A Laser Flash Photolysis Kinetic Study of Reactions of the Cl_2^- Radical Anion with Oxygenated Hydrocarbons in Aqueous Solution

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ABSTRACT: A laser photolysis–long path laser absorption (LP-LPLA) experiment has been used to determine the rate constants for H-atom abstraction reactions of the dichloride radical anion (Cl_2^-) in aqueous solution. From direct measurements of the decay of Cl_2^- in the presence of different reactants at pH = 4 and I = 0.1 M the following rate constants at T = 298 K were derived: methanol, $(5.1 \pm 0.3) \cdot 10^4$ M^{-1} s^{-1}; ethanol, $(1.2 \pm 0.2) \cdot 10^5$ M^{-1} s^{-1}; 1-propanol, $(1.01 \pm 0.07) \cdot 10^5$ M^{-1} s^{-1}; 2-propanol, $(1.9 \pm 0.3) \cdot 10^5$ M^{-1} s^{-1}; tert.-butanol, $(2.6 \pm 0.5) \cdot 10^4$ M^{-1} s^{-1}; formaldehyde, $(3.6 \pm 0.5) \cdot 10^4$ M^{-1} s^{-1}; diethylether, $(4.0 \pm 0.2) \cdot 10^5$ M^{-1} s^{-1}; methyl-tert.-butylether, $(7 \pm 1) \cdot 10^4$ M^{-1} s^{-1}; tetrahydrofuran, $(4.8 \pm 0.6) \cdot 10^5$ M^{-1} s^{-1}; acetone, $(1.41 \pm 0.09) \cdot 10^3$ M^{-1} s^{-1}. For the reactions of Cl_2^- with formic acid and acetic acid rate constants of $(8.0 \pm 1.4) \cdot 10^4$ M^{-1} s^{-1} (pH = 0, I = 1.1 M and T = 298 K) and $(1.5 \pm 0.8) \cdot 10^3$ M^{-1} s^{-1} (pH = 0.42, I = 0.48 M and T = 298 K), respectively, were derived.

A correlation between the rate constants at T = 298 K for all oxygenated hydrocarbons and the bond dissociation energy (BDE) of the weakest C-H-bond of log k_{2nd} = (32.9 $\pm$ 8.9) − (0.073 $\pm$ 0.022) · BDE/kJ mol^{-1} is derived.

From temperature-dependent measurements the following Arrhenius expressions were derived:

$$k\,(Cl_2^- + HCOOH) = (2.00 \pm 0.05) \cdot 10^{10} \cdot \exp(-(4500 \pm 200)\,K/T)\,M^{-1}\,s^{-1},$$
$$E_a = (37 \pm 2)\,kJ\,mol^{-1}$$

$$k\,(Cl_2^- + CH_3COOH) = (2.7 \pm 0.5) \cdot 10^{10} \cdot \exp(-(4900 \pm 1300)\,K/T)\,M^{-1}\,s^{-1},$$
$$E_a = (41 \pm 11)\,kJ\,mol^{-1}$$

$$k \, (\text{Cl}_2^- + \text{CH}_3\text{OH}) = (5.1 \pm 0.9) \cdot 10^{12} \cdot \exp(-(5500 \pm 1500) \, K/T) \, \text{M}^{-1} \, \text{s}^{-1},$$
$$E_a = (46 \pm 13) \, \text{kJ} \, \text{mol}^{-1}$$

$$k \, (\text{Cl}_2^- + \text{CH}_2(\text{OH})_2) = (7.9 \pm 0.7) \cdot 10^{10} \cdot \exp(-(4400 \pm 700) \, K/T) \, \text{M}^{-1} \, \text{s}^{-1},$$
$$E_a = (36 \pm 5) \, \text{kJ} \, \text{mol}^{-1}$$

Finally, in measurements at different ionic strengths (I) a decrease of the rate constant with increasing I has been observed in the reactions of Cl_2^- with methanol and hydrated formaldehyde. © 1999 John Wiley & Sons, Inc. Int J Chem Kinet 31: 169–181, 1999

INTRODUCTION

In aqueous solution, the chloride ion can effectively be oxidized by reactive radicals X; for example, reaction (1),

$$X + \text{Cl}^- \longrightarrow X^- + \text{Cl} \qquad (1)$$

$$\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^- \qquad (2)$$
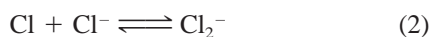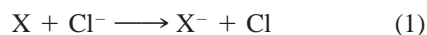
The chlorine atoms formed are converted to dichloride radical anions in the presence of excess chloride in reaction (2) ($K_2 = 1.9 \cdot 10^5 \, \text{M}^{-1}$ [1]). The same reaction sequence is possible for oxidants such as SO_4^-, OH, and NO_3 radicals. The reaction with the hydroxyl radical, however, involves several complex equilibria [1] and is only effective in acidic solution.

In the tropospheric liquid phase, chloride is one of the most abundant species [2]. In chloride containing aqueous aerosols and smaller cloud droplets, Cl_2^- is therefore expected to be formed provided other radicals are present [3]. The conversion of the highly reactive radicals such as OH, NO_3, and SO_4^- into Cl_2^- may lead to a gradual decrease of the oxidizing capacity of the tropospheric aqueous phase.

Soluble oxygenated organic compounds represent an important class of tropospheric species. They are known to originate either from gas-phase oxidation of volatile organic compounds or from direct emissions [4]. Due to their polar character, these compounds are expected to be readily transferred into the tropospheric aqueous phase where they may undergo further degradation in competition with the corresponding gas-phase processes.

Rate coefficients for reactions of Cl_2^- in liquid solution have been studied in a number of previous investigations. The results are summarized in a review by Neta et al. [5]. Several pulse radiolysis studies have been performed including reactions of Cl_2^- with nucleic acid constituents [6], surfactants and pyrimidines [7], amino acids [8], and organic nucleophiles [9]. Moreover, in order to elucidate the mechanism of electron transfer reactions of Cl_2^-, Storer et al. [10], Lierse et al. [11] and Gogolev et al. [12] studied reactions

with platinum coordination compounds, selected actinides, and complexes of the transition metal ions Co(II), Fe(II), and Mn(II), respectively. The most comprehensive study has been performed by Hasegawa and Neta [13]. These authors determined rate constants for reactions of Cl_2^- with a wide variety of organic and inorganic compounds in aqueous solution containing 1 M NaCl in order to unravel different reaction mechanisms such as electron transfer, H-atom abstraction, and addition. Because a large number of reactions of the dichloride radical anion have only been measured at room temperature and in aqueous solution [5], Shoute et al. [14], Padmaja et al. [15, 16], and Alfassi et al. [17] investigated the temperature and solvent dependence of the rate constants of reactions with inorganic ions as well as unsaturated alcohols and hydrocarbons. Recently, Maruthamuthu et al. [18] presented results of a laser flash photolysis study of reactions of Cl_2^- with haloacetates.

In the present article we present the application of a laser flash photolysis–long path laser absorption technique for the study of reactions of Cl_2^- with oxygenated hydrocarbons in diluted aqueous solution. The advantage of this technique is that it provides sensitive detection and therefore allows us to carry out experiments with small initial concentrations of Cl_2^-. Additionally, the temperature dependencies of the rate constants for the reactions of Cl_2^- with formic and acetic acid, methanol, and hydrated formaldehyde have been determined.

