and that only at very high pH can hydrolysis into formic acid and HCl compete successfully.

Experimental Section

Vinyl chloride (Fluka, 99%) and chloroform and dichloromethane (>99% Merck) were used without further purification. All reactions were carried out in Milli-Q-purified (Millipore) water. Ozone was generated from oxygen (SWO-70, WEDECO, Herford), and its concentration in aqueous solutions was determined spectrophotometrically (ϵ(260 nm) = 3314 $dm^3\ mol^{-1}\ cm^{-1}$).[19] The stopped-flow setup (BIOLOGIC SFM-3) was equipped with a diode array spectrophotometer (TIDAS-16, J&M Anal. Mess-und Regeltechnik, Aalen) and a home-made conductivity detection system (Wheatstone bridge arrangement,[18] 30-μL cuvette, rise time 2 ms) whose further details will be described elsewhere.

For pulse radiolysis the aqueous solutions were purged with either argon (99.99%) or N_2O to free the solutions from oxygen. A 2.7 MeV Van de Graaff electron accelerator was run at its highest possible dose per pulse (ca. 60 Gy at electron pulses of 4-μs duration).[17] Details of the conductometric system have been described.[17,18]

Carbon monoxide was determined with an electrochemical sensor (MWG 2502; Gesellschaft für Gerätebau, Dortmund). The detector is placed in a circuit containing the reaction vessel (12 mL), a peristaltic pump, and a reference loop (11 μL) (Figure 1). The gas volume of this circuit is pumped through the system until it reaches an equilibrium between the gas and water phase. The concentration of CO formed was quantified by filling the reference loop with CO as an external standard. Due to different rates of CO supply from the reference loop and the purged sample, different response profiles are obtained (insets A and B in Figure 1). In addition, some fading of the signals occurs at longer times. Although this may cause a systematic error in the order of 10%, quantitation of CO yields is satisfactory (*cf.* inset C in Figure 1). Carbon monoxide down to concentrations of 5×10^{-6} mol dm^{-3} can be measured with this setup. For measuring the pH dependence of CO formation, phosphate and borate buffers (Merck) were used in the pH range where acid formation could shift the pH significantly. For high pH, 1 M NaOH was diluted appropriately.

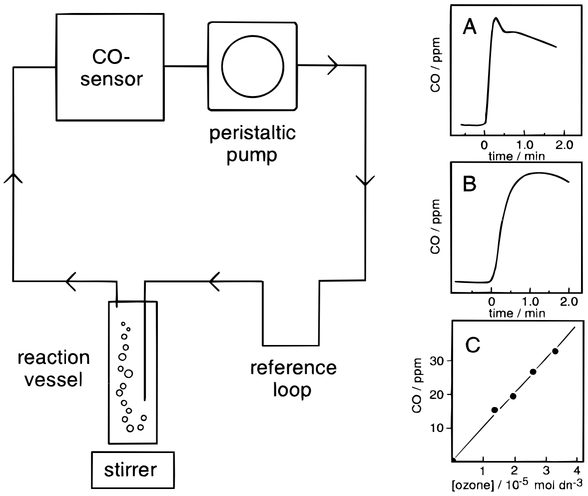

Figure 1. CO detection setup: schematic scheme of the CO gas flow. Insets: (A) calibration; (B) measurement of a CO-containing aqueous solution; (C) CO yield as a function of ozone concentration in the ozonation of vinyl chloride.

Formaldehyde was measured by the method of Hantzsch,[20] and hydrogen peroxide and organic hydroperoxides were determined with Allen's reagent.[21] Chloride and formate ions were measured by high-performance ion chromatography (Dionex DX-100; Ion Pac AS-9 column with an Ion Pac AG9 pre-column, eluent 2×10^{-3} mol dm^{-3} of $NaHCO_3$). Product yields increased linearly with ozone concentration (10^{-5} to 2×10^{-4} mol dm^{-3}).

