On the Nonsensitized Photo-oxidation of

1,1,1-Trichloroethane Vapour in Air

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The nonsensitized photo-oxidation of 1,1,1-trichloroethane in air
has been studied. The only quantitatively important products detected
were hydrogen chloride, carbon oxides, and phosgene, but some
acetic acid (or acetyl chloride) and 1,1,1,2-tetrachloroethane were
also traced. The kinetics of phosgene formation was studied and its
quantum yield determined as about 1.3, independent of both the light
intensity and the partial pressure of 1,1,1-trichloroethane. The yield
of consumption of 1,1,1-trichloroethane was shown to be 2.5 — 3 times
that of phosgene formation.

A mong chlorinated hydrocarbons used by industry for degreasing purposes
1,1,1-trichloroethane has gained some popularity in recent years. As
welding may be performed in degreasing shops, it is of great practical importance
to know whether the ultraviolet light from the welding may induce oxida-
tion of the solvent vapour to toxic gases, as has been shown to be the case
with trichloroethylene.[1,2] The work reported below was done to fill the lack
of knowledge on this point, and it will be followed-up with a study on welding
in air contaminated with 1,1,1-trichloroethane to be published elsewhere.[3]

EXPERIMENTAL

The kinetic experiments. As a light source a deuterium lamp (Original Hanau D 102)
was used in the kinetic experiments. The reaction vessel was a 10 cm flow-through
cuvette described earlier.[2] Because of the low output from the lamp in the absorption
range of 1,1,1-trichloroethane and the weak absorption of this light the use of a mono-
chromator turned out to be impossible, and the total output from the lamp was thus
directed towards the front window of the reaction vessel through a 1 cm cuvette with
water. The absorbed amount of light was determined in the following way: Firstly, the
total intensity, I_0, at the site of the reaction vessel was measured by means of potassium
ferrioxalate actinometry.[4] Likewise the intensity was measured with a 0.02 M solution
of cadmium bromide in the water cuvette. This gave the fraction, F, of the emission
absorbed by the $CdBr_2$-filter. Secondly, the spectral distribution of this part was deter-
mined by directing the light through the water cuvette — with and without $CdBr_2$-
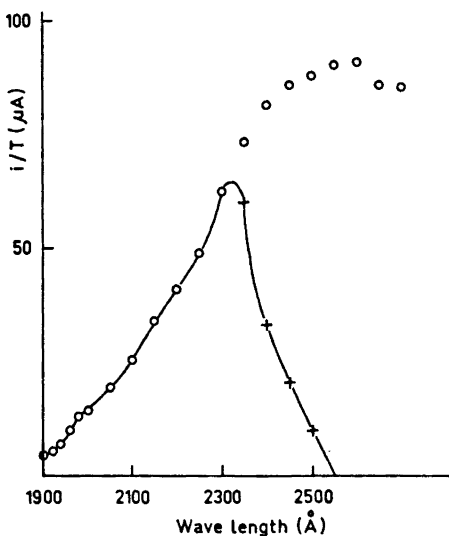
Fig. 1. Relative intensity of the lamp and absorption of CdBr$_2$-filter, respectively, against wavelength. i, the deflection of the galvanometer; T, the relative transmission of the monochromator; O relative intensity of the lamp without CdBr$_2$-filter; + relative intensity absorbed by CdBr$_2$-filter.
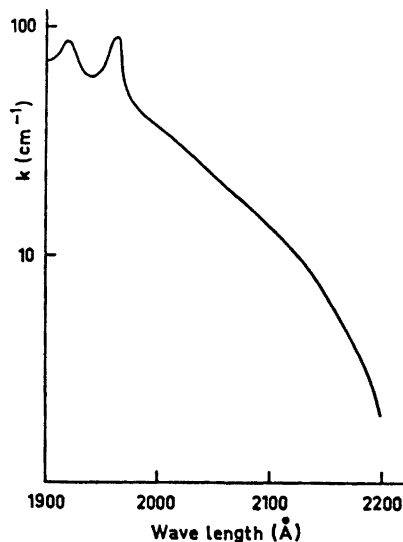
Fig. 2. Absorption spectrum av 1,1,1-trichloroethane.

