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# PHOTOOXIDATION OF EXHAUST POLLUTANTS

III. Photooxidation of the chloroethenes: Degradation efficiencies, quantum yields and products

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#### Abstract

The photochemical decomposition and oxidation of the chloroethenes  $C_2H_{4-x}Cl_x$  (x=1-4) was investigated in the gas phase by irradiation with a low pressure mercury lamp in an oxygen atmosphere.

Degradation efficiencies directly depend on the number of chlorine atoms both at 185 and 254 nm. The quantum yields for degradation increase from 2-3 for vinyl chloride to > 100 for tri- and tetrachloroethene at 185 nm in the  $10^{-3}$  bar concentration range. At 254 nm we measured nearly time independent quantum yields of around 10 for tri- and 40 for tetrachloroethene.

The photooxidation products and their mechanism of formation are discussed in detail.

## 1. Introduction

The family of chloroethenes plays a vital role in a variety of industrial applications and achieved rapid growth rates after the Second World War. Except for vinyl chloride as gaseous substance the other chlorinated ethenes are colorless liquids with a sweetish odor. Vinyl chloride (monomer; VCM) is one of the world's most important industrial chemicals with a world consumption in 1984 of 12-15 millions t. Nearly the total production is used for polymerisation to PVC. 1,1- and 1,2-dichloroethene are often found as an isomeric mixture produced in small quantities as by-products. Trichloroethene and even more tetrachloroethene are very good solvents for organic compounds, e.g. fat and grease. Tetrachloroethene is safe and reliable in commercial use because it is neither flammable nor does it forms explosive mixtures with air. Therefore, its replacement is difficult without loss of safety [1].

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With more stringent environmental regulations production rates of chlorinated hydrocarbons (CHC) declined because of replacement by other solvents and reduced losses by improved chemical plants and user facilities. Emission of chlorinated ethenes to soil and the atmosphere causes a general pollution problem and contributes to smog formation and to the reduction of ozone in the higher atmosphere [2]. Also, their carcinogenic potential may cause hazard to human health. For these reasons waste gases containing Cl-ethenes have to be cleaned.

Photooxidation by UV-radiation is a possible alternative to the adsorption on charcoal for achieving the necessary cleaning of the pollutants at normal pressure without heating. The decomposition process is based on radical chains which are started by UV-photolysis and are comparable to those in combustion reactions with photolysis replacing thermal decomposition. While products such as HCl and phosgene can easily be removed by alkaline wet gas cleaning, we will show in the following that the observed chloroacetyl chlorides may become a new problem due to their high degree of chlorination and considerable stability towards photooxidation.

## 2. Experimental

The experimental and analytical set-up for UV-photooxidation of chlorinated hydrocarbons has already been described in detail in Paper II of this series [3]. A 20 Watt low pressure mercury lamp (HNS Osram 20W/U/OZ) was used for the measurements at 185 nm with an ozone filter placed in front to eliminate the 254 nm radiation. Our examinations in the 254 nm region were performed with an "ozone free" 15 Watt low pressure mercury lamp (Heraeus TNN 15-32) without further spectral dispersion. For an exact measurement the evacuated photolysis cell (volume 36,2 cm<sup>3</sup>) was fed with a defined concentration of each substance and then filled with oxygen to atmospheric pressure [4,5]. The cell was equipped with Suprasil-I-quartz-windows for the UV-beam and NaCl-windows for the IR-beam. For time-resolved IR analysis we used a FTIR-spectrometer (Perkin-Elmer FTIR Series 1600) typically operating with a resolution of 4 cm<sup>-1</sup>. If necessary, somewhat higher resolution (2 cm<sup>-1</sup>) was used. Typically 16 interferograms were averaged in order to get a good signal to noise ratio, leading to approximately 60 s to record one absorption spectrum. During IR-analysis the UV-shutter was closed.

