

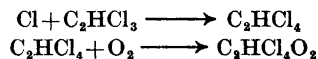
The Non-sensitized Photo-oxidation of Trichloroethylene in Air

JAN ANDERS DAHLBERG

The Chemical Laboratory, Uddeholms AB, S-663 00 Skoghäll, Sweden

The non-sensitized photo-oxidation of trichloroethylene has been kinetically investigated. The results can be interpreted in terms of a chain reaction which probably is initiated by a reaction between an excited trichloroethylene molecule and another trichloroethylene molecule in the ground state. The chain reaction yields mainly dichloroacetyl chloride, the maximum quantum yield of which is found to be about 20 at high partial pressures of trichloroethylene and oxygen. The quantum yield of phosgene is about 1/5 of that of dichloroacetyl chloride.

Since Erdmann's early work¹ several studies on trichloroethylene photo-oxidation have been reported. The gas-phase reaction sensitized by chlorine has been investigated by Müller and Schumacher² and by Huybrechts and Meyers.³ To explain the chain initiation and propagation the following steps are proposed in both papers:



To complete their scheme Müller and Schumacher propose steps that contain only one radical per step (even in the terminating one), whereas Huybrechts and Meyers in order to allow for the facts that the oxidation rate is proportional to I_a and the chlorination rate to $I_a^{1/2}$, assume both propagation and termination steps which are bimolecular regarding the radical $\text{C}_2\text{HCl}_4\text{O}_2$. As in the non-sensitized oxidation the initiating and also the terminating reactions might be different to those of the chlorine-sensitized one, we have felt the former to be worth a kinetic study. Not only for scientific reasons is the reaction interesting; in workshops where welding and degreasing by means of trichloroethylene are going on simultaneously health hazards may occur⁴ and emission of trichloroethylene vapour is supposed to be one cause of the formation of photochemical smog.⁵ As in these cases the partial pressure of trichloroethylene is very low (of the order of 10^{-4} atm or lower) and since so far as we know all earlier studies of the non-sensitized oxidation have concerned the liquid or concentrated vapour phases only, we have

in this investigation used partial pressures of the same order of magnitude as the threshold limit values of trichloroethylene ($\sim 10^{-4}$ atm). This turned out to be the very range where the concentration of trichloroethylene is beginning to influence the value of the quantum yield strongly. From a practical point of view it is also important to know how the quantum yield depends on the wave-length of the exciting light, as the spectra of different welding arcs differ widely. The wave-length dependence of the quantum yield may also throw some light on the nature of the primary process.

EXPERIMENTAL

For each experiment freshly distilled, unstabilized trichloroethylene was fetched direct from the plant to which this laboratory is connected. The purity of the samples was always better than 99.9 %, the impurities being mainly chloroform, 1,1,2-trichloroethane, and perchloroethylene.

As a light source for the photochemical experiments a deuterium lamp (originally intended for a Beckman DU spectrophotometer) was used in most cases. The reaction vessel was placed at the exit slit of a Bausch & Lomb 500 mm Grating Monochromator (the grating blazed at 2000 Å) and could easily be pushed out of the light path in which — behind the reaction vessel — a photomultiplier was placed in order to monitor the intensity of the light. The reaction vessel was a cylindrical flow-through cuvette (length 100 mm, internal diameter 38 mm). The front and back windows were made of synthetic silica (Suprasil) and the cylinder of Pyrex glass. The inlet and outlet tubes were placed about 1 cm from each window. The gas mixture was fed to the vessel through the tube near the front window. The photomultiplier (RCA 931-A) was made sensitive to UV below 3000 Å by means of a thin layer of sodium salicylate sprayed on the tube (about 1 mg/cm²). This should give the photomultiplier a response proportional to the incident light intensity (quanta/cm² sec) and independent of the wave-length according to Watanabe and co-workers.^{6,7} The salicylate layer was protected against oxidation, dust and mechanical damage by surrounding the tube with a nitrogen atmosphere inside a small housing with a Suprasil window. The ratio between the absolute light intensity and the anode current was determined by means of potassium ferrioxalate actinometry at 2537 Å.⁸ All runs were performed at about 25°C.

