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On the Formation of Phosgene and Trichloroacetyl Chloride in the Non-sensitized Photo-oxidation of Perchloroethylene in Air

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The non-sensitized photo-oxidation of trichloroethylene (tri) and 1,1,1-trichloroethane in the gas phase have earlier been reported.^{1,2} In this paper the non-sensitized photo-oxidation of perchloroethylene (per) at low vapour pressures in air is described. The experimental technique has been described in the paper on photo-oxidation of trichloroethylene by Dahlberg.¹

In the tri case the initiating step was shown to be a reaction between one tri molecule in the excited state and one in the ground state in competition with a pseudo first-order deactivation step.¹ However, for perchloroethylene we have shown that the initiating step is a dissociation of a per molecule upon light absorption. It is further shown that phosgene is probably formed not only according to the scheme by Huybrecht *et al.*³ for the chlorine-sensitized photo-oxidation, but also by a parallel chain mechanism.

The results of the kinetic measurements are shown in Figs. 1 and 2. Obviously there are linear relationships between the rates of formation (v) of trichloroacetyl chloride (TCAC) and phosgene, respectively, and the absorbed light (I_{abs}). Thus all measurements made at the oxygen pressure 0.2 atm and at I_{abs} above 8.5×10^{-13} einstein/s fit well to the following equations calculated by the method of least squares:

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Fig. 1. v_{phosgene} (measured) plotted vs. I_{abs} at different p_{per} : O, $p_{\text{per}} = 5$ Pa; Δ , $p_{\text{per}} = 10$ Pa; $\square$, $p_{\text{per}} = 30$ Pa; $\bullet$, $p_{\text{per}} = 50$ Pa; +, $p_{\text{per}} = 100$ Pa.

Fig. 2. v_{TCAC} (measured) plotted vs. I_{abs} at different p_{per} : O, $p_{\text{per}} = 5$ Pa; Δ , $p_{\text{per}} = 10$ Pa; $\square$, $p_{\text{per}} = 30$ Pa; $\bullet$, $p_{\text{per}} = 50$ Pa; +, $p_{\text{per}} = 100$ Pa.

$$v_{\text{TCAC}} = 31.9 I_{\text{abs}} - 263 \times 10^{-13} \text{ mol s}^{-1}$$

$$v_{\text{phosgene}} = 27.6 I_{\text{abs}} - 177 \times 10^{-13} \text{ mol s}^{-1}$$

The slopes of these lines, *i.e.* the quantum yields, seem to be independent of the per pres-

sure, which suggests other absorption and chain-initiating steps than in the tri case. Hence, we assume in agreement with Horowitz and Rajbenbach⁴ that absorption of UV light in this region causes dissociation of the per molecule according to the formula:

Now, the chlorine atom may initiate the chain mechanism proposed by Huybrecht *et al.*³ for the chlorine-sensitized oxidation:

The terminating steps are:

The $\text{C}_2\text{Cl}_4\text{O}$ formed in step 6 is either TCAC or perchloroethylene epoxide.

According to Huybrecht *et al.*³ phosgene is formed by cleavage of $\text{C}_2\text{Cl}_2\text{O}$ and further oxidation of the CCl_3 radical. As to the fate of the C_2Cl_3 radical we have detected dichloroacetylene as a photolysis product of perchloroethylene by gas chromatography contrary to Horowitz and Rajbenbach.⁴ We thus propose the following step:

The C_2Cl_3 radical might also give rise to an alternative route to phosgene:

This chain would terminate by step 10 and by:

This also implies a switch-over to the TCAC-forming chain.

If we assume that k_4 is much greater than k_8 [C_2Cl_3] + $2(k_5 + k_9)[\text{C}_2\text{Cl}_2\text{O}_2]$ a stationary state treatment of the TCAC-forming chain gives the kinetic equation

$$v_{\text{TCAC}} = I_{\text{abs}} \times 2k_6/A$$

where $A = k_4k_8/k_2[\text{O}_2] + k_7k_4^2/k_2^2[\text{O}_2]^2 + k_9$

Likewise a stationary state treatment of the phosgene-forming chain gives the equation:

$$v_{\text{phosgene}} = I_{\text{abs}} \frac{2k_{12}k_{11}[\text{O}_2]}{k_{12}k_{10} + k_{10}k_{14} + k_{14}k_{11}[\text{O}_2]}$$

The derived equations are both compatible with the fact that the quantum yields are independent of I_{abs} and the per pressure. The

Table 1. Relationship between phosgene and TCAC+epoxide formation.

Exp. No.	$n_{\text{phosgene}} 10^{-10} \text{ mol}$	$n_{\text{epoxide}} 10^{-10} \text{ mol}$	Phosgene/TCAC+epoxide
1	416	368	0.49
2	367	368	0.47
3	376	350	0.48

phosgene route proposed above could thus afford an explanation to the high phosgene/TCAC ratio — about 1 in this reaction compared to about 1/3 in the chlorine-sensitized one. Contrary to this, the ratios of the corresponding reactions of trichloroethylene are almost equal. However, in this connection one shall also take into consideration the formation of epoxides isomeric to the acetyl chlorides. The results of measurements of epoxides are given in Table 1. The values in the last column are calculated assuming a [phosgene]/[TCAC] ratio = 28/32. Obviously the $[\text{COCl}_2]/[\text{C}_2\text{Cl}_2\text{O}]$ ratio is still rather high compared to the corresponding value of the chlorine-sensitized reaction. This suggests a contribution to the phosgene formation from the chain proposed above, i.e. steps 11–13.

An objection against the dissociative absorption step may be that all chemical evidence in the trichloroethylene case favours a non-dissociative absorption process.¹ The perchloroethylene molecule, however, has a much greater symmetry, which might afford an explanation to this problem. A result of this greater symmetry should thus be that the number of vibrational modes is rather strongly diminished in the excited state in comparison with trichloroethylene. The chance that the excitation energy will concentrate in a CCl-bond should therefore be greatly enhanced. The probability that the $\text{N} \rightarrow \text{V}$ transition will cause dissociation of a CCl bond would thus increase when going from tri- to perchloroethylene.

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