The substances used were:

- acetone 99,5 % p.A. (Riedel-de-Haen)
- vinyl chloride 99,95 % (Merck-Schuchardt)
- trans-1,2-dichloroethene 98 % (Janssen)
- tetrachloroethene 99 % (Janssen)
- carbon dioxide 4.5 (Messer Griesheim)
- oxygen 5.0 (Messer Griesheim)

- ethene 3.5 (Messer Griesheim)
- 1,1-dichloroethene 99 % (Janssen; Roth)
- trichloroethene 99 % (Roth)
- phosgene 20 % in toluene (Fluka)
- carbon monoxide 99,5 % (Merck-Schuchardt)
- trichloroacetyl chloride 98 % (Merck-Schuchardt)

# 3. Results

#### 3.1 Degradation products and efficiency

As shown in Fig. 1 the absorption cross sections of the chloroethenes are high at 185 nm but comparatively low in the 254 nm range.



Fig.1 : Absorption cross sections of the chloroethenes [6]

In fig. 2 and 3 the degradation efficiencies of the chloroethenes are shown as function of irridation time at 185 and 254 nm for low concentrations (around 1 mbar  $C_2H_{4-x}Cl_x$  in 1000 mbar oxygen).



Fig.2: Degradation efficiencies of the chloroacetylenes as function of time at 185 nm

1:	2,1 mbar vinyl chloride	at	1619,8 cm <sup>-1</sup>	analysis wavenumber
2.	2,5 mbar trans-1,2-dichloroethene	at	829,7 cm <sup>-1</sup>	
2':	1,9 mbar 1,1-dichloroethene	at	1627,9 cm <sup>-1</sup>	
3:	1,9 mbar trichloroethene	at	935,4 cm <sup>-1</sup>	
4:	0,9 mbar tetrachloroethene	at	916,4 cm <sup>-1</sup>	
	V V			
p/p		<b>X</b>		* * * *
0	A A A A A A A A A A A A A A A A A A A	×	*	



Fig.3: Degradation efficiencies of the chloroethenes as function of time at 254 nm

1:	2,5 mbar vinyl chloride	at	1619,8 cm <sup>-1</sup>	analysis wavenumber
2.	2,0 mbar trans-1,2-dichloroethene	at	829,7 cm <sup>-1</sup>	
2':	1,2 mbar 1,1-dichloroethene	at	1627,9 cm <sup>-1</sup>	
3:	0,9 mbar trichloroethene	at	935,4 cm <sup>-1</sup>	
4:	0,9 mbar tetrachloroethene	at	916,4 cm <sup>-1</sup>	

As shown in Fig.1 the absorption of the mono- and dichloroethenes is negligible at 254 nm. VCM does not decompose at all at 254 nm, while (E)-1,2-dichloroethene slowly disappears after several hours of irradiation, c. f. fig. 3. After a period of restrained degradation a sudden decomposition is observed in case of the dichloroethenes which probably results from start of a chain mechanism. When the number of radicals propagating the chain surpasses the number of radicals which are inactivated by collisions with other molecules or the walls of the vessel fast degradation is observed. Trichloroethene and in particular tetrachloroethene are decomposed very fast without delay, despite their absorption cross sections in the 254 nm region are still small, c.f. fig. 1. The UV-radiation acts as a kind of "catalyst" which supplies Cl-radicals to start the chain reaction. The small light penetration depth at high CHC concentrations certainly contributes to the retardation. With increasing degradation in the penetration zone and appearance of more transparent photooxidation products, the light is able to penetrate deeper and to generate more radicals from photolysis. The observed induction periods are probably due to the times required to build up stationary-state radical concentrations necessary for efficient chain propagation and degradation. For this reason dichloroethene and trichloroethene decompose slower at small concentrations than at large ones. In case of chlorine gas addition the degradation rate will enhance because of the greater amount of free Cl-radicals being available [17].



Fig.4: FTIR-spectrum of 28 mbar trichloroethene after photooxidation at 185 nm using a 20 Watt low pressure mercury lamp

Qualitative analysis, i.e. identification of the main and side products, was performed by FTIR spectroscopy and GC/MS analysis combined with computer-aided mass spectrometry library search. In Fig.4 the FTIR-spectra of trichloroethene are shown at different irradiation times. The degradation products of all examined chloroethenes are listed in Table 1. Beside CO<sub>2</sub>, CO and HCl we observed COCl<sub>2</sub> and different acid chlorides as main products.