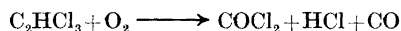
Because of the pronounced tendency of trichloroethylene, and still more its oxidation products, to adsorb on the walls of the reaction vessel the experiments had to be performed with streaming gas mixtures. This made it possible to keep the partial pressure of trichloroethylene at a constant level throughout an experiment and to avoid inner filter effects by the presence of absorbing products. The amount of light absorbed could thus be easily calculated from the partial pressure of trichloroethylene, its absorption coefficient at the wave-length used and the anode current from the photomultiplier, when the cuvette was pushed out of the light path. The gas mixtures were prepared by means of a flow dilution system in which a small current of air was saturated with trichloroethylene at room temperature and fed together with the diluting gas into a mixing flask where the hold up time was at least 1 min. The partial pressure of trichloroethylene in the mixtures was varied between 40 and 3000 μ atm. The flow rate through the reaction vessel was in most cases about 20 ml/min. In the gas leaving the cuvette usually two products were determined, dichloroacetyl chloride (DCAC) and phosgene. DCAC was absorbed in isopropyl alcohol and the ester then formed was determined by means of gas liquid chromatography using electron capture detection. The samples for phosgene determination were taken out of the effluent gas flow with a gastight Hamilton syringe and immediately analyzed in the same chromatographic equipment. In both cases silicon oil DC-200 was used as a stationary phase. The analytical methods will be described in full details elsewhere.⁹ As DCAC is very strongly absorbed in all kinds of soft tubings, the connection between the reaction vessel and the absorption train containing the alcohol had to be an all-glass one. This glass connection was also furnished with a short branch tube closed by means of a piece of Viton tubing through which the needle of the Hamilton syringe could be inserted into the gas flow.

RESULTS AND DISCUSSION

Earlier investigations have shown that the stoichiometry of the main reaction is properly described by



where $\text{C}_2\text{HCl}_3\text{O}$ is DCAC or — at least in the liquid phase reaction — trichloroethylene epoxide. By consecutive or side reactions certain amounts of phosgene, hydrogen chloride, and carbon monoxide are also formed.



That this general picture is valid for the non-sensitized gas-phase oxidation too, was confirmed not only by our kinetic data regarding DCAC and phosgene but also by a few experiments, in which the total amount of easily hydrolysable or free chloride and the amount of epoxide were determined. The chloride determination was done by absorbing the effluent gas in water and titrating with AgNO_3 (potentiometric indication). According to the reaction formulae above the titratable chloride amount should equal the amount of DCAC + 3 × the amount of phosgene formed. For the epoxide determination a train of absorption vessels containing sodium iodide in acetone was connected to the outlet of the reaction cuvette. As the epoxide gives 1.5 mole I_2 ¹⁰ the amount of epoxide formed should be given by (iodine formed — phosgene absorbed):1.5. The results of these measurements are given in Table 1.

Table 1. Analytical experiments.

Determination		Run No. 1	Run No. 2	Run No. 3
DCAC	mole/min	366×10^{-9}	89×10^{-10}	—
Phosgene	»	60×10^{-9}	18×10^{-10}	6×10^{-10}
Total Cl^- expected	»	546×10^{-9}	143×10^{-10}	—
Total Cl^- formed	»	500×10^{-9}	120×10^{-10}	—
Epoxide	»	40×10^{-9}	—	7×10^{-10}

The very different amounts of products in the three runs are mainly due to differences in light intensity. The discrepancy between found and expected chloride is not too large to be ascribed to experimental error, and the results thus indicate that there is no other significant path to hydrogen chloride than the one that also gives phosgene.

Although the epoxide can rearrange to DCAC even at the temperature at which the runs were performed ($\sim 25^\circ\text{C}$), the time for the gas to flow from the inlet of the reaction vessel to the absorption train is too short for the rearrangement to take place to any appreciable degree and the conclusion may thus be allowed that the main path of the oxidation is to DCAC directly and not *via* the epoxide.