Rate constants of reactions involving neutral reactants are influenced by ionic strength due to the primary kinetic salt effect [19]. To quantify the effect of ionic strength, reactions with methanol and formaldehyde have been studied in the presence of variable amounts of a neutral salt (NaClO_4).

EXPERIMENTAL

Measurements of rate constants have been performed using a laser photolysis–long path laser absorption apparatus (LP-LPLA). The experimental set-up is shown
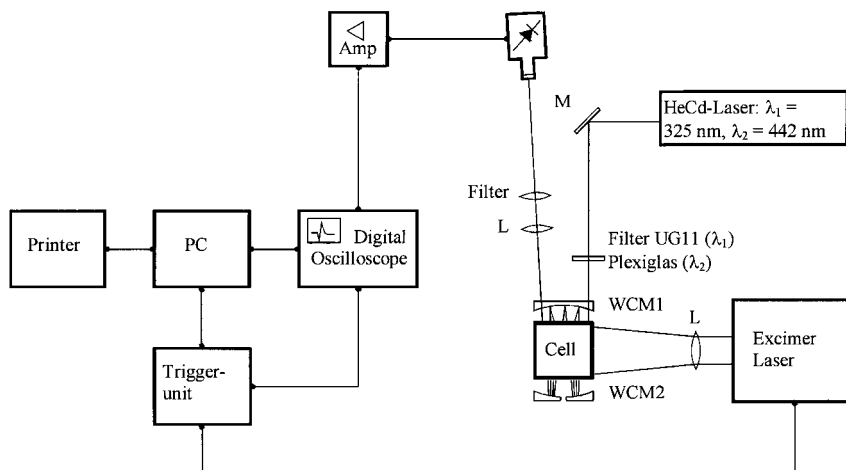
Figure 1 Experimental set-up of the laser photolysis–long path laser absorption (LP-LPLA) experiment.

in Figure 1 and has been described in detail elsewhere [20]. Briefly, it consists of a cubic reactor equipped with quartz windows through which the solution is pumped. The reactions studied are initiated by laser pulse photolysis ($\lambda = 248$ nm) of sodium peroxodisulfate using an excimer laser (Lambda Physik, LPX 100):

$$S_2O_8^{2-} + h\nu \longrightarrow 2\ SO_4^{-} \qquad (3)$$
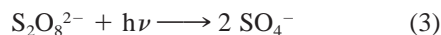
Peroxodisulfate concentrations of $5 \cdot 10^{-4}$ M have been applied. Under these conditions typical initial radical concentrations of $2 \cdot 10^{-7}$ M were generated.

The SO_4^{-} radical anion was converted to Cl_2^{-} in the presence of 0.1 M NaCl via reactions (1) and (2). As has been shown in a previous study [2], reaction (1) is the rate determining step for the formation of Cl_2^{-}. With a rate constant of $k_1 = (3.3 \pm 0.5) \cdot 10^8$ $M^{-1}\ s^{-1}$ at infinite dilution, it may be estimated that under the conditions applied more than 99.5% of the SO_4^{-} radical anions are converted to Cl_2^{-} in less than 0.2 μs. By using Cl^- concentrations of 0.1 M instead of 1 M as applied in the early study by Hasegawa and Neta [13], the effects of ionic strength were minimized. This procedure is in agreement with the more recent studies by Shoute et al. [14] and Padmaja et al. [15, 16], following the work of Hasegawa and Neta from the same group. In these recent studies, halogenide concentrations of 0.1 M were applied in investigations of dihalogenide radical anion reactions (Cl_2^{-}, Br_2^{-}).

The perpendicular axis of the reactor was used for time resolved detection of the Cl_2^{-} radical anion using a Helium-Cadmium laser (Omnichrome, 2056-15/35 M) as a light source. With a mirror system in White

configuration the light path was folded 16 times providing an overall absorption path length of 112 cm. The HeCd laser emits simultaneously at 325.0 nm and 441.6 nm, of which the visible line was blocked with a filter (Schott, UG11) and Cl_2^{-} was monitored by its absorption at 325.0 nm ($\varepsilon = 8.3 \cdot 10^3\ M^{-1}\ cm^{-1}$ [1]). The optical signals were detected with a photodiode and registered by a digital storage oscilloscope (Gould 4050). Usually 8 to 16 single experiments were averaged and transmitted to a personal computer for least-square analysis to extract the first-order rate constant. Usually, four different reactant concentrations were used to derive second-order rate constants.
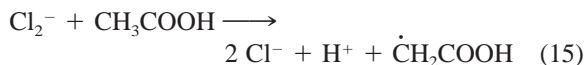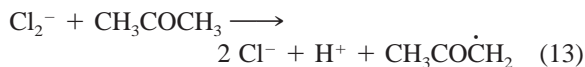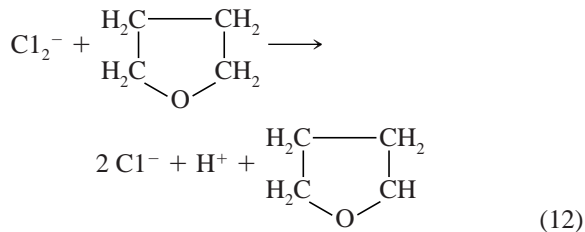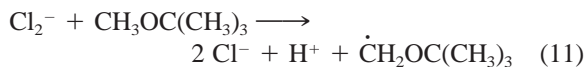
Solutions were prepared using double distilled, Millipore filtered water ($R_{H2O} \geq 18$ MΩ). Sodium chloride and sodium peroxodisulfate were obtained from Fluka. The pH of the solution was adjusted to 4, except for the acids that were measured at pH = 0 (formic acid) and pH = 0.42 (acetic acid), by addition of concentrated $HClO_4$ (Fluka). The reactants used were supplied by Fluka in high purity grade and were used without further purification.

Stock solutions of formaldehyde obtained from Fluka are stabilized with methanol. The concentrations of both compounds were analyzed by Fluka and verified by quantitative ^{1}H-NMR measurements. Moreover, the formaldehyde concentration was determined by titration with NaOH after reaction with sodium sulphite [21]. The individual concentrations determined by both methods are in agreement within the error limits. The measured first-order rate constants in the reaction with formaldehyde have been corrected for the reaction of Cl_2^{-} with methanol using the second-order rate constant determined for the same temperature and ionic strength.

