# Hydroxyl Radical Reactions with Halogenated Ethanols in Aqueous Solution

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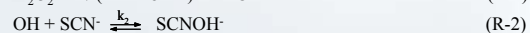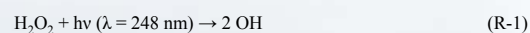
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## Motivation

Halogenated alcohols have been suggested as alternative to CFCs and HCFCs, therefore their atmospheric concentrations are expected to increase in the near future. Due to their polarity, uptake by cloud water and rain might be a significant sink for these chemicals in the atmosphere. In the aqueous phase, fluorinated and chlorinated alcohols are suggested to react mainly with OH radical. However, only few kinetic data are available in the literature, thus the reactions of OH radical with the following organic compounds have been studied: (1) 2-fluoroethanol, (2) 2,2- difluoroethanol, (3) 2,2,2-trifluoroethanol, (4) 2-chloroethanol, (5) 2,2-dichloroethanol, and (6) 2,2,2-trichloroethanol. In the present study, a laser-photolysis long-path absorption (LP-LPA) set-up (Figure 1) was used for indirect kinetic studies of OH radical reactions with halogenated alcohols in the aqueous phase. The kinetic data obtained here will be used as input parameters in forthcoming versions of the multiphase reaction mechanism CAPRAM.

## Experimental



**Figure 1:** Laser-photolysis long-path-absorption (LP-LPA) set-up for kinetic investigation

Because the OH radical absorbs weakly in the UV region of the spectrum with only a small extinction coefficient of ($\varepsilon \sim 600$ [l mol$^{-1}$cm$^{-1}$] at $\lambda \sim 235$ [nm]) and due to the overlapping of the organic peroxyl radicals formed in parallel to the OH decay an OH radical absorption measurement is difficult. Thus, the OH radical concentration is followed indirectly by using the common competition kinetics method. A much-applied competition kinetic system for the study of OH reactions in aqueous solution is the thiocyanate system which has been applied in this work. This competition kinetic system is based on the reactions (R-1) - (R-4):

$$H_2O_2 + h\nu \ (\lambda = 248 \ nm) \rightarrow 2 \ OH \qquad \text{(R-1)}$$
$$OH + SCN^- \ \overset{k_2}{\rightleftharpoons} \ SCNOH^- \qquad \text{(R-2)}$$
$$SCNOH^- \ \overset{k_3}{\rightleftharpoons} \ SCN + OH^- \qquad \text{(R-3)}$$
$$SCN + SCN^- \ \overset{k_4}{\rightleftharpoons} \ (SCN)_2 \qquad \text{(R-4)}$$

The product $(SCN)_2^-$ absorbs strongly in the blue region of the spectrum with peak absorbance at $\lambda = 475$ [nm] and extinction coefficient of $\varepsilon = 7600$ [l mol$^{-1}$ cm$^{-1}$]. In this work the temperature dependent rate constant of reaction (R-2) reported by Chin and Wine (k = $1.24 \cdot 10^{10}$ [l mol$^{-1}$ s$^{-1}$] at 298 K) was applied as a reference data.
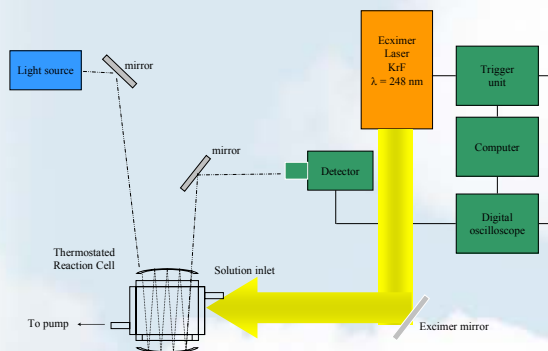
## Results and Discussions

In Table 1 the observed rate constants at 298 K and the activation parameters obtained from the temperature dependent measurements of OH radical reactions towards halogenated alcohols are summarized.