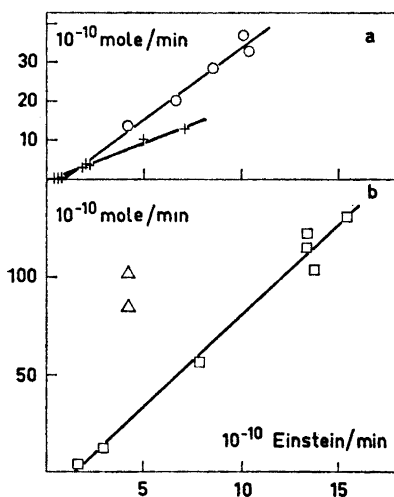


Fig. 1. v_{DCAC} (measured) plotted vs. I_{abs} at different p_{tri} .

- (+) $p_{\text{tri}} \approx 40 \times 10^{-6}$ atm.
 (O) $p_{\text{tri}} \approx 75 \times 10^{-6}$ atm.
 (□) $p_{\text{tri}} \approx 400 \times 10^{-6}$ atm.
 (Δ) $p_{\text{tri}} \approx 3000 \times 10^{-6}$ atm.

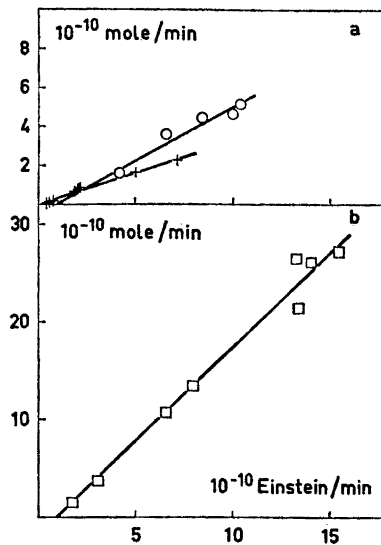


Fig. 2. v_{phosgene} (measured) plotted vs. I_{abs} at different p_{tri} . Symbols the same as in Fig. 1.

Hence the kinetic investigation was restricted to the rate of formation (v) of DCAC and phosgene. In Figs. 1–2 the measured rates are plotted against the amount of light absorbed per minute in the reaction vessel (I_{abs}) at constant partial pressures of oxygen and trichloroethylene. It is quite evident that the velocities of formation of both DCAC and phosgene are linearly dependent on the absorbed light intensity, as is the case in the chlorine-sensitized reaction.

On the other hand the straight lines generally do not pass through the origin but cut the v -axis at negative values, *i.e.* there is some dark reaction consuming the products of the photochemical one at rates v_{d} , which are almost

Table 2. Rates of product-consuming dark reaction at different p_{tri} .

$p_{\text{tri}} \times 10^6$ (atm)	v_{d} (DCAC) $\times 10^{10}$ (mole/min)	v_{d} (COCl ₂) $\times 10^{10}$ (mole/min)
40	0.63	-0.03
75	3.25	0.48
400	14.48	1.92

independent of the concentrations of DCAC and phosgene. From Table 2 it seems obvious that a correlation exists between the partial pressure of trichloroethylene and v_d for both DCAC and phosgene. This correlation suggests the presence of some minor impurity present in trichloroethylene, capable of reacting with acyl chlorides. The dark reaction was not further investigated.

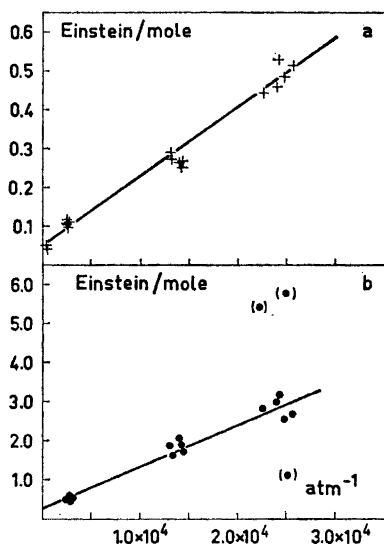


Fig. 3. I_{abs}/v plotted vs. $1/p_{\text{tri}}$.
a. DCAC; b. Phosgene.