Kinetic simulations were made using the Gear algorithm.[22,23]

Results and Discussion

Ozonation of Vinyl Chloride. The rate of the reaction of ozone with vinyl chloride was determined by stopped-flow by monitoring the decay of ozone at 260 nm as a function of the vinyl chloride concentration which was present in large excess with respect to ozone. From the linear dependence of k_{obs} as a function of the vinyl chloride concentration a rate constant of $k = 1.7 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$ is calculated.

For product studies, saturated vinyl chloride solutions (solubility of vinyl chloride at 20 °C = 4.32×10^{-2} mol dm^{-3})[24] were mixed with varying amounts of ozone. The product yields increased linearly with increasing amounts of added ozone (*cf.* inset C in Figure 1). A full material balance is obtained: (mol of products/mol of ozone) 1.05 mol of chloride, 0.06 mol of formate, 1.01 mol of carbon monoxide, and 1.08 mol of hydroxymethyl hydroperoxide. The formation of hydroxymethyl hydroperoxide was ascertained by (i) the formation of formaldehyde and (ii) the kinetics of its reaction with Allen's reagent (essentially KI). A kinetic trace of the formation of I_3^- at 350 nm when ozonated vinyl chloride solutions were reacted with this reagent is shown in Figure 2. An authentic sample (from formaldehyde and hydrogen peroxide; at 20 °C the stability constant of hydroxymethyl hydroperoxide is $1.3 \times 10^4\ dm^3\ mol^{-1}$)[25] showed the same kinetics. For comparison, a similar experiment has been made with hydrogen peroxide (inset in Figure 2). It can be seen from this figure that the reaction of hydroxymethyl hydroperoxide is considerably slower than that of hydrogen peroxide.

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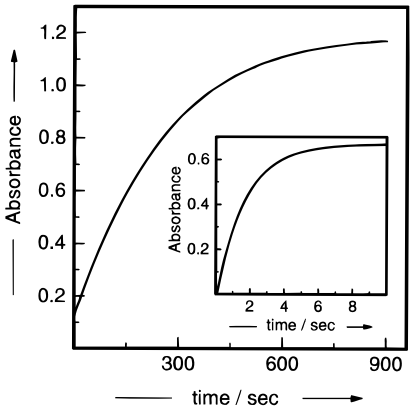


Figure 2. Reaction of Allen's reagent with the peroxidic product formed in the reaction of vinyl chloride with ozone. Kinetics of the buildup of I_3^- measured at 350 nm. Inset: The kinetics of Allen's reagent with H_2O_2.

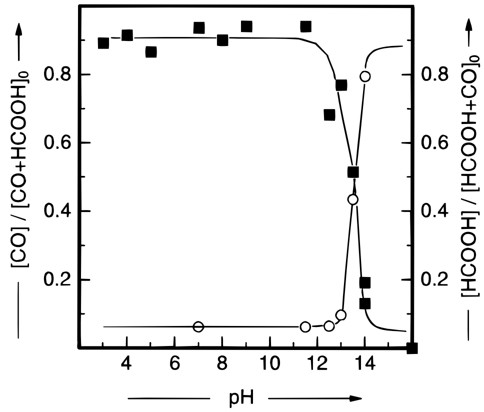
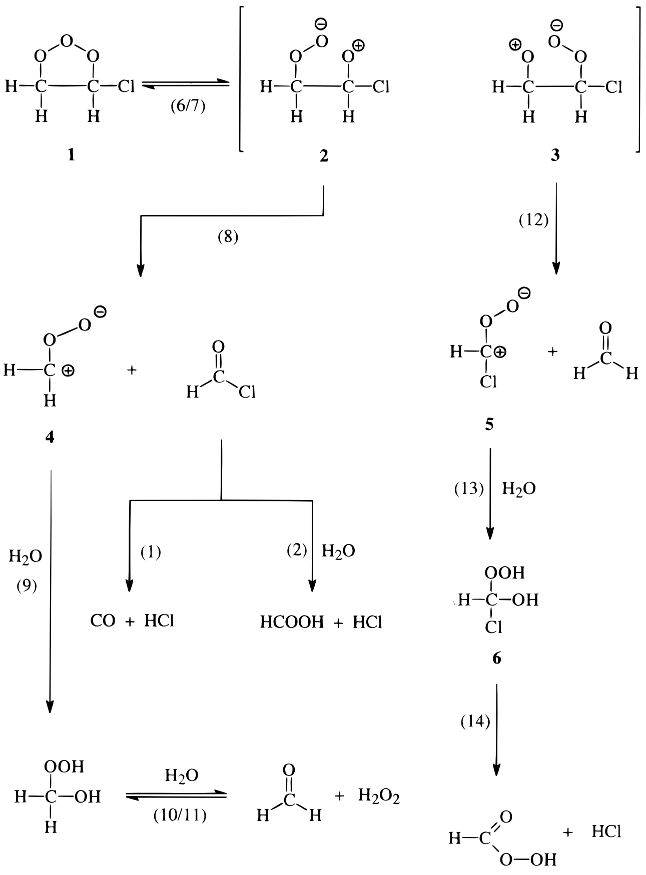