RESULTS

Kinetics of Reactions of Cl_2^- with a Series of Oxygenated Hydrocarbons at $T = 298$ K

The rate coefficients for the reactions

$$Cl_2^- + CH_3OH \longrightarrow 2\, Cl^- + H^+ + \dot{C}H_2OH \quad (4)$$

$$Cl_2^- + CH_3CH_2OH \longrightarrow \\ 2\, Cl^- + H^+ + CH_3\dot{C}HOH \quad (5)$$

$$Cl_2^- + CH_3CH_2CH_2OH \longrightarrow \\ 2\, Cl^- + H^+ + CH_3CH_2\dot{C}HOH \quad (6)$$

$$Cl_2^- + (CH_3)_2CHOH \longrightarrow \\ 2\, Cl^- + H^+ + (CH_3)_2\dot{C}OH \quad (7)$$

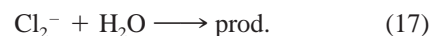$$Cl_2^- + (CH_3)_3COH \longrightarrow \\ 2\, Cl^- + H^+ + (\dot{C}H_2)(CH_3)_2COH \quad (8)$$

$$Cl_2^- + H_2C(OH)_2 \longrightarrow \\ 2\, Cl^- + H^+ + H\dot{C}(OH)_2 \quad (9)$$

$$Cl_2^- + CH_3CH_2OCH_2CH_3 \longrightarrow \\ 2\, Cl^- + H^+ + CH_3\dot{C}HOCH_2CH_3 \quad (10)$$

$$Cl_2^- + CH_3OC(CH_3)_3 \longrightarrow \\ 2\, Cl^- + H^+ + \dot{C}H_2OC(CH_3)_3 \quad (11)$$

$$Cl_2^- + \quad \begin{array}{c} H_2C\!-\!\!-\!\!CH_2 \\ | \qquad\quad | \\ H_2C \quad\quad CH_2 \\ \diagdown O \diagup \end{array} \longrightarrow$$

$$2\, Cl^- + H^+ + \quad \begin{array}{c} H_2C\!-\!\!-\!\!CH_2 \\ | \qquad\quad | \\ H_2C \quad\quad \dot{C}H \\ \diagdown O \diagup \end{array}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad (12)$$

$$Cl_2^- + CH_3COCH_3 \longrightarrow \\ 2\, Cl^- + H^+ + CH_3CO\dot{C}H_2 \quad (13)$$

$$Cl_2^- + HCOOH \longrightarrow 2\, Cl^- + H^+ + \dot{C}OOH \quad (14)$$

$$Cl_2^- + CH_3COOH \longrightarrow \\ 2\, Cl^- + H^+ + \dot{C}H_2COOH \quad (15)$$
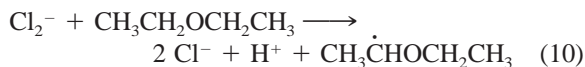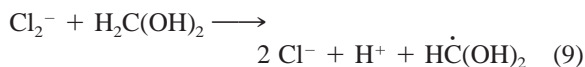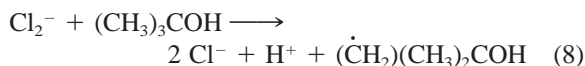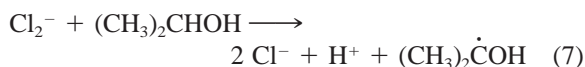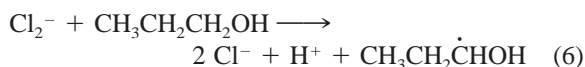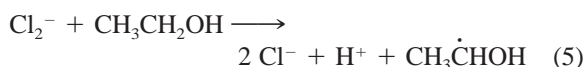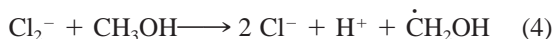
have been determined using the LP-LPLA method. For this purpose, the decays of Cl_2^- in the presence of excess reagent have been observed. All experiments were performed at pH = 4 and $T = 298$ K, except for the acids that were measured at pH = 0 (formic acid) and pH = 0.42 (acetic acid).

Although the products from the reactions (4–15) have not been quantified directly, it is most likely that organic radicals as a result of H-atom abstraction reactions are formed (see later). The radical reaction products (alkyl radicals) may contribute to an additional loss of Cl_2^-. However, it is known that these radicals react rapidly with dissolved oxygen generating organic peroxyl radicals, which in general have a very low reactivity [22]. Their maximum concentrations are in the order of the initial concentration of Cl_2^- (i.e., $2 \cdot 10^{-7}$ M). Using a rate coefficient for $RO_2 + Cl_2^-$ of $1 \cdot 10^9$ M^{-1} s^{-1}, a first-order contribution to the loss of Cl_2^- of 200 s^{-1} can be calculated and hence can be neglected when compared to the significantly higher pseudo-first order rate coefficients which were observed.

When investigating the decay of Cl_2^- in aqueous solution not only the reaction with the reactant A, but also the loss of Cl_2^- (and, by implication of the rapidly established equilibrium (2), of Cl atoms) in the reaction with H_2O, viz.

$$Cl_2^- + A \longrightarrow prod. \qquad (16)$$

$$Cl_2^- + H_2O \longrightarrow prod. \qquad (17)$$

$$Cl + H_2O \longrightarrow prod. \qquad (18)$$

need to be taken into account.

The decay of the sum of the radicals $[R] = [Cl] + [Cl_2^-]$ is then given by:

$$-\frac{d[R]}{dt} = k_{16}[Cl_2^-][A] + k_{17}[Cl_2^-][H_2O] \\ + k_{18}[Cl][H_2O] \qquad (I)$$

Upon substitution of $[Cl] = [Cl_2^-]/(K_2\,[Cl^-])$ the following equation for the decay of Cl_2^- is derived:

$$-\frac{d[Cl_2^-]}{dt} \\ = \frac{\left(\left(k_{17} + \dfrac{k_{18}}{K_2[Cl^-]}\right)[H_2O] + k_{16}[A]\right)[Cl_2^-]}{1 + \dfrac{1}{K_2[Cl^-]}} \qquad (II)$$

It should be noted that an additional reaction between Cl atoms and the reactant A is neglected because of the small amount of chlorine atoms present at $[Cl^-]$ = 0.1 M. Moreover, the denominator of equation (II) is close to unity at $[Cl^-]$ = 0.1 M and, therefore, to a good approximation:
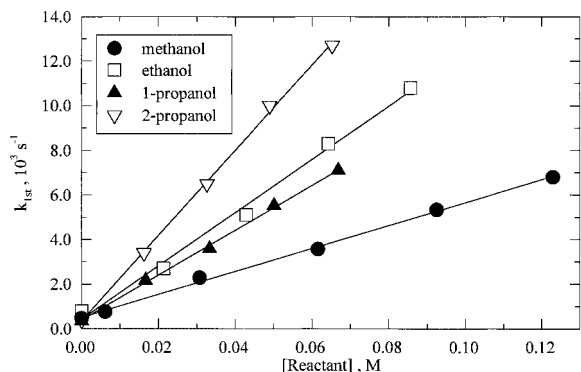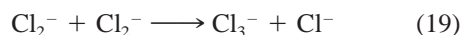
Figure 2 Plots of k_{1st} vs. reactant concentrations for the reactions of Cl_2^- with methanol, ethanol, 1-propanol, and 2-propanol; pH = 4, I = 0.1 M, T = 298 K.

Figure 4 Plots of k_{1st} vs. reactant concentrations for the reactions of Cl_2^- with diethylether and tetrahydrofuran ; pH = 4, I = 0.1 M, T = 298 K.

$$- \frac{d \ln [Cl_2^-]}{dt}$$
$$= k_{1st}$$
$$= \left(k_{17} + \frac{k_{18}}{K_2[Cl^-]} \right) [H_2O] + k_{16}[A] \quad (III)$$

Hence, the measured first order rate constants for the decay of Cl_2^- depend linearly on the concentration of reactant A, because the first part of the right hand side of equation (III) is constant for all experiments in which [A] has been varied.