How the photochemical reaction rate depends on the partial pressure of trichloroethylene is shown in Fig. 3. Here the values of I_{abs}/v (where $v = v_{\text{measured}} + v_d$) are plotted vs. $1/p_{\text{tri}}$. For both DCAC and phosgene the plots fit reasonably to straight lines, the equations of which can be transformed to:

$$v_{\text{DCAC}}/I_{\text{abs}} = 20 \frac{2770 p_{\text{tri}}}{1 + 2770 p_{\text{tri}}} \text{ moles/einstein}$$

$$v_{\text{COCl}_2}/I_{\text{abs}} = 3.7 \frac{2510 p_{\text{tri}}}{1 + 2510 p_{\text{tri}}} \text{ moles/einstein}$$

The formulae should be valid at $\lambda = 2130 \text{ \AA}$ and $p_{\text{O}_2} = 0.2 \text{ atm}$. The unit for p_{tri} is atm.

The relation between the yields of phosgene and DCAC is in agreement with the relation found in the chlorine-sensitized reaction.^{2,3} The fact that v_{DCAC} and v_{COCl_2} are almost identical functions of p_{tri} suggests further that the mechanisms of the oxidation to DCAC and to phosgene are essentially the same, only differing in the last steps.

The oxygen-dependence has not been investigated systematically but preliminary experiments indicate that the rate is changed very little by varia-

Table 3. Runs at different oxygen pressure. $p_{\text{tri}} \approx 4 \times 10^{-4}$ atm. $\lambda = 2130 \text{ \AA}$.

p_{O_2} (atm)	$I_{\text{abs}} \times 10^{10}$ (einstein/min)	$v_{\text{DCAC}} \times 10^{10}$ (mole/min)	Remarks
4.6×10^{-3}	10.9	87.5	
9.2×10^{-4}	11.0	83.5	
2.0×10^{-5}	1.7	4.9	^a
2.0×10^{-1}	1.7	6.3	^a
2.0×10^{-1}	11.0	89.0	Interpolated from Fig. 1b

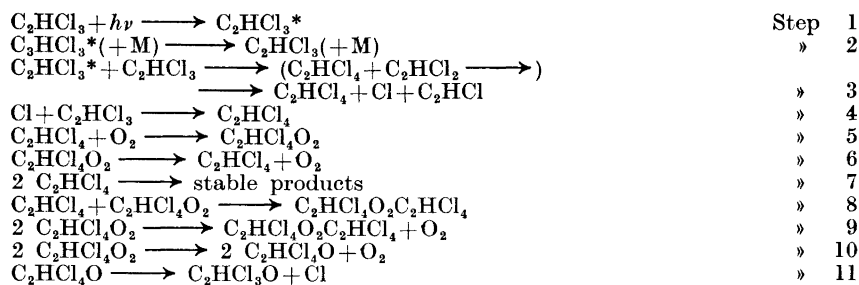
^a These values are somewhat higher than the corresponding value in Fig. 1b. This is not surprising because of the low intensity, at which a change of v_{d} causes a great relative change in the measured v .

tions in the oxygen pressure above 10^{-4} atm. This can be seen in Table 3, where the results of three runs with low oxygen pressure are presented together with comparable data obtained at the oxygen pressure 0.2 atm.

For the chlorine-induced oxidation³ a fairly marked effect of changing the oxygen pressure is evident already below 10^{-1} atm (at 363°K).

The apparent difference in oxygen dependence between the sensitized and the non-sensitized oxidations may however well be an effect of temperature. Thus, if the propagating and terminating steps proposed by Huybrechts and Meyers³ for the chlorine-sensitized reaction were operative also in the non-sensitized one, the pronounced oxygen-independence at 298°K and likewise the order of magnitude of the maximum quantum yield would be a consequence, as will be seen from below. Further this should explain the similar stoichiometry in the two cases and why the rates of both reactions are proportional to the first power of the light intensity.

Thus, to explain the kinetic results the following reaction mechanism is proposed:



In this scheme steps 4–11 are identical with steps 2, 8–12, 14, and –9 proposed by Huybrechts and Meyers³ to explain the kinetics of the chlorine-sensitized oxidation. Assuming stationary state conditions and $k_6 \gg k_8[\text{C}_2\text{HCl}_4] + (k_9 + k_{10})[\text{C}_2\text{HCl}_4\text{O}_2]$ the above scheme leads to the following kinetic formula:

$$v_{\text{chain}} = k_{11} [\text{C}_2\text{HCl}_4\text{O}] = I_{\text{abs}} \frac{(k_3/k_2) [\text{C}_2\text{HCl}_3]}{1 + (k_3/k_2) [\text{C}_2\text{HCl}_3]} A$$

$$\text{where } A = \frac{2}{\frac{k_9}{k_{10}} + \frac{k_8 k_6}{k_{10} k_5 [\text{O}_2]} + \frac{k_7 k_6^2}{k_{10} k_5^2 [\text{O}_2]^2}}$$