Figure 3. Ozonation of vinyl chloride in aqueous solution with yields of CO and formic acid as a function of pH.

The CO yield does not depend on the pH in acid solutions but strongly decreases at high pH (Figure 3). At approximately pH 13.6 its yield drops to half of its maximum value. The drop in the CO yield is accompanied by an increase in the yield of formic acid (○ in Figure 3; at these high pH values hydroxide ions have to be neutralized and formate determinations are fraught with a considerable error due to the high background of salt). Due to the high rate constant of the reaction of vinyl chloride with ozone it can be excluded that this drop in the CO yield is due to the reaction of hydroxide ions with ozone (k = 48 $dm^3\ mol^{-1}\ s^{-1}$)[14] and the subsequent reactions of vinyl chloride with the OH radicals thus formed.

When a saturated vinyl chloride solution is reacted with ozone the half-life of the reaction falls into the microsecond time range, *i.e.* it is much faster than the resolution of our stopped-flow setup, both with optical (ca. 2 ms) and conductometric (ca. 1 ms) detection. Under such conditions the conductivity change due to the formation of HCl (and of minor amounts of formic acid) is instantaneous, and no longer-lived acid-releasing intermediates are detected.

Scheme 1



These observations lead to the following mechanistic proposal: Electrophilic ozone addition to the double bond leads to the primary zwitterion (not shown) which closes to the ozonide **1**. The ozonide **1** can open to the secondary zwitterions **2** and **3** (equilibrium 6/7). The secondary zwitterion **2** decays to formyl chloride and the tertiary zwitterion **4** (reaction 8). In its reaction with water, **4** yields hydroxymethyl hydroperoxide (reaction 9) which is in equilibrium with formaldehyde and hydrogen peroxide (equilibrium 10/11); $K = 1.3 \times 10^4$ $dm^3\ mol^{-1}$).[25] Formyl chloride decomposes into CO and HCl (reaction 1), and in competition it hydrolyses into HCl and formic acid (reaction 2). The alternative route, formation and decay of zwitterion **3** (reactions 12−14), which leads to performic acid, can be neglected. This peracid is formed when *cis*- or *trans*-dichloroethene is ozonated. Its rate of reaction with Allen's reagent is 1.8×10^3 $dm^3\ mol^{-1}\ s^{-1}$, i.e. nearly 1000 times faster than that of hydrogen peroxide. The very small intercept in Figure 2 mainly results from the time elapsed by manually mixing the reagent with the ozonated solution. In a stopped-flow experiment this intercept has been narrowed down to <2% (the hydrolysis of performic acid is relatively slow but 5 times faster ($k = 1.6 \times 10^{-4}\ s^{-1}$; Dowideit and von Sonntag, to be published) than that of acetic peracid ($k = 3.5 \times 10^{-5}\ s^{-1}$, *cf.* reference 26).

It has been mentioned above that the formation of HCl is faster than the resolution of the conductometric detection system of our stopped-flow setup. Hence $k_1 + k_2$ must be considerably faster than 300 s^{-1}. In addition, due to the much lower yield of formic acid reaction 2 must be considerably slower than reaction 1. An OH^--induced hydrolysis only sets in at very high pH (*cf.* Figure 3). In order to assess the rate constant of reaction 1, a method is required which not only generates formyl chloride on the microsecond time scale but also allows the measurement of its decomposition in this time range. To this end, pulse radiolysis experiments have been carried out.