A deviation from first-order behavior of the decay of Cl_2^- may arise due to the fast self-reaction (19) of the dichloride radical anion, viz.

$$Cl_2^- + Cl_2^- \longrightarrow Cl_3^- + Cl^- \quad (19)$$

For this reaction a second-order rate constant of $k_{19} =$

$(1.8 \pm 0.1) \cdot 10^9 \ M^{-1} \ s^{-1}$ at $I \rightarrow 0$ and T = 298 K has been determined within this study in reasonable agreement with the former determination of this rate coefficient by McElroy of $k_{19} = 7 \cdot 10^8 \ M^{-1} \ s^{-1}$ [23]. With the initial radical anion concentration of $2 \cdot 10^{-7}$ M we estimate a maximum "first-order" contribution of 140 s^{-1} for the additional loss due to reaction (19). This is low compared to the measured first-order rate constants in all our experiments. Indeed, the decay profiles of the Cl_2^- radical anion concentration were always found to reflect first-order behavior within the experimental error limits with the first-order rate coefficients being proportional to the concentrations of the reactants.

From the slopes of the plots of first-order decay constant versus reactant concentration (Figs. 2–5) second-order rate coefficients of $k_4 = (5.1 \pm 0.3) \cdot 10^4$ $M^{-1} \ s^{-1}$; $k_5 = (1.2 \pm 0.2) \cdot 10^5 \ M^{-1} \ s^{-1}$; $k_6 =$
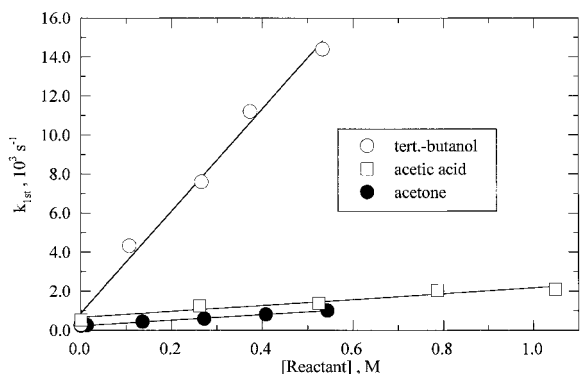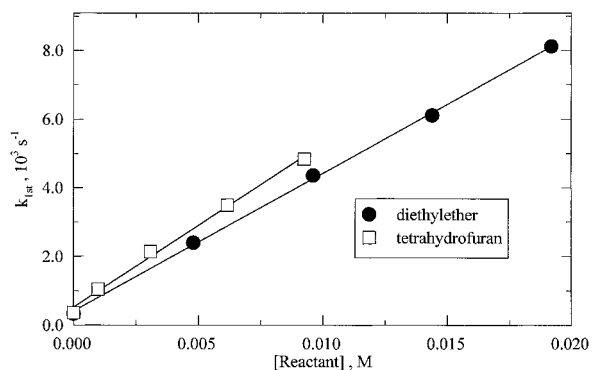

Figure 3 Plots of k_{1st} vs. reactant concentrations for the reactions of Cl_2^- with tert.-butanol, acetone (pH = 4, I = 0.1 M, T = 298 K) and acetic acid (pH = 0.42, I = 0.48, T = 298 K).
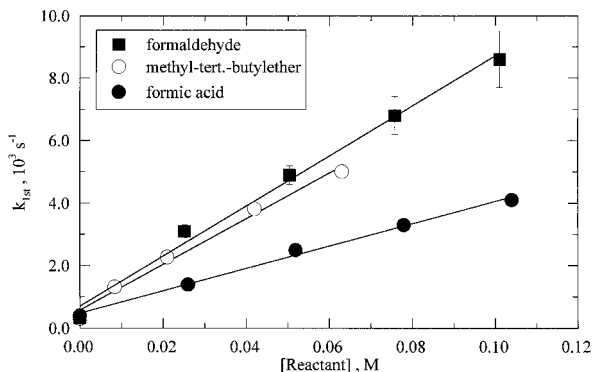

Figure 5 Plots of k_{1st} vs. reactant concentrations for the reactions of Cl_2^- with formaldehyde, methyl-tert.-butylether (pH = 4, I = 0.1 M, T = 298 K) and formic acid (pH = 0, I = 1.1 M, T = 298 K).

$(1.01 \pm 0.07) \cdot 10^5$ M^{-1} s^{-1}; $k_7 = (1.9 \pm 0.3) \cdot 10^5$ M^{-1} s^{-1}; $k_8 = (2.6 \pm 0.5) \cdot 10^4$ M^{-1} s^{-1}; $k_9 = (3.6 \pm 0.5) \cdot 10^4$ M^{-1} s^{-1}; $k_{10} = (4.0 \pm 0.2) \cdot 10^5$ M^{-1} s^{-1}; $k_{11} = (7 \pm 1) \cdot 10^4$ M^{-1} s^{-1}; $k_{12} = (4.8 \pm 0.6) \cdot 10^5$ M^{-1} s^{-1}; $k_{13} = (1.41 \pm 0.09) \cdot 10^3$ M^{-1} s^{-1}; $k_{14} = (8.0 \pm 1.4) \cdot 10^4$ M^{-1} s^{-1}; and $k_{15} = (1.5 \pm 0.8) \cdot 10^3$ M^{-1} s^{-1} were obtained. In all experiments the ionic strength was 0.1 M due to the sodium chloride added except for the acids that were investigated at $I = 1.1$ M (formic acid) and $I = 0.48$ M (acetic acid).

Temperature Dependence and Ionic Strength Effect for the Reaction of Cl$_2^-$ with Methanol

Since the rate constant for reaction (4)

$$Cl_2^- + CH_3OH \longrightarrow 2\ Cl^- + H^+ + \dot{C}H_2OH \quad (4)$$

is so far only known for $T = 298$ K [13,27], it has also been measured as a function of temperature at pH = 4 and $I = 0.1$ M. The rate constants in the temperature range 289–328 K may be summarized by the Arrhenius expression (cf. Fig. 6):

$$k_4 = (5.1 \pm 0.9) \cdot 10^{12}$$
$$\cdot \exp(-(5500 \pm 1500)K/T)\ M^{-1}\ s^{-1} \quad (IV)$$

which corresponds to an activation energy of $E_{a4} = (46 \pm 13)$ kJ mol^{-1}.