solution — towards the entrance slit of a monochromator furnished with a quantum counting photomultiplier device.[5] After correction for the relative transmittancy of the monochromator [5] these readings gave the curve in Fig. 1. The area, A, under this curve corresponds to the part of light absorbed by the CdBr$_2$-filter, and by dividing this area into narrow wavelength intervals, $A\lambda$, the intensities of these intervals could be calculated. A combination of these intensities with absorption coefficients, $k\lambda$, of 1,1,1-trichloroethane (see Fig. 2) gave the amount of light absorbed in an experiment. Thus, the absorbed amount of light within a certain interval around the wavelength λ should be

$$I_\lambda(\text{abs}) = I_0 \, FA_\lambda/A \, [1 - \exp(-k_\lambda \, 10 \times p \times 273/T)]$$

In this equation p is the pressure of 1,1,1-trichloroethane (in atm) and T the absolute temperature. The totally absorbed amount of light was calculated by adding the values of I_λ (abs) of all 10 Å-intervals between 1900 and 2210 Å. The intensity of wavelengths shorter than 1900 Å was considered negligible and so was the absorption above 2210 Å. The gas mixture made by flow dilution [2,6] was fed continuously because of adsorption of trichloroethane and its products on the reaction vessel. The hold-up time in the reaction vessel was 5 — 10 min. The temperature was about 22°C in all runs.

In the kinetic experiments only phosgene was determined, because this was the only product for which we had a method that was fast and sensitive enough.[7] The samples were taken by means of a 1 ml gas tight syringe and immediately injected in a gas chromatograph furnished with an EC-detector.

The analytical experiments. For these runs more light was needed, so a high pressure mercury lamp was placed as to illuminate the reaction vessel through its back window. From the reactor the gas mixture was led directly through all-glass connections to a 10 cm IR-cuvette or to impinger flasks for analysis. In a few experiments (Nos. 7 — 9) air saturated with trichloroethane was enclosed in a quartz flask and exposed for 50 — 70

h to the light from the deuterium lamp, whereupon a part of the gas mixture was brought into an evacuated 10 cm IR-cuvette and analysed.

In experiments Nos. 2, 4, and 6 the gas mixture was also analysed by absorption in 0.1 M NaOH in a train of two impinger flasks connected to the reaction vessel. In the solution were determined total chloride, carbonate and in one case the consumption of hydroxyl ions. The chloride was determined by titration with $Hg(NO_3)_2$ and should give the sum of [HCl], 2[COCl₂], [CH₃COCl] and any other easily hydrolysable chlorine (*e.g.* Cl₂) present in the product mixture. Carbonate was determined gravimetrically as BaCO₃ and should give the sum of [CO₂] and [COCl₂]. The surplus in hydroxyl consumption not accounted for by HCl, COCl₂, and CO₂ was ascribed to CH₃COCl.

In experiments 3 and 5 the products were absorbed in two impinger flasks containing an acetone solution of 2.5 % NaI. This should show the formation of any iodide-oxidizing product other than phosgene, when the iodine formed is compared to the phosgene figures determined by IR.

Chemicals. The trichloroethane used in this study was a non-stabilized product made in our laboratory. Gas liquid chromatography showed that it contained at least 99.5 % of 1,1,1-trichloroethane, the main impurities being the 1,1,2-isomer and vinylidene chloride.

The potassium ferrioxalate was made according to Parker.[4] The cadmium bromide was a commercial *p.a.* product. The air used was taken from a compressed air tube and had therefore a very low water content.

RESULTS AND DISCUSSION

The results of the analytical measurements are presented in Table 1. The [Cl]/[C] ratio found by dividing [HCl] + 2[COCl₂] with [CO] + [CO₂] + [COCl₂] should equal 1.5 if these four substances and water were the only products

Table 1. Results of the analytical measurements.