Pulse Radiolysis of Dichloromethane and Chloroform Solutions. Formyl chloride may be generated pulse-radiolytically from dichloromethane or chloroform via the dichloromethyl radical and (the potentially very short-lived; *cf.* reference 9) dichloromethanol (reactions 4 and 5). In the radiolysis of

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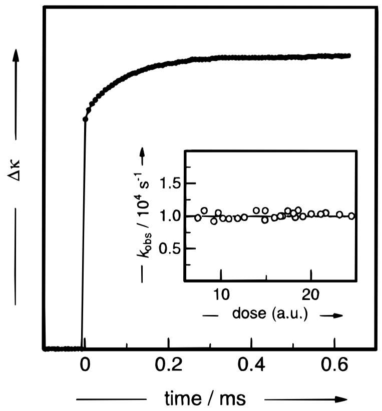

Figure 4. Pulse radiolysis of Ar-saturated aqueous solutions of chloroform (2×10^{-3} mol dm^{-3}). Kinetics of the buildup of conductivity. Inset: Dependence of the rate of the slower part of the conductivity buildup as a function of the dose per pulse.

water OH radicals, solvated electrons and H atoms are formed as short-lived intermediates. Hydroxyl radicals and solvated electrons are formed in about equal amounts ($G(^{\bullet}OH) \approx G(e_{aq}^{-}) \approx 2.8 \times 10^{-7}$ mol J^{-1}), while the yield of H atoms is considerably lower ($G(^{\bullet}H) \approx 0.6 \times 10^{-7}$ mol J^{-1}).[27]

$$H_2O \xrightarrow{\text{ionizing radiation}} e_{aq}^{-}, OH, H^{\bullet}, H^{+}, OH^{-}, H_2O_2, H_2 \qquad (15)$$

Dichloromethyl radicals may be formed in the reaction of (i) chloroform with the solvated electron (*cf.* reaction 16) or (ii) dichloromethane with OH radicals (*cf.* reaction 28). The dichloromethyl radicals must then react with OH radicals (reaction 4). This requires a relatively high OH-radical concentration which can be achieved by high doses per pulse. Under such conditions dichloromethanol and formyl chloride are formed very rapidly, and their decomposition/hydrolysis can be followed by changes in conductivity. Both routes (i) and (ii) will be discussed.

Chloroform reacts very fast with the solvated electrons to yield the desired dichloromethyl radicals (reaction (16), $k_{16} = 3 \times 10^{10}$ dm^3 mol^{-1} s^{-1})[13] while the OH radicals and the H atoms react with chloroform much more slowly (reaction 17, $k_{17} = 5 \times 10^6$ dm^3 mol^{-1} s^{-1}, and reaction 18, $k_{18} = 1.1 \times 10^7$ dm^3 mol^{-1} s^{-1}).[13] Thus conditions can be met where a considerable part of the OH radicals react with the dichloromethyl radicals (reaction 4). As far as conductance change is concerned, reactions of two OH radicals (reaction 19, $k_{19} = 1.1 \times 10^{10}$ dm^3 mol^{-1} s^{-1}),[13] the reaction of OH radicals with the H atom (reaction 20, $k_{20} = 7.0 \times 10^9$ dm^3 mol^{-1} s^{-1})[13], and the combination of dichloromethyl radicals and trichloromethyl radicals (reactions 21−23; estimated at $k_{22} = k_{23} = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}) are invisible, apart from reducing the yield of dichloromethanol/formyl chloride (reaction 4, estimated at $k_4 = 6 \times 10^9$ dm^3 mol^{-1} s^{-1} on the basis of the high self-termination rate constant of the OH radical). The reaction of the trichloromethyl radical with the OH radical, a minor reaction under appropriately chosen conditions, leads to the formation of trichloromethanol and subsequently to phosgene (reactions 24 and 25). The rate of their decomposition/hydrolysis has been determined before ($k_{25} > 7 \times 10^5$ s^{-1}; $k_{26} = 9$ s^{-1}),[9] and it will be shown that the slow hydrolysis of phosgene does not interfere with the decay process of interest.