Moreover, the influence of ionic strength on the rate constant for reaction (4) has also been investigated. In these experiments, the ionic strength I of the solution was adjusted by adding variable amounts of NaClO$_4$. A decrease of the rate coefficient with increasing ionic strength has been found for $I \leq 2$ M (Fig. 7). At still higher ionic strength no further decrease of the second-order rate constant has been observed and a limiting
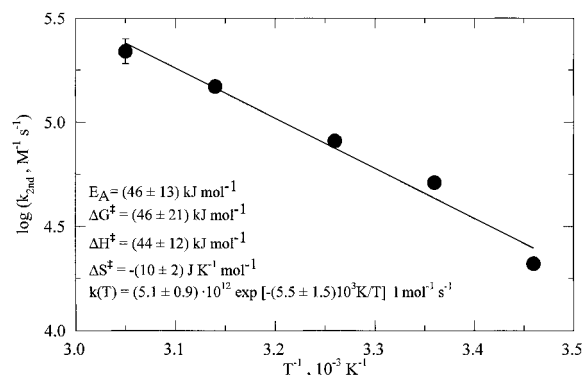
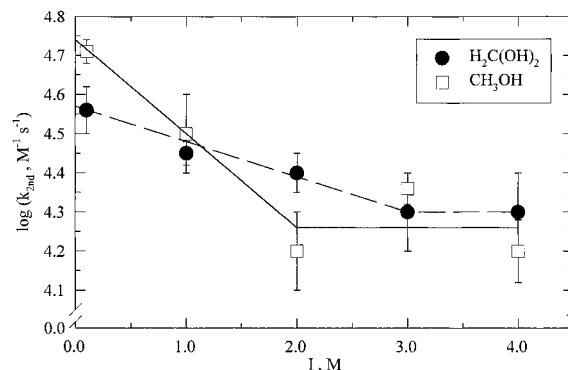**Figure 6**   Arrhenius plot for reaction (4) Cl$_2^-$ + CH$_3$OH → 2 Cl$^-$ + H$^+$ + CH$_2$OH; pH = 4, $I = 0.1$ M.

Figure 7   Plot of k_{2nd} vs. ionic strength for the reactions of Cl$_2^-$ with methanol and formaldehyde, pH = 4, $T = 298$ K (see text).

value of $k\ (I \to \infty) = (1.8 \pm 0.9) \cdot 10^4$ M^{-1} s^{-1} is reached. The linear decrease of log k vs. I may be explained based on the activity coefficients of the neutral reagents [19,25], viz.

$$\log k = \text{const.} + \beta \cdot I \quad (V)$$

where β is the so-called kinetic salting coefficient (cf. later). From the data of Figure 7 we obtain

$$\beta_4 = -(0.24 \pm 0.06)\ M^{-1} \quad \text{for} \quad I \leq 2\ M$$
$$\text{at} \quad pH = 4 \quad \text{and} \quad T = 298\ K.$$

Temperature Dependence and Ionic Strength Effect for the Reaction of Cl$_2^-$ with Formaldehyde

In aqueous solution formaldehyde is almost completely hydrated, as shown in the following:

$$HCHO + H_2O \longleftrightarrow H_2C(OH)_2 \quad (20)$$
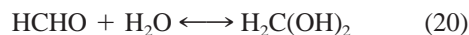
Bell [26] recommended a dimensionless equilibrium constant of $K_{20} = 2000$ at $T = 298$ K for diluted solutions. Using $\Delta H_{20} = 33$ kJ mol^{-1} [26], K_{20} reduces to 610 at 327 K, the highest temperature used in our experiments. Therefore, under all of our conditions less than 0.2% of the reactant is present as HCHO, and methanediol H$_2$C(OH)$_2$ is the reactive species in aqueous solution. However, equilibrium (20) is expected to be influenced not only by the temperature but also by the ionic strength of the solution. Gruen and McTigue [27] investigated the influence of ionic strength on the equilibrium constants of several higher aldehydes in the presence of different salts. They found a decrease of the amount of the hydrated form of the aldehydes with increasing ionic strength and

$E_A = (36 \pm 5)$ kJ mol^{-1}

$\Delta G^{\ddagger} = (47 \pm 11)$ kJ mol^{-1}

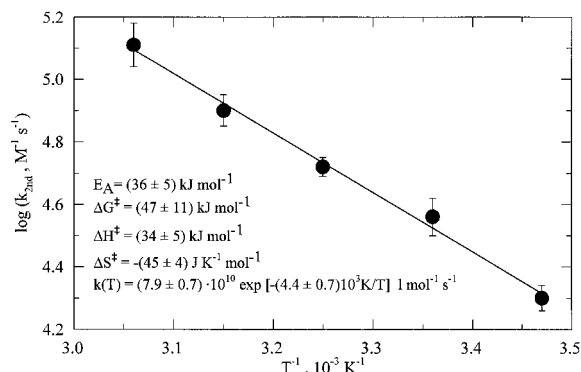$\Delta H^{\ddagger} = (34 \pm 5)$ kJ mol^{-1}

$\Delta S^{\ddagger} = -(45 \pm 4)$ J K^{-1} mol^{-1}

$k(T) = (7.9 \pm 0.7) \cdot 10^{10}$ exp $[-(4.4 \pm 0.7)10^3$K/T] l mol^{-1} s^{-1}

Figure 8 Arrhenius plot for reaction (9) $Cl_2^- + CH_2(OH)_2 \rightarrow 2\ Cl^- + H^+ + CH(OH)_2$; pH = 4, I = 0.1 M.

suggested that this is mainly due to the decrease of the water activity accompanying the increase of the electrolyte concentration. This result is further confirmed by the fact that the change of the equilibrium constants investigated are comparable for different aldehydes. Using the results of Gruen and McTigue [27], a decrease of the equilibrium constant to $K_{20} = 710$ at $I = 4$ M and $T = 298$ K can be predicted.

Rate measurements for reaction (9)

$$Cl_2^- + H_2C(OH)_2 \longrightarrow$$
$$2\ Cl^- + H^+ + H\dot{C}(OH)_2 \quad (9)$$
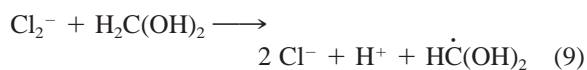
have been performed in the temperature range of 288–327 K. The results for different temperatures are summarized in Figure 8. From the data of this figure an Arrhenius expression of

$$k_9 = (7.9 \pm 0.7) \cdot 10^{10}$$
$$\cdot \exp(-(4400 \pm 700)\text{K}/T)\ \text{M}^{-1}\ \text{s}^{-1} \quad \text{(VI)}$$

corresponding to an activation energy of $E_{a9} = (36 \pm 5)$ kJ mol^{-1}, is obtained.

Reaction (9) was also investigated at various ionic strengths between 0.1 and 4 M at $T = 298$ K. The rate constants obtained are shown in Figure 7. Similar to the reaction of Cl_2^- with methanol, a decrease of the rate coefficient k_9 with increasing ionic strength is observed. On a logarithmic scale, this decrease is linear for $I \leq 3$ M and results in a kinetic salting coefficient of $\beta_9 = -(0.09 \pm 0.04)$ M^{-1} at $T = 298$ K and pH = 4 to be derived. For higher ionic strengths (i.e., $I \geq 3$ M) a limiting value of $k\ (I \rightarrow \infty) = (1.9 \pm 0.5) \cdot 10^4$ M^{-1} s^{-1} is predicted.

For the explanation of the observed ionic strength effects the occurrence of ion pairs (here: NaCl$_2$) may also be considered [28]. Then the "saturation behavior" observed in the plots of Figure 7 may be the result

of the occurrence of parallel reactions of Cl_2^- at low ionic strength and of the predominant reaction of the ion-paired species NaCl$_2$ in the high ionic strength regime. In the case where ion-pairing occurs, the extracted salt-coefficients do not only represent activity coefficients but are also influenced by the equilibrium between Cl_2^- and NaCl$_2$. The data presented here will be treated accordingly in a forthcoming paper where kinetic ionic strength effects observed in reactions of different radicals are discussed [28].