Experiment No.	1	2	3	4	5	6	7	8	9
$p_{C_2H_3Cl_3}$ (atm)	0.005	0.005	0.005	0.005	0.01	0.12	0.12	0.12	0.12
p_{COCl_2} (torr)	1.3	1.0	1.0	1.5	1.7	4.5	6.1	3.7	6.1
p_{CO_2} (torr)	3.9	4.0	3.5	4.5	11.0	4.5	5.1	6.5	7.7
p_{CO} (torr)	3.0	1.7	1.0	2.0	3.0	13.5	10.2	15.2	14.4
p_{HCl} (torr)	6.1	6.5	4.3	6.9	11.8	17.6	8.1	25	20
[Cl]/[C]	1.1	1.3	1.1	1.2	1.0	1.2	0.9	1.3	1.1
[COCl₂]/([COCl₂]+[CO₂]+[CO])	0.16	0.15	0.18	0.19	0.11	0.20	0.28	0.15	0.22
[Cl⁻] (mmol/l air) titr.		0.45		0.49		1.78			
” IR		0.48		0.58		1.56			
[CO₃²⁻] (mmol/l air) grav.		0.25		0.31		0.66			
” IR		0.28		0.35		0.52			
NaOH-consumption (mmol/l air)						3.16			
I₂-formation (mmol/l air) titr.			0.075		0.135				
I₂-formation expected from IR			0.056		0.10				

of the oxidation. In fact it ranges from 0.9 to 1.3. The deficit in the Cl-account might be due to formation of elementary chlorine, which cannot be detected by IR. However, the essential agreement between the chloride figures obtained in the titration of the absorption solutions and those calculated for the corresponding runs from the IR-determinations does not support the assumption

of Cl_2-formation. The gravimetric carbonate determinations, moreover, give evidence for that the sum of the $[COCl_2]$ and $[CO_2]$ measurements by IR is fairly correct. The ratio $[COCl_2]/([COCl_2]+[CO_2]+[CO])$ is rather constant (apart from two runs) with a mean value of 0.18. As no other quantitatively important product containing carbon was detected, we may therefore conclude that the quantum yield of the consumption of trichloroethane is 2.5 to 3 times that of phosgene formation.

The iodine formation in experiments 3 and 5 is appreciably higher than to be expected from IR-figures for phosgene. The cause may be Cl_2-formation, but as was mentioned above this assumption is not in good accordance with the chloride titrations in experiments 2, 4, and 6. We therefore suppose that the difference between iodine found and expected is due mainly to some peroxide and may be in part to ozone and/or chlorine.

The formation of a little acetic acid was shown by several IR-bands. The difference in experiment 6 between $[OH^-]$ consumed and $[Cl^-]+2[CO_3^{2-}]$ formed is not more than 0.06 mmol/l gas passed through the solution, and that is probably within experimental error. Otherwise it would correspond to a partial pressure of about 1 torr for acetic acid, which anyhow is low compared to the IR-determinations for HCl, CO, CO_2, and $COCl_2$. The acetic acid would have been formed in a hydrolysis process following the formation of acetyl chloride in the oxidation, which evidently must yield some water too, accounting for the deficit in hydrogen in the IR-analysis.

Neither chloral nor formaldehyde was formed, according to both chemical aldehyde tests and to IR. Chloral might have been expected through a reaction between oxygen and the radical CCl_3CH_2, which has been postulated as an intermediate in the chlorine-sensitized oxidation of trichloroethane.[8] Formaldehyde might result from a decomposition of the radical CCl_3CH_2O, a reaction analogous to the phosgene-forming step in the oxidations of, e.g., tri- and perchloroethylene and pentachloroethane.[9,10] The cleavage of this radical should also give CCl_3, which with oxygen would give phosgene. The absence of chloral and formaldehyde among the products evidently supports the view that phosgene is not mainly formed via the oxidation of the CCl_3CH_2-radical. Yet the presence of this radical in the reacting gas mixture may be deduced from the formation of some 1,1,1,2-tetrachloroethane that was detected among the products by means of gas liquid chromatography.

The kinetics of the reaction was studied only by determining phosgene, as was mentioned above. This may be justified by the finding that the ratio $[COCl_2]/([COCl_2]+[CO]+[CO_2])$ remained constant when the trichloroethane pressure was changed in the analytical experiments.