$$e_{aq}^{-} + CHCl_3 \rightarrow {}^{\bullet}CHCl_2 + Cl^{-} \qquad (16)$$

$$^{\bullet}OH + CHCl_3 \rightarrow H_2O + {}^{\bullet}CCl_3 \qquad (17)$$

$$^{\bullet}H + CHCl_3 \rightarrow H_2 + {}^{\bullet}CCl_3\ (HCl + {}^{\bullet}CHCl_2) \qquad (18)$$

$$2^{\bullet}OH \rightarrow H_2O_2 \qquad (19)$$

$$^{\bullet}OH + {}^{\bullet}H \rightarrow H_2O \qquad (20)$$

$$2^{\bullet}CHCl_2 \rightarrow C_2H_2Cl_4 \qquad (21)$$

$$^{\bullet}CHCl_2 + {}^{\bullet}CCl_3 \rightarrow C_2HCl_5 \qquad (22)$$

$$2^{\bullet}CCl_3 \rightarrow C_2Cl_6 \qquad (23)$$

$$^{\bullet}OH + {}^{\bullet}CCl_3 \rightarrow HOCCl_3 \qquad (24)$$

$$HOCCl_3 \rightarrow Cl_2CO + HCl \qquad (25)$$

$$Cl_2CO \rightarrow CO_2 + 2HCl \qquad (26)$$

When argon-purged aqueous solutions of chloroform (2×10^{-3} mol dm^{-3}) are subjected to high-energy electron pulses of 4-μs duration, an increase in conductivity equivalent to ~3 $\times 10^{-7}$ mol J^{-1} is observed 20 μs after the pulse, *i.e.* when the excess conductivity due to the formation of H$^+$ and OH$^-$ formed during the pulse (reaction 15) has largely decayed. At the high doses used in these experiments (up to 60 Gy; equivalent to a total radical concentration of up to 3.7×10^{-5} mol dm^{-3}) the first half-life of the radicals is 5 μs and the radical reactions are practically complete after 25 μs (estimated by computer simulation). Hence most of the dichloromethanol is already formed during the first 25 μs. Vicinal chlorohydrins, e.g. trichloromethanol,[9] the OH-radical adducts to halogenated olefins,[8,28] and the *ipso*-OH adducts to chlorinated anisols[29] show HCl release within a few microseconds.

Thus this first and fast increase in conductivity can be accounted for not only by reactions 15 followed by 16 but also to a large extent by reactions 5 and 25.

Following this initial fast conductivity buildup there is a slower one with a half-life of ca. 80 μs and a yield of approximately 0.8×10^{-7} mol J^{-1} (Figure 4). The half-life of this second conductivity increase is independent of the dose per pulse (inset in Figure 4). We attribute this second phase of conductivity increase to the decay and hydrolysis of formyl chloride (reactions 1 and 2). The overall rate constant is calculated at $k \approx 10^4$ s^{-1}. For the applied dose of about 60 Gy the formation of $CHCl_2OH$ is ≈30% of the primary OH radical's yield (estimated by computer simulation). The measured yield of the second conductivity increase agrees with this estimate.

Confirmation of the above rate constant is obtained by the experiments using dichloromethane as a source of dichloromethyl radicals. In this approach N_2O-purged solutions of dichloromethane (10^{-3} mol dm^{-3}) were pulse-irradiated. In the N_2O-saturated solutions ($[N_2O] = 2 \times 10^{-2}$ mol dm^{-3}) the solvated electrons are converted into OH radicals (reaction 27, $k_{27} = 9.1 \times 10^9$ dm^3 mol^{-1} s^{-1})[13] so that the total yield of these radicals increases to about 5.8×10^{-7} mol J^{-1}. The OH radicals and the H atoms react with dichloromethane (reactions 28 and 29, $k_{28} = 5.8 \times 10^7$ dm^3 mol^{-1} s^{-1}, $k_{29} = 4 \times 10^6$ dm^3