Temperature Dependencies for the Reactions of Cl_2^- with Formic Acid and Acetic Acid

Measurements of the rate coefficient for reaction (14), that is

$$Cl_2^- + HCOOH \longrightarrow 2\ Cl^- + H^+ + \dot{C}OOH \quad (14)$$

have been performed in the temperature range of 288–328 K at pH = 0 and $I = 1.1$ M. The results for the different temperatures are summarised in Figure 9. From the data of this plot, an Arrhenius expression of

$$k_{14} = (2.00 \pm 0.05) \cdot 10^{10}$$
$$\cdot \exp(-(4500 \pm 200)\text{K}/T)\ \text{M}^{-1}\ \text{s}^{-1} \quad \text{(VII)}$$

corresponding to an activation energy of $E_{a14} = (37 \pm 2)$ kJ mol^{-1}, is obtained.

The second-order rate coefficients for reaction (15)

$$Cl_2^- + CH_3COOH \longrightarrow$$
$$2\ Cl^- + H^+ + \dot{C}H_2COOH \quad (15)$$
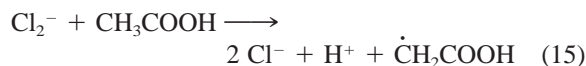
were measured in the temperature range of 288–328 K at pH = 0.42 and $I = 0.48$ M. The results of these

$E_A = (37 \pm 2)$ kJ mol^{-1}

$\Delta G^{\ddagger} = (51 \pm 4)$ kJ mol^{-1}

$\Delta H^{\ddagger} = (35 \pm 2)$ kJ mol^{-1}

$\Delta S^{\ddagger} = -(56 \pm 1)$ J K^{-1} mol^{-1}

$k(T) = (2.00 \pm 0.05) \cdot 10^{10}$ exp $[-(4.5 \pm 0.2)10^3$K/T] l mol^{-1} s^{-1}
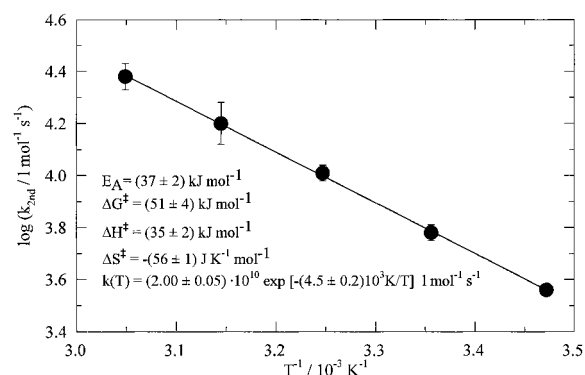
Figure 9 Arrhenius plot for reaction (9) $Cl_2^- + HCOOH \rightarrow 2\ Cl^- + H^+ + COOH$; pH = 0, I = 1.1 M.
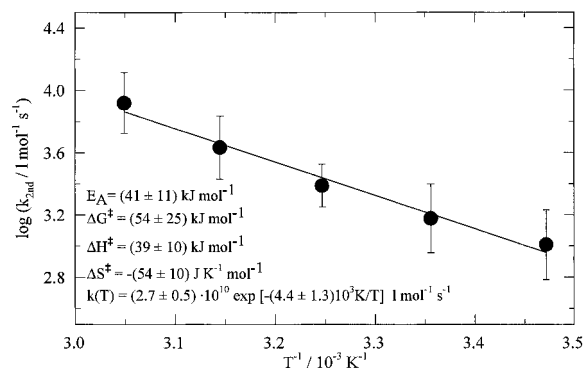
Figure 10 Arrhenius plot for reaction (9) Cl_2^- + $CH_3COOH \rightarrow 2\ Cl^- + H^+ + CH_2COOH$; pH = 0.42, I = 4.8 M.

measurements are shown in Figure 10. From these data, an Arrhenius expression of

$$k_{15} = (2.7 \pm 0.5) \cdot 10^{10}$$
$$\cdot \exp(-(4900 \pm 1300)K/T)\ M^{-1}\ s^{-1} \quad \text{(VIII)}$$

corresponding to an activation energy of E_{a15} = (41 ± 11) kJ mol^{-1}, is obtained.

DISCUSSION

Rate Coefficients for H-Atom Abstraction Reactions of Cl_2^- at 298 K

The rate constants for H-atom abstraction reactions of the dichloride radical anion as obtained in the present work together with previous literature data are summarized in Table I. In comparing these data, it needs to be noted that the majority of the previous studies have not been performed in dilute solutions but rather at moderate ionic strength ($I = 1$ M). Only for reaction (7) with 2-propanol previous investigations in dilute aqueous solution have been performed. The rate constant from the present work is in good agreement, within the experimental errors, with previous data obtained from both laser photolysis [29] and pulse radiolysis studies [10].

A number of reactions have been investigated in aqueous solutions containing 1 M NaCl [13]. The rate coefficients obtained for the reactions with methanol, ethanol, 2-propanol, tert.-butanol are lower than the values derived in the present study. These differences range between a factor of 1.6 in the case of 2-propanol and more than one order of magnitude in the case of methanol and tert.-butanol. Although in the present work it has been shown that increasing ionic strength

can decrease the rate constant for H-atom abstraction reactions of Cl_2^-, the rate constant for reaction (4) with methanol measured at $I = 1$ M in the presence of $NaClO_4$ is still a factor of 8 higher than the value found by Hasegawa and Neta [13]. This difference remains unexplained. However, it should be noted that for the reaction (13) of Cl_2^- with acetone no such difference between the rate coefficients from both studies is obvious and therefore cannot be assigned as a systematic effect. In the study of Hasegawa and Neta the reactions of Cl_2^- with formic acid and acetic acid have also been investigated and the rate coefficients found are in good agreement with the values of the present study.

Measurements of k_4, k_5, and k_{13} reported in the literature were performed in pure solutions of methanol, ethanol, and acetone, respectively, and were carried out using the pulse radiolysis/time-resolved absorption technique [24,30,31]. In all of these studies the first-order decay of Cl_2^- was monitored and used for calculations of second-order rate coefficients. Fel'dman et al. [24] and Khmelinskii et al. [30] obtained results for reactions (4) and (5) with methanol and ethanol that are approximately one order of magnitude lower than the values reported here. Contrary to these results, the value obtained by Broszkiewicz et al. [31] for k_{13} in pure acetone is 25% larger than our value. These discrepancies probably arise from differences in salvation effects of reactants, intermediates, and products. Padmaja et al. [15] and Alfassi et al. [17] reported results of laser flash photolysis studies of Cl_2^- with unsaturated alcohols and hydrocarbons in acetonitrile/water solutions and other solvent mixtures, respectively, with different solvent composition. They found a decrease of the rate coefficients at $T = 298$ K with the mole fraction of acetonitrile for both the alcohols and the hydrocarbons, and they concluded that for an addition mechanism the overall rate constant is mainly influenced by the stabilization of the intermediate due to the different solvent molecules. However, the reactions of Cl_2^- with methanol, ethanol, and acetone probably follow an H-atom abstraction mechanism in which a proton and two chloride ions are generated besides the organic radicals. Cl_2^- and these ions are strongly solvated in water, but less so in organic solvents. The organic reactants, on the other hand, are much better solvated in the pure organics. In the case of methanol and ethanol the overall rate constant for reaction with Cl_2^- is increased in aqueous solutions due to the better solvation of the ionic products, whereas this effect is probably in part compensated in the reaction of Cl_2^- with acetone in pure acetone.

