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Abstract

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On Some Regularities of the Liquid-Phase Direct Photooxidation of Trichloroethylene

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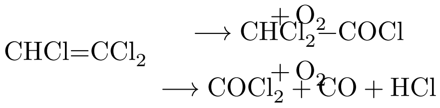
It is known that, upon oxidation of trichloroethylene, dichloroacetyl chloride, phosgene, carbon monoxide, and hydrogen chloride are formed:



$$CHCl{=}CCl_2 \begin{cases} \xrightarrow{+O_2} CHCl_2{-}COCl \\ \xrightarrow{+O_2} COCl_2 + CO + HCl \end{cases}$$

Only the chlorine-sensitized process of photooxidation of trichloroethylene by oxygen has been studied in detail (^{1}), as one having practical significance (^{2}). It has been established that under these conditions the reaction proceeds as a radical-chain reaction. Photoexcitation of chlorine is assumed to be the primary act, since the process can be initiated by radiation with $\lambda = 4368$ Å (^{3}).

We have shown (^{4}) that, for the purpose of obtaining dichloroacetic acid chloride, it is rational to carry out direct (not halogen-sensitized) photooxidation of trichloroethylene in the liquid phase at the boiling temperature of the reaction mass. In this case high yields of the acid chloride are obtained, in contrast to dark oxidation (^{5}) or direct low-temperature photooxidation (^{6}).

In the present communication the main results are set forth of studies of the regularities of the oxidation reaction of trichloroethylene under the conditions proposed by us. Oxidation of trichloroethylene was carried out in quartz or Pyrex vessels by bubbling oxygen through liquid trichloroethylene under irradiation with PRK-2 and PRK-7 mercury-quartz lamps. The rate of oxygen feed was set by a flowmeter. The intensity of irradiation was varied by changing the distance to the radiation source and was determined with a photochemical actinometer. In a number of experiments a monochromator or light filters were used.

The course of the process was followed by taking, at definite time intervals, samples of the reaction liquid, in which, after hydrolysis, the content of acid chloride was determined from the difference between the total acidity and the content of hydrochloric acid. The amount of phosgene formed was established from the diphenylurea obtained when the gaseous reaction products were passed into a solution of aniline in acetic acid. The quantum yield of the reaction was determined by the uranyl oxalate method.

In carrying out the experiments, the temperature, rate of oxygen feed, irradiation intensity, wavelength of the radiation, solvents, and concentration of the chloroolefin were varied; various additives affecting the rate of the process were used.

Figure 1 presents characteristic kinetic curves for the oxidation. As can be seen, when trichloroethylene (1) is completely consumed, the maximum yield of acid chloride (2) is reached, after which its decrease is observed with a simultaneous increase in the rate of formation of gaseous products (3), which is a consequence of oxidative decomposition

chloroanhydride (4). The presence of an induction period in the reaction and the S-shaped course of curves 1 and 2 (Fig. 1) may indicate a radical-chain or autocatalytic character of the process. The experiment confirms both assumptions.

It is seen from Table 1 that in the dark the oxidation reaction does not develop for a long time either at 20° or at 85° (experiments Nos. 1, 2). Under ultraviolet irradiation the reaction rate is high and increases with increasing temperature (experiments Nos. 3–6). This shows that the total rate of the process is determined by both photochemical and thermal stages.

Fig. 1

Fig. 2

Fig. 1. Dependence on time of the consumption of trichloroethylene (1), the formation of dichloroacetyl chloride (2), and the yield of gaseous products (3) at a temperature of 85° and UV irradiation.

Fig. 2. Yield of dichloroacetyl chloride under different oxidation conditions (explanations in the text)

Table 1

Experiment Nos.	Conditions of the experiments	Conditions of the experiments	Conditions of the experiments	Conditions of the experiments	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Quantum yield of the reaction*
Experiment Nos.	temp., °C	irradiation spectral region	irradiance, W/cm^2	additions to CHClCCl	1	2	3	4	Quantum yield of the reaction*
1	20	No	–	–	0	0	0	0	–
2	85	»	–	–	0	0	0	0	–
3	20	248–577	0.133	–	10.2	20.5	30.7	37.7	10
4	30	248–577	0.133	–	20.6	39.6	49.0	55.4	17
5	55	248–577	0.133	–	21.8	51.4	67.0	71.1	23
6	85	248–577	0.133	–	27.6	54.0	77.4	80.0	35
7	20	No	–	B_2O_2	0	0	0	0	–
8	85	»	–	B_2O_2	12.3	27.4	41.0	56.5	–
9	85	248–577	0.133	Iodine	2.1	8.7	15.3	28.9	6
10	85	248–577	0.133	Pyridine	4.2	12.5	19.8	26.7	11