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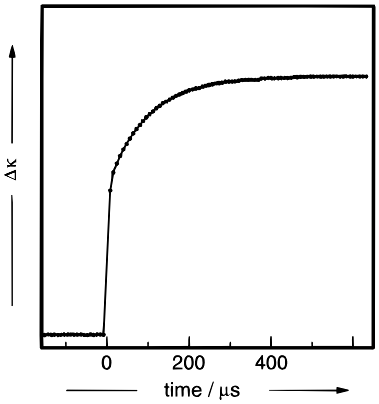

Figure 5. Pulse radiolysis of N_2O-saturated aqueous solutions of dichloromethane (10^{-3} mol dm^{-3}). Kinetics of the buildup of conductivity.

mol^{-1} s^{-1}).[13]

$$e^-_{aq} + N_2O \rightarrow {}^\bullet OH + N_2 + OH^- \qquad (27)$$

$$^\bullet OH + CH_2Cl_2 \rightarrow H_2O + {}^\bullet CHCl_2 \qquad (28)$$

$$H^\bullet + CH_2Cl_2 \rightarrow H_2 + {}^\bullet CHCl_2(HCl + {}^\bullet CH_2Cl) \qquad (29)$$

Due to the slowness of reaction 29 and the low dichloromethane concentration some of the OH radicals do not only undergo reaction 28 but also combine to a considerable extent with the dichloromethyl radicals (reaction 4). As shown in Figure 5, two phases of conductivity change are observed: a fast one which includes the decomposition of dichloromethanol and a slower one of again $k \approx 10^4$ s^{-1} which is attributed to the decay and hydrolysis of formyl chloride (reactions 1 and 2). Again, computer simulations confirm the observed HCl yields.

Conclusion

In aqueous solution, formyl chloride mainly decays into CO and HCl and only a minor fraction hydrolyzes. Assuming that in the ozonolysis experiments the second pathway (reactions 12−14) does not play a role and that all of the formic acid arises from reaction 2, one calculates that only 6% of the formyl chloride hydrolyzes (reaction 2), in competition with its decay into CO and HCl (reaction 1). In fact, since some formic acid is likely to arise from the second pathway this percentage could be even lower. The rate constant for the hydrolysis of phosgene[9] is 9 s^{-1} and that of tetrachlorosuccinic dichloride[8] is 5 s^{-1}. Formyl chloride may also hydrolyze (reaction 2) at a similar rate. In view of this, and since only a small percentage of formyl chloride follows this reaction, it is concluded that the observed rate constant is practically entirely determined by k_1.

In strongly basic solutions the formation of CO is suppressed (Figure 3), reaching half of its maximum value at pH 13.6. This implies that at this pH the rate of reaction 1 is equal to the rate of the OH^--induced hydrolysis of formyl chloride; i.e. the rate constant of the latter reaction is 2.5×10^4 dm^3 mol^{-1} s^{-1}. This is very close to the value, 2.8×10^4 dm^3 mol^{-1} s^{-1},[9] of the OH^--induced hydrolysis of phosgene.

It has been mentioned in the Introduction that from theoretical calculations[3] it is estimated that in the gas phase formyl chloride should show a lifetime on the order of 10^{13} years, while it has now been shown that in aqueous solutions it decomposes with a half-life of 80 μs. This drastic lowering of the activation energy must be due to a change in the mechanism. It is likely that in aqueous solution formyl chloride decomposes by an ionic pathway, similar to the dehydration of formic acid to CO under strongly acidic conditions, and that the high solvation energies[30] of the proton (273 kcal mol^{-1}) and the chloride ion (90 kcal mol^{-1}) assist the decomposition. It may be speculated that the relatively fast decay of formyl chloride observed in gas phase laboratory experiments[2,4] (which depended on the size of the reaction vessel and was altogether poorly reproducible) is due to its fast hydrolysis at moist surfaces.

Acknowledgment. This work was supported by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie (Projects 02-WT-9288 and 02-WT-9583) and by the DVGW (Deutscher Verein des Gas- und Wasserfachs e.V.) under the Project 09/93. The technical assistance of B. Mienert and F. Reikowsky is gratefully acknowledged. We also thank Dr. O. Leitzke (WEDECO) for having provided us with an ozonator.

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