chloroethene	degradation products		
vinyl chloride monomer	formyl chloride, monochloroacetaldehyde, acetylene,		
(VCM)	carbon monoxide, carbon dioxide, monochloroacetyl		
	chloride, hydrochlorid acid*, formic acid*		
1,1-dichloroethene	formyl chloride, monochloroacetyl chloride, phosgene,		
	formic acid *, hydrochloric acid *, carbon monoxide,		
	carbon dioxide		
(E)-1,2-dichloroethene	monochloroacetyl chloride, carbon monoxide, carbon		
	dioxide, formyl chloride, formic acid*, hydrochloric acid*,		
	phosgene		
trichloroethene	dichloroacetyl chloride, phosgene, carbon monoxide,		
	carbon dioxide		
tetrachloroethene	trichoroacetyl chloride, phosgene, carbon monoxide, carbon		
	dioxide		

Table 1: Photooxidation products of the chloroethenes

\* in the presence of water vapour

#### 3.2 Quantum yields

According to the principles of actinometry described in paper I of this series [7], we used ethene at 185 nm and acetone at 254 nm as chemical actinometers with well-known quantum yields for photodecomposition of nearly one [8] and 0.5 [9] respectively.

Using actinometry, only relative decomposition rates have to be determined to calculate the  $C_2H_{4-x}Cl_x$  photooxidation quantum yields.

$$\Phi_{C_2H_{4-x}Cl_x} = \frac{\Delta[C_2H_{4-x}Cl_x]_t \bullet \left(1 - e^{-\sigma_{Ac}} \bullet [Ac] \bullet 1\right)}{\Delta[Ac]_t \bullet \left(1 - e^{-\sigma_{C_2H_{4-x}Cl_x}} \bullet [C_{2H_{4-x}Cl_x}] \bullet 1\right)} \bullet \Phi_{Ac}$$

Here  $\Delta [x]_t$  is the concentration change of x at a certain time t by photooxidation,  $\sigma_x$  the absorption coefficients,  $[x]_t$  the concentration, I the effective absorption path length and  $\Phi$  the quantum yields.

As shown in Fig. 5 we observed quantum yields  $\Phi$  of about 100 for tri- and tetrachloroethene, < 100 for 1,1dichloroethene and about 10 for (E)-1,2-dichloroethene and 2-3 for vinyl chloride at 185 nm. At 254 nm the absorption coefficients for mono- and dichloroethene are too small to be determined reliably so that quantum yields could not be given here. For tri- and tetrachloroethene we observed nearly time-independent differential quantum yields of around 10 and 40 resp. in the  $10^{-3}$  bar concentration range.  $\Phi >> 1$  points to the importance of secondary reactions and chain branching steps.



Fig.5: Quantum yields for degradation of chloroethenes in the 1000 ppm range at irradiation of 185 nm



Fig.6: Quantum yields for degradation of chloroethenes in the 1000 ppm range at irradiation of 245 nm

# 4. Discussion

## 4.1 Oxidation of vinyl chloride monomer (VCM)

VCM shows the lowest degradation rate (Fig. 2 and 3) of all examined chloroethenes. This is in agreement with the fact that acetylene production is another important primary photolysis channel beside Cl-production. Very little Cl-production prohibits the formation of long reaction chains hence low quantum yields for photodegradation are observed, c.f. Fig. 5. Photooxidation of VCM leads to CO, CO<sub>2</sub>, HCl, formyl chloride, monochloroacetaldehyde and acetylene. The primary formed formyl chloride is photochemically and thermodynamically unstable and decomposes to  $CO_2$ , CO and HCl or hydrolyses to formic acid in the presence of water vapour.

We propose the following mechanism for VCM photooxidation, compare also [10]:

 $CH_2$ =CHCl + 185 nm →  $CH_2$ =CH· + Cl· → HC=CH + HCl

The initially formed Cl-radicals add to the vinylic  $\pi$ -bond which leads to secondary reaction products [11]:

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\begin{array}{rcl} \text{CH}_2=\text{CHCl} + \text{Cl} & \rightarrow & \text{CH}_2\text{Cl}\text{-CHCl} & \\ \text{CH}_2\text{Cl}\text{-CHCl} + \text{O}_2 & \rightarrow & \text{CH}_2\text{Cl}\text{-CHCl}\text{-O} & \stackrel{2x}{\longrightarrow} & 2 \text{ CH}_2\text{Cl}\text{-CHCl}\text{-O} + \text{O}_2 \\ \text{CH}_2\text{Cl}\text{-CHCl}\text{-O} & \rightarrow & \text{CH}_2\text{Cl} + \text{H}\text{-COCl} \\ & \rightarrow & \text{CH}_2\text{Cl} + \text{H}\text{-COCl} \\ & \rightarrow & \text{CH}_2\text{Cl} + \text{CO} + \text{HCl} \\ & \rightarrow & \text{CH}_2\text{Cl}\text{-CHO} + \text{Cl} & (\text{Cl}\text{-elimination}) \\ \end{array}
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In line with the low quantum yields Cl-elimination is less important in comparison to the other decomposition channels.