**Table 1:** Rate constants and the activation energy ($E_A$) and the preexponential factor (A) for the reactions of OH with halogenated alcohols.

| Compound | k(298K) [l mol$^{-1}$ s$^{-1}$] | A [l mol$^{-1}$ s$^{-1}$] | $E_A$ [kJ mol$^{-1}$] |
|---|---|---|---|
| 2-fluoroethanol | $(5.4 \pm 1.8) \cdot 10^8$ | $(1.2 \pm 0.1) \cdot 10^{12}$ | $(18 \pm 8)$ |
| 2,2-difluoroethanol | $(2.8 \pm 0.7) \cdot 10^8$ | $(4.5 \pm 0.5) \cdot 10^9$ | $(7 \pm 7)$ |
| 2,2,2-trifluoroethanol | $(8.5 \pm 2.5) \cdot 10^7$ | $(2.0 \pm 0.1) \cdot 10^{11}$ | $(20 \pm 7)$ |
| 2-chloroethanol | $(8.6 \pm 0.7) \cdot 10^8$ | $(3.0 \pm 0.2) \cdot 10^{10}$ | $(9 \pm 4)$ |
| 2,2-dichloroethanol | $(3.9 \pm 0.8) \cdot 10^8$ | $(2.1 \pm 0.2) \cdot 10^{10}$ | $(10 \pm 4)$ |
| 2,2,2-trichloroethanol | $(1.7 \pm 0.8) \cdot 10^8$ | $(1.6 \pm 0.1) \cdot 10^{10}$ | $(10 \pm 5)$ |

The rate constant data show clearly that the halogenated ethanols are less reactive than the parent compound, ethanol (k = $2.1 \cdot 10^9$ [l mol$^{-1}$ s$^{-1}$]). The available kinetic data suggest that the H abstraction occurs predominantly from the $CH_2$ group of the ethanols. It is proposed that the relatively large reductions in reactivity of the halogenated ethanols are mainly due to the inductive effects in the transition states. Halogen substitution in the $CH_3$ group will reduce the electron density on the H atoms in the $CH_2$ group and thus destabilise the transition state compared to that formed with $CH_3CH_2OH$. These transition states will be increasingly destabilised as the degree of charge separation increases.

Figure 2 shows a plot of the rate constants at 298 K as a function of the electronegativity of the $CX_3$ group (SPE). For the numbers 8-15 the correlation found here can be expressed by the following equation:

$$\log (k \ /l \ mol^{-1} \ s^{-1}) = (11 \pm 0.9) - (0.2 \pm 0.08) \ SPE \qquad n = 7; \ r = 0.96$$
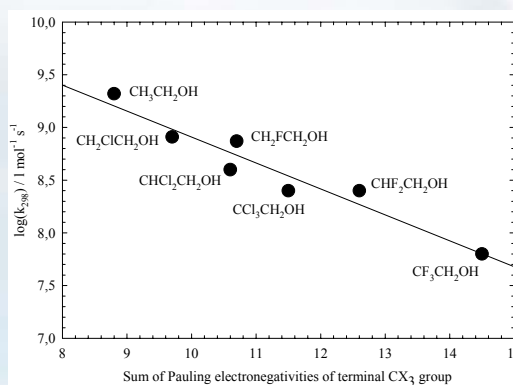


**Figure 2:** Plot of the logarithm of rate constant vs. sum of Pauling electro negativities of terminal $CX_3$ group.

This regression line may be used to estimate rate constants at 298 K for the reactions of OH with halogenated alcohols in aqueous solution when measured data are not available. The linearity of the plot supports the view that the electron withdrawing effects of the halogen atoms in the methyl group play an important role in the stability of the transition state. This method can also be used to estimate the kinetics of unknown radical reactions.

## References

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## Summary and Conclusions

To the best of the authors' knowledge currently no systematic measurements of OH radical reactions with halogenated alcohols in aqueous solution are available. Rate constants for the reactions of the OH with halogenated alcohols in aqueous solution were determined as a function of temperature. Another function of the current study was to investigate the effect of correlation between the observed rate constants and sum of Pauling electronegativities (SPE) of terminal $CX_3$ group for halogenated alcohols. The correlation have been proved that a terminal $CX_3$ group for halogenated alcohols have a strong influence on the rate constants of their reactions with OH radicals in the aqueous phase.

## Acknowledgement