From measurements at 363 and 403°K Huybrechts and Meyers³ calculated:

$$\log_{10} \left(\frac{k_8 k_6}{k_{10} k_5} \right) = - \frac{14520}{4.576T} + 3.54$$

$$\log_{10} \left(\frac{k_{10}}{k_9} \right) = - \frac{3400}{4.576T} + 4.03$$

$$\log_{10} k_7 = - \frac{500}{4.576T} + 9.56$$

$$\log_{10} \left(\frac{k_8 k_5}{k_6} \right) = \frac{20530}{4.576T} + 3.14$$

By extrapolation to 298°K these equations give the following set of values:

$$k_9/k_{10} = 3 \times 10^{-2}$$

$$k_8 k_6 / (k_{10} k_5) = 8 \times 10^{-8} \text{ mole/l and}$$

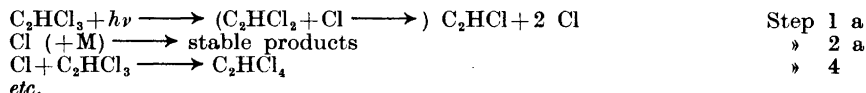
$$k_7 k_6^2 / (k_{10} k_5^2) = \sim 10^{-16} \text{ mole}^2/\text{l}^2$$

From this it is evident that the oxygen-dependent factor, A , *i.e.* the quantum yield at high trichloroethylene pressures, will assume a maximum value of 60 to 70 and half of this value at an oxygen pressure of about 6×10^{-5} atm. These estimates are not incompatible with the maximum yield found (about 25) and the oxygen pressure at which a substantial lowering of the rate was noticeable remembering the extreme extrapolation inherent in the estimation.

Now turning to the deactivating step 2 and the chain initiating step 3 these explain the trichloroethylene dependent factor of the experimental kinetic equations. We have also confirmed the formation of chloroacetylene in the photolysis of trichloroethylene by means of gas liquid chromatography. If the chain propagation and termination steps of the chlorine-sensitized oxidation are the mainly operative ones even in the non-sensitized reaction this implies that chlorine atoms or C_2HCl_4 radicals are formed in the initiating steps and further that the radical C_2HCl_2 (if formed) should decompose almost instantly. In the mixture of condensed products from the trichloroethylene photolysis in absence of oxygen we have identified all the main bands in the IR-spectrum of 1,1,2,3,4,4-hexachlorobutene-2 (m.p. 80°C). However the mechanism of its formation, this product shows that dichloromethyl groups are formed without the action of oxygen on trichloroethylene and thus, affords

some evidence for the migration of a chlorine atom in one way or another in the oxidation initiating steps.

Another initiating mechanism should also be considered:



With the same assumptions as earlier this scheme gives the following rate expression:

$$v_{\text{chain}} = I_{\text{abs}} \frac{\frac{2k_4}{Ak_{2a}} [\text{C}_2\text{HCl}_3]}{1 + \frac{2}{A} + \frac{2k_4}{Ak_{2a}} [\text{C}_2\text{HCl}_3]} A$$

As $2/A \ll 1$, this formula is compatible with the experimentally found relationship. The dissociation of trichloroethylene upon excitation is analogous to what has been assumed for *cis*-dichloroethylene¹¹ and for tetrachloroethylene.¹² The continuous appearance of the N→V-band of chloroethylene spectra may also be a result of dissociation.¹³