Experiment Nos.	Conditions of the experiments	Conditions of the experiments	Conditions of the experiments	Conditions of the experiments	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Yield of dichloroacetyl chloride during the process, in hours, % of theoretical	Quantum yield of the reaction*
11	85	248—577	0.133	Diphenylamine	0.4	6.1	10.0	15.3	6
12	85	248—577	0.133	Phenol	0	0	0	0	0
13	85	300—420**	0.035	—	6.5	13.4	17.8	27.0	285
14	85	248—577	0.003	—	12.5	27.8	11.2	52.3	660
15	85	320—577***	0.300	—	2.7	8.8	17.5	28.5	6

* In all cases the quantum yield was determined for the reaction period between the first and second hours.
** With UVS-4 light filter.
*** Oxidation is carried out in a Pyrex apparatus.

Figure 2 presents the kinetic curves for the initial period of oxidation in experiments where trichloroethylene before the ultraviolet radiation was switched on either was not subjected (1) or was subjected (2) to the action of oxygen. The absence of an induction period on curve 2 shows that in the dark process, despite the apparent invariability of the reac-

of the reaction mass (experiment No. 2, Table 1), compounds are formed that are necessary for the rapid development of photochemical processes. Such com-

Fig. 3 and Fig. 4

Figure 1: Fig. 3 and Fig. 4

pounds may be peroxides, whose presence we established by qualitative reactions.

The introduction of benzoyl peroxide, as a radical-forming additive, helps eliminate the induction period of the photoprocess (3). In the dark

Fig. 3

Fig. 4

Fig. 3. Kinetics of the formation of dichloroacetyl chloride. 1 –under UV irradiation, 2 –the same with the addition of 1% dichloroacetyl chloride before the start of the process, 3 –the same, with irradiation switched off at point A, 4 –dark process, 5 –the same with the addition of 1% dichloroacetyl chloride, 6 –the same, with irradiation switched off at point B; 1, 2, 6 –photoinitiated process; 3, 4, 5 –dark process

Fig. 4. Isotherms of the photooxidative decomposition of dichloroacetyl chloride in carbon tetrachloride (1) and dichloroethane (2)

process, benzoyl peroxide does not initiate the reaction at 20°, but it substantially affects it at 85°, i.e., under conditions favorable for the thermal decomposition of the peroxide (cf. experiments Nos. 1, 7, 2, 8 in Table 1). Additions to the reaction mass of substances that form stable compounds with radicals (Table 1), such as iodine (experiment No. 9), pyridine (experiment No. 10), diphenylamine (experiment No. 11), or phenol (experiment No. 12), substantially inhibit the photooxidation reaction of trichloroethylene (experiment No. 6).

The data presented indicate a radical-chain mechanism for the reaction under study. This is confirmed by a quantum yield from 6 to 660, depending on the intensity and character of the irradiation (experiments Nos. 13–15), and by the possibility of carrying out the reaction at a high rate even after irradiation has ceased (curve 3, Fig. 3).

On the other hand, the possibility of oxidation without an induction period in the presence in the reaction mass of the reaction product dichloroacetyl chloride (Fig. 3), both in irradiated (1 and 2) and dark (4 and 5) processes, or with their different sequence (3 and 6), indicates the autocatalytic character of the reaction. From Fig. 4 it is seen that the rate of oxidative decomposition of dichloroacetyl chloride in the medium of the chlorine-radical-transferring solvent CCl_4 is considerably higher than, for example, in dichloroethane, which is characteristic of processes proceeding by a radical mechanism. This, apparently, is also the reason for the catalytic influence of acid chloride on the oxidation of trichloroethylene.

The question of the primary act of chain initiation in the nonsensitized gas-phase photooxidation of trichloroethylene is of interest. The process cannot be caused by photoexcitation of oxygen or trichloroethylene,

since it is initiated by radiation with $\lambda > 320$ mμ (UFS-4 light filters, Pyrex), not absorbed by oxygen ($\lambda_{\text{max}} < 200$ mμ) and trichloroethylene ($\lambda_{\text{max}} < 266$ mμ). The primary act may be the radical decomposition of trichloroethylene peroxide initiated by irradiation or by thermal energy. It is known that, under the action of atmospheric oxygen, chloroolefins readily form peroxides, which decompose explosively and cause rapid radical polymerization of the monomer (7).

We observed that, under ultraviolet irradiation, trichloroethylene in the absence of oxygen does not form polymerization products. The presence of small amounts of oxygen causes the reaction of polymer formation. With a large excess of oxygen, the polymerization chain passes into the oxidation chain, and the principal reaction