How the rate depends on the light intensity was studied at four levels of the trichloroethane pressure, from 0.0003 to 0.003 atm. As seen in Fig. 3, all the determinations fit fairly well to one single straight line irrespective of the trichloroethane pressure. The equation of this line is: $v=1.29 \times I_{abs}-2.3 \times 10^{-11}$ (calculated according to the method of least squares). We assume that the negative value of v at $I_{abs}=0$ is due to a dark reaction consuming phosgene at a rate v_d approximately independent of its concentration. Hence we conclude that the quantum yield of phosgene is about 1.3 independent of the trichloroethane pressure. How the quantum yield depends on the oxygen pressure
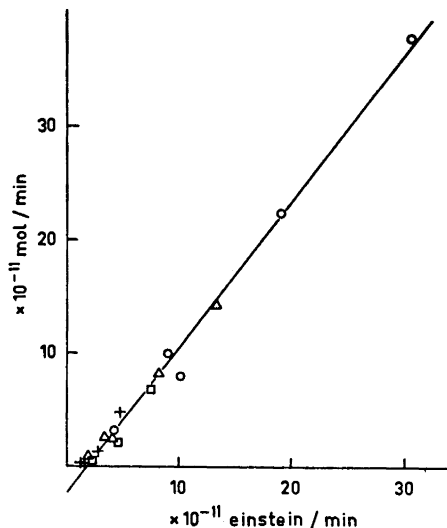
Fig. 3. v_{obs} plotted *vs.* I_{abs} at different $p_{C_2H_3Cl_3}$. ◯ 0.003 atm; △ 0.001 atm; ☐ 0.0005 atm; + 0.0003 atm.

was not investigated, but one single determination at $p_{O_2} = 0.00002$ atm, $p_{C_2H_3Cl_3} = 0.003$ atm and $I_{abs} = 16.9 \times 10^{-11}$ einstein/min gave $v_{obs} = 13.0 \times 10^{-11}$ mol/min. This is as much as *ca.* 2/3 of the velocity at $p_{O_2} = 0.2$ atm, which indicates a very weak dependence of the quantum yield on the oxygen pressure above 0.0001 atm.

Any discussion of the reaction mechanism on this preliminary stage of knowledge must be very speculative. However, the absorption of UV radiation in this wavelength area (about 2000 Å) by saturated chlorinated hydrocarbons is generally ascribed to the excitation of a non-bonding electron on a chlorine atom to an anti-bonding σ-orbital between that chlorine atom and the carbon atom to which it is attached.[11] As the energy of the bond between these atoms is very much lower than the excitation energy, the most probable primary process should be: $CH_3CCl_3 + h\nu \rightarrow CH_3CCl_2 + Cl$. The radicals $CHCl_2CCl_2$ and CCl_3CCl_2 have been shown to give the corresponding acetyl chlorides and some phosgene on reaction with oxygen,[8] so the formation of acetyl chloride is to be expected in this case. However, as the quantum yield of the primary process should be 1, and as the amount of acetic acid or acetyl chloride found is only a small fraction of that of phosgene, which is formed with a quantum yield of the order of 1, the fate of the radical CH_3CCl_2 is generally not the oxidation to acetyl chloride. By analogy with the oxidation of the radicals $CHCl_2CCl_2$ and CCl_3CCl_2 one may assume the radicals $CH_3CCl_2O_2$ and CH_3CCl_2O to be formed in this case, and the latter may decompose to phosgene and the methyl radical as well as to acetyl chloride and a chlorine atom. If this is the main route to phosgene, this would evidently give an explanation to both the order of magnitude of the quantum yield, the velocity dependence of the light intensity and the independence of the trichloroethane pressure.

The chlorine atom formed in the primary process is supposed to react with another trichloroethane molecule giving HCl and the radical CCl_3CH_2. The oxidation of this radical and of the methyl radical should then yield carbon oxides, hydrogen chloride, and perhaps some phosgene. Nothing can be said about the mechanism of these reactions except that it might involve the liberation of another chlorine atom, thus making the oxidation of further trichloroethane molecules possible.

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