Chloroacetaldehyde is subject to an  $\alpha$ -cleavage well known as "Norrish-I-reaction".

 $CH_2Cl-CHO + 185 \text{ nm} \rightarrow CH_2Cl + CHO$ 

The COH-radical reacts with oxygene to CO, CO2 and HO2 [26].

 $CHO + O_2 \rightarrow CO + HO_2 \cdot OH + CO \rightarrow CO_2 + H \cdot$ 

The CH<sub>2</sub>Cl-radical is oxidized to formyl chloride which decomposes probably to COH- and Cl-radicals, c.f.  $\cdot$ CH<sub>3</sub>Cl photooxidation in paper II of this series.

 $CH_2Cl + O_2 \rightarrow CH_2Cl - O - 2x \rightarrow 2 CH_2Cl - O + O_2$   $CH_2Cl - O + O_2 \rightarrow H - COCl + H - O_2$ 

The HO<sub>2</sub>-radical reacts comparably slow and is probably not able to propagate a chain.

The proposed mechanism explains the absence of long chains, all observed reaction products and even the absence of phosgene.

#### 4.2.1 Photooxidation of (E)-1,2-dichloroethene

The photooxidation of 1,2-dichloroethene is faster than VCM-photooxidation. Primary products are formyl chloride and in small amounts monochloroacetyl chloride and dichloroacetaldehyde which are photooxidized as well and decompose to form phosgene, formyl chloride, formaldehyde, CO, CO<sub>2</sub> and HCl. We propose the following radical chain mechanism, compare also [12]:

 $\begin{array}{l} \text{CHCl}=\text{CHCl} + 185 \text{ nm} \rightarrow \text{CH}=\text{CHCl} + \text{Cl} \\ \text{CHCl}=\text{CHCl} + 185 \text{ nm} \rightarrow \text{CHCl}_2\text{-CHCl} \\ \text{CHCl}=\text{CHCl} + 102 \rightarrow \text{CHCl}_2\text{-CHCl} \\ \text{CHCl}_2\text{-CHCl} + 102 \rightarrow \text{CHC}_2\text{-CHCl} \\ \text{CHCl}_2\text{-CHCl} + 102 \rightarrow \text{CHC}_2\text{-CHC} \\ \text{CHCl}_2\text{-CHC} + 102 \rightarrow \text{CHC}_2\text{-CHC} \\ \text{CHC}_2\text{-CHC} + 102 \rightarrow \text{CHC}_2\text{-CHC} + 102 \rightarrow \text{CHC}_2\text{-CHC} \\ \text{CHC}_2\text{-CHC} + 102 \rightarrow \text{CHC}_2\text{-CHC} + 102 \rightarrow 102$ 

The intermediate radical stabilises through tautomerisation

 $CHCl_2$ - $CHCl_{\cdot} \leftrightarrow CH_2Cl_{\cdot}-CCl_2$ .

and is oxidized either to monochloroacetyl chloride or to phosgene and  $CH_2CI$ 

 $CH_2CI-CCl_2 + O_2 \xrightarrow{2x} CH_2CI-CCl_2 - O + O_2 \rightarrow CH_2CI-COCI + Cl + Cl + COCI_2 + CH_2CI$ 

which is oxidized to H-COCl as already discussed.

## 4.2.2. Photooxidation of 1,1-dichloroethene

The photooxidation of 1,1-dichloroethene leads to monochloroacetylchloride or to phosgene and formyl chloride as detailed above.