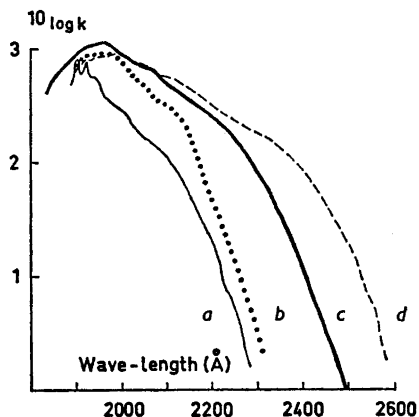
Step 2 a on the other hand should be imagined as a series of reactions in which the first one, the irreversible adhesion of Cl to the wall or some molecule in the gas phase, is rate-determining. This step is quite hypothetical and does not — to our knowledge — gain any support from published data. Further if dissociation were the way of formation of chloroacetylene this formation should not be dependent of the trichloroethylene partial pressure, but in fact it is. An estimate of this dependence was made in two photolysis runs in which p_{tri} was 3.2×10^{-3} and 3.4×10^{-4} atm, respectively. The relative quantum yields were determined at essentially constant I_{abs} by gas liquid chromatography. At the higher pressure the yield was 3.1 times that of the lower. The relation between the yields of DCAC at these two pressures is 1.8 according to the experimental formula given above. Evidently the formation of chloroacetylene is at least as dependent on the trichloroethylene pressure as is the oxidation and thus, if a dissociative mechanism is operative in the oxidation initiation it has to be more complicated than the one discussed above. Possibly chloroacetylene could be formed in a reaction between trichloroethylene and the C_2HCl_2 -radical, but from reasons already stated this radical should be very short-lived (*cf.* Ref. 11). Hence the experimental results favours the steps 1, 2, and 3 rather than 1 a and 2 a.

The continuous N→V-band of the spectra of chloroethylenes does not necessarily imply that the molecules dissociate in the excited state. As the V-state is twisted and its C—C distance longer than the C—C distance in the planar N-state the molecules will—according to the Franck-Condon principle—by N→V-excitation get into a multiplicity of close-lying vibrational states, that would give the spectrum its continuous appearance.^{14,15}

Fig. 4. Absorption spectra of chloroethylenes. The measurements were made by means of a recording spectrophotometer and with streaming mixtures of vapour and air through the cuvette. If the unit for the partial pressure of the absorbing molecule is atm, the absorption coefficient is defined by

$$k = \frac{T}{p \times 273 \times l} \cdot \ln \frac{I_0}{I} \text{ (cm}^{-1}\text{)}$$

a, *cis*-Dichloroethylene.
b, *trans*-Dichloroethylene.
c, Trichloroethylene.
d, Tetrachloroethylene.



The wave-length 2130 Å was chosen for the above-mentioned runs mostly from practical reasons: as is shown in Fig. 4 the absorption coefficient of trichloroethylene is rapidly decreasing with increasing wave-length above 2200 Å and below 2100 Å the output from the exit slit of the monochromator rapidly became too low to make measurement convenient. However, as was pointed out in the introduction, the wave-length dependence of the quantum yield has both practical and theoretical importance, so some attempts have been made to perform a few elucidative experiments regarding this dependence. The conditions and results are presented in Table 4.

Table 4. Runs at different wave-lengths. $p_{O_2} = 0.2$ atm.

λ (Å)	$p_{tri} \times 10^6$ (atm)	$I_{abs} \times 10^{10}$ (einstein/min)	$v_{DCAC} \times 10^{10}$ (mole/min)	$v_{COCl_2} \times 10^{10}$ (mole/min)
1930	326	1.7	6.6	0.68
2030	271	1.5	<i>a</i>	0.59
2030	281	1.6	<i>a</i>	0.62
2130	306	1.7	6.3	0.79
2280	301	1.4	<i>a</i>	0.92
2280	283	1.4	<i>a</i>	0.78
2130	2700	4.2	102	<i>a</i>
2130	2960	4.2	85	<i>a</i>
2280	2730	4.6	153	<i>a</i>
2280	3000	3.8	96	<i>a</i>
2400	2830	3.1	21	<i>a</i>
2400	3030	3.2	29	<i>a</i>

a not determined.

In spite of limited experimental accuracy the results seem to demonstrate that the quantum yield is nearly constant at wave-lengths shorter than 2300 Å. Two measurements at 2400 Å on the other hand show a much lower quantum

yield, thus indicating a rapid drop of the yield at wave-lengths above 2300 Å. This should not be incompatible with either of the discussed mechanisms. In the case of step 3 it suggests an activation energy, whereas a predissociation mechanism should be involved in step 1 a, if this is the operative one.

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