For all reactions of the Cl_2^- radical anion investigated in the present work an H-atom abstraction mechanism is suggested. Indirect support of this suggestion

Table I   Comparison of Previous Literature Data for Rate Coefficients of H-atom Abstraction Reactions of Cl_2^- with Results from the Present Work at 298 K.

Reaction No.	Reactant	k (298 K), $M^{-1} S^{-1}$	pH	I, M	Technique[a]	Reference
(4)	methanol	$(3.5 \pm 0.7) \cdot 10^{3b}$	1	1	PR	[13]
		$4 \cdot 10^{3c}$		1	PR	[24]
		$(5.1 \pm 0.3) \cdot 10^4$	4	0.1	LFP	This work
		$(2.9 \pm 0.8) \cdot 10^{4d}$	4	1	LFP	This work
(5)	ethanol	$(4.5 \pm 0.9) \cdot 10^{4b}$	1	1	PR	[13]
		$1.4 \cdot 10^{4e}$		10.3	LFP	[30]
		$(1.2 \pm 0.2) \cdot 10^5$	4	0.1	LFP	This work
(6)	1-propanol	$(1.01 \pm 0.07) \cdot 10^5$	4	0.1	LFP	This work
(7)	2-propanol	$(1.2 \pm 0.2) \cdot 10^{5b}$	1	1	PR	[13]
		$1.5 \cdot 10^{5b}$	1	0.1	LFP	[25]
		$(1.9 \pm 0.3) \cdot 10^5$	0.3	0.5	PR	[10]
		$(1.9 \pm 0.3) \cdot 10^5$	4	0.1	LFP	This work
(8)	tert.-butanol	$\sim 700^b$	1	1	PR	[13]
		$(2.6 \cdot 0.5) \cdot 10^4$	4	0.1	LFP	This work
(9)	formaldehyde	$(3.6 \pm 0.5) \cdot 10^4$	4	0.1	LFP	This work
(10)	diethylether	$(4.0 \pm 0.2) \cdot 10^5$	4	0.1	LFP	This work
(11)	methyl-tert.-butylether	$(7 \pm 1) \cdot 10^4$	4	0.1	LFP	This work
(12)	tetrahydrofuran	$(4.8 \pm 0.6) \cdot 10^5$	4	0.1	LFP	This work
(13)	acetone	$(1.4 \pm 0.3) \cdot 10^{3b}$	1	1	PR	[13]
		$1.8 \cdot 10^{3f}$		0.25	PR	[31]
		$(1.41 \pm 0.09) \cdot 10^3$	4	0.1	LFP	This work
(14)	formic acid	$6.7 \cdot 10^{3b}$	1	1.1	PR	[13]
		$(8.0 \pm 1.4) \cdot 10^4$	0	1.1	LFP	This work
(15)	acetic acid	$<10^{4b}$	1	1.1	PR	[13]
		$(1.5 \pm 0.8) \cdot 10^3$	0.42	0.48	LFP	This work

[a] PR = Pulse Radiolysis; LFP = Laser Flash Photolysis

[b] Room temperature

[c] Experiments with 1 M LiCl in pure methanol

[d] Experiments in the presence of 0.1 M NaCl and 0.9 M $NaClO_4$

[e] Experiments with 10.3 M HCl in pure ethanol

[f] Experiments with 0.25 M LiCl in pure acetone

is lent by the work of Henglein [29], who presented evidence for the formation of the 1-hydroxy-1-methyl ethyl radical in reaction (7) of Cl_2^- with 2-propanol. The intermediate was identified by the reaction with tetranitromethane in the presence and absence of oxygen. Moreover, Hasegawa and Neta [13] reported a similar pattern of reactivity for hydrogen abstraction by H atoms and Cl_2^- and concluded that the reaction rate is mainly controlled by the energy of the C-H bond being ruptured [13].

In Table II the bond dissociation energy (BDE) of the weakest C-H bonds of the reactants are summarized together with the measured rate constants for the reactions with Cl_2^-. Because no experimental determination is available from literature, several bond dissociation energies were calculated from standard formation enthalpies using the method proposed by Benson [32]. It may be assumed that the differences of the rate constants at $T = 298$ K are mainly due to different activation energies, which are dependent on the BDEs of the ruptured bonds. Figure 11 shows a plot of the logarithm of the measured rate constant divided by the number of equivalent H-atoms ($k_H = k_{2nd}/n$) versus BDE of the weakest bond. A decrease of the rate constant with increasing BDE is found, indicating that the H-atom abstraction mechanism is

Table II Rate Constants for H-atom Abstraction Reactions of Cl_2^- at pH = 4, I = 0.1 M and T = 298 K and Bond Dissociation Energy of the Weakest CH bond.

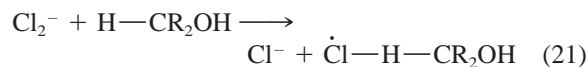| Reactant	$\log (k_H/M^{-1} s^{-1})^a$	Weakest bond (—H)	BDE, kJ mol^{-1}	Reference
methanol	4.23 ± 0.03	(H—)CH$_2$OH	402.3 ± 1.3	[34]
ethanol	4.78 ± 0.07	(CH$_3$CH(—H)OH	389 ± 4	[35]
1-propanol	4.70 ± 0.03	CH$_3$CH$_2$CH(—H)OH	385	c
2-propanol	5.28 ± 0.07	(CH$_3$)$_2$C(—H)OH	381 ± 4	[35]
tert.-butanol	3.46 ± 0.08	(CH$_3$)$_2$[CH$_2$(—H)]COH	410	c
diethylether	5.00 ± 0.02	CH$_3$CH(—H)OCH$_2$CH$_3$	383.7 ± 1.7	[35]
methyl-tert.-butylether	3.77 ± 0.06	(CH$_3$)$_3$COCH$_2$(—H)	410	c
tetrahydrofuran	4.78 ± 0.05	H$_2$C——CH$_2$ / H$_2$C CH(−H) / O	385 ± 4	[35]
acetone	2.37 ± 0.03	CH$_3$COCH$_2$(—H)	411.3 ± 7.5	[35]
formic acid	4.90 ± 0.05^b	(H—)COOH	387	c
acetic acid	2.7 ± 0.2^b	(H—)CH$_2$COOH	410 ± 8	[36]

^{a} This study.
^{b} Measurements at pH = 0.42, I = 0.47 M and T = 298 K [33].
^{c} Calculated using the method proposed by Benson [32].