 $\begin{array}{rcl} \text{CH}_2=\text{CCl}_2 + \text{Cl} & \rightarrow & \text{CCl}_2\text{-CH}_2\text{Cl} \\ \text{CH}_2\text{Cl}\text{-CCl}_2 + \text{O}_2 & \xrightarrow{2x} & \text{CH}_2\text{Cl}\text{-CCl}_2\text{-O} + \text{O}_2 & \rightarrow & \text{CH}_2\text{Cl}\text{-COCl} + \text{Cl} \\ & \rightarrow & \text{COCl}_2 + \text{CH}_2\text{Cl} \end{array}$ 

## 4.3 Photooxidation of Trichloroethene

Again the formation of Cl-radicals by UV-photolysis is considered to be the rate-determining reaction step. Polar and steric effects favour attack at the less substituted carbon forming dichloroacetyl chloride, c.f. Fig. 7 [13]. The formation of trichloroactaldehyde could not be observed in our experiments.





Fig. 7 Degradation plots of four chloroethenes at 185 nm with the distribution of the main products as function of time

### 4.4 Tetrachloroethene

As shown in Fig.2 the photooxidation of tetrachloroethene is the most efficient of all examined chloroethenes. We attribute this to high amounts of chain carrying Cl-radicals which are formed by photolysis and secondary reactions. We measured quantum yields of around 100 at 185 nm and 40 at 254 nm (Fig.5 and 6). Two main reaction path ways are proposed in the following. In the first path ("TCAC-path") mainly trichloroacetyl chloride is formed, while the other path ("COCl<sub>2</sub>-path") mainly leads to phosgene.

UV-excitation of tetrachloroethene leads to dissoziation of a C-Cl-bond Cl<sub>2</sub>C=CCl<sub>2</sub> + 254 nm  $\rightarrow$  Cl<sub>2</sub>C=CCl<sub>2</sub> + Cl<sub>2</sub>

The "TCAC-path" is comparable to the photooxidation of the other chloroethenes

 $\begin{array}{rcl} \text{Cl}_2\text{C}=\text{CCl}_2 + \text{Cl} & \rightarrow & \text{Cl}_3\text{C}-\text{CCl}_2 \\ \text{Cl}_3\text{C}-\text{CCl}_2 + \text{O}_2 & \rightarrow & \text{O}-\text{O}-\text{CCl}_2-\text{CCl}_3 & \xrightarrow{2x} & \text{O}-\text{CCl}_2-\text{CCl}_3 & \rightarrow & \text{CCl}_3\text{-COCl} + \text{Cl} \end{array}$ 

The intermediate radical O-CCl<sub>2</sub>-CCl<sub>3</sub> is also able to decompose to phosgene and OCl<sub>3</sub> which is oxidized to form phosgene as well.

Regarding a phosgene to trichloroacetylchloride product ratio of 1:1 in the non-sensitized reaction as observed here in contrary to the 1:3 ratio in the chlorine-sensitized one examined by Anderson et al. [11] we consider the existence of a second reaction path beside the TCAC-path, the so-called "COCl<sub>2</sub>-Path".

 $\text{Cl}_2\text{C}=\text{CCl}\cdot \ + \ \text{O}_2 \ \rightarrow \ \text{Cl}_2\text{C}=\text{CCl}\text{-O}\text{-O}\cdot \ \rightarrow \ \text{COCl}_2 \ + \ \text{COCl}\cdot$ 

·COCl probably oxidizes to CO, CO2 or recombines to phosgene.

#### 5. Kinetic simulation

Kinetic modelling of chemical reaction sequences is of considerable help to clarify complex reaction mechanisms. We tried to simulate the photooxidation of tetrachloroethene using the program "HOMREA" [14, 15]. Homogenous mixture of the reactants, the homogeneous illumination and isothermal conditions were assumed. We obtained the reaction rates either from the literature or adopted them from analogous reactions [4, 18]. While we were able to simulate the experimental results with fair precision [18], we feel that too little is known about the respective reaction rates and radical intermediates to trust the simulation. Hence we decided that it is too early to publish the results here.

#### 6. Conclusion

The photooxidation of the higher chlorinated ethenes is efficient with quantum yields >> 1 exhibiting chain reactions. For all chloroethenes, however, we observed chloroacetyl chlorides or chloroacetaldehydes as major products with considerable photooxidation stability. The formation of these products makes the practical use of photooxidation for removal of CHC pollutants less attractive.

## 7. References

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