dominating in all of the reactions investigated. From a least-square fit for the reactions with the organic compounds the following empirical equation is obtained:
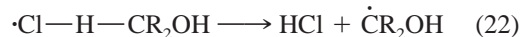
$$\log k_H = (32.9 \pm 8.9) - (0.073 \pm 0.022) \cdot BDE/kJ\ mol^{-1} \quad (IX)$$

At high dissociation energies of BDE > 400 kJ mol^{-1} the correlation is very weak as expressed by the low regression coefficient of r = 0.92. The large differences in the rate constants for compounds with BDE ≈ 410 kJ mol^{-1} may reflect the formation of different intermediates during the hydrogen abstraction process. It may be speculated that the reaction

occurs via an addition/elimination mechanism according to

$$Cl_2^- + H—CR_2OH \longrightarrow Cl^- + \dot{C}l—H—CR_2OH \quad (21)$$

followed by

$$\cdot Cl—H—CR_2OH \longrightarrow HCl + \dot{C}R_2OH \quad (22)$$

As can be seen from the Arrhenius plots for the reactions of Cl_2^- radical anion with formaldehyde, acetic acid, formic acid, and methanol, the activation parameters differ mostly for the activation entropies. For the reaction of Cl_2^- with methanol a much lower activation entropy is found than for the other reactions. This can be understood because the C-atom from which the H-atom is abstracted is only bonded to one O-atom in the case of methanol and not to two O-atoms as in the case of the other reactants investigated in this study. Therefore, the activated complex formed in the reaction of Cl_2^- with methanol should be less sterically hindered.

Ionic Strength Effects

The rate constants of reactions involving a neutral molecule may change at high ionic concentration because of a joint effect of the added salt on both the initial reagents and transition states [19,37]. Recently,
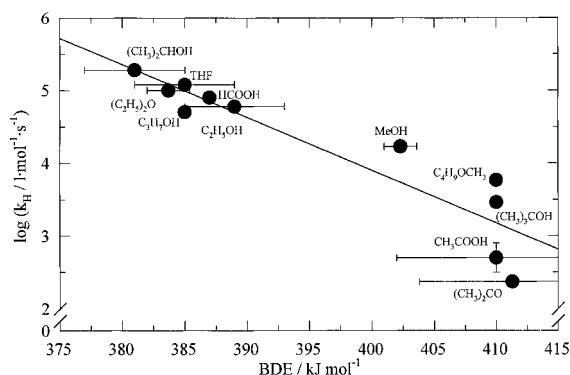

Figure 11 Plot of log k_H vs. bond dissociation energy for H-atom abstraction reactions of Cl_2^- with a number of oxygenated hydrocarbons; I = 0.1 M, T = 298 K.

salt effects for rates of radical reactions in aqueous solution have been reported for reactions involving one [38] or two neutral molecules [20]. For bimolecular reactions these effects can be expressed by the activity coefficients of the reactants and the activated complex. The activity coefficients of non-electrolyte solutes in aqueous salt solutions have been reviewed by Long and McDevit [35]. They found two contrary effects of electrolytes on activity coefficients of polar non-electrolytes. The coefficient increases with the molar volume of the non-electrolyte, whereas an increasing dipole moment leads to a decrease of the activity coefficient. Moreover, the effect of each salt is different. Unfortunately, no experimental determination of activity coefficients of methanol and formaldehyde, respectively, in the presence of $NaClO_4$ is available. Wilcox and Schrier [40] reported equations for calculating activity coefficients of different alcohols in salt solutions containing NaCl, NaBr, and NaI, respectively. For methanol, they found in each case an increase of the activity coefficient at ionic strengths higher than $I = 1$ M; for example, in the presence of 3 M NaCl the activity coefficient is 50% higher compared to diluted solutions. From these results it may be concluded that the activity coefficient of methanol also increases in the presence of dissolved sodium perchlorate. Moreover, the increase of the activity coefficient of hydrated formaldehyde is probably smaller due to the higher dipole moment compared to methanol.

However, for the rate constants of the reactions of Cl_2^- with methanol and formaldehyde as investigated in this study, a decrease of rate coefficients has been found with higher ionic strength (Fig. 7). These results show that the effect of the increasing activity coefficients of the involved neutral molecules is compensated by the influence of the added salt on the activity coefficient of Cl_2^- and the activated complex, respectively.

No information is available on the change of the activity coefficient of Cl_2^- in salt solution. However, the activity coefficient of chloride, which can be calculated for solutions with mixed electrolytes using the method proposed by Meissner and Kussik [41], may be used for a qualitative comparison. For this calculation the activity coefficients of the single electrolytes NaCl, $NaClO_4$ and $Na_2S_2O_8$ are used [42,43]. The results show a slightly reduced activity coefficient of Cl^- at higher ionic strength. However, this reduction cannot explain the much more reduced rate of coefficients at higher ionic strength, even when taking into account the probable increase of the activity coefficients of the neutral molecules in both reactions.

Ion pairing is a well-known effect for concentrated aqueous salt solutions [44]. Therefore, we propose that ion-pairing between the Cl_2^- radical anions and the Na^+ cations may occur. Qualitatively, the $NaCl_2$ complex might have a reduced reactivity compared to the free Cl_2^- radical anion, which would explain the kinetic ionic strength effects found in this study. This effect of ion-pairing in kinetic salt effect will be discussed in more detail elsewhere [28].

CONCLUSION

The present study has provided rate constants for H-atom abstraction reactions of Cl_2^- with oxygenated hydrocarbons at $T = 298$ K and $I = 0.1$ M in aqueous solution. Six of the reactions have previously been investigated by Hasegawa and Neta [13], who performed investigations in the presence of 1 M NaCl. These data are not in agreement with the results found here. Because the discrepancies do occur in both directions they may, at least partly, be attributed to the effects of ionic strength. However, since the dichloride radical anion is in equilibrium with the chlorine atom, this equilibrium is shifted to Cl_2^- by an increasing chloride concentration. A similar effect, however, might be expected when the elimination of chloride from the activated complexes formed in the reactions of organic substrates with Cl_2^- is considered. Only the determination of chlorine atom rate coefficients with the substrates studied here will allow us to quantify possible contributions of the direct chlorine atom reaction.

To our knowledge, only the rate constant for the reaction with 2-propanol has previously been measured in diluted aqueous solution [29]. This value is in excellent agreement with our results. For the five H-abstraction reactions with 1-propanol, hydrated formaldehyde, diethylether, tert.-butyl-methylether, and tetrahydrofuran, the rate coefficients for the reactions with Cl_2^- have been determined for the first time within the present study.

The rate constants obtained for a large number of oxygenated hydrocarbons are in the range of $1.4 \cdot 10^3 - 7 \cdot 10^5$ M^{-1} s^{-1} and show a correlation with the bond dissociation energy of the weakest C-H bond. The rate coefficients at $T = 298$ K are considerably lower than rate constants for electron transfer and addition reactions of Cl_2^- [5,14–17]. The rate constants for the reactions of Cl_2^- with methanol and with formaldehyde have also been studied as a function of ionic strength. In both cases a decrease of the rate coefficients with increasing salt concentrations has been found.

The rate constants and the correlation obtained in the present study may be used for the development of advanced aqueous phase chemical mechanisms for a better description of aqueous phase chemical conversions in the troposphere, including cloud droplet and aqueous aerosol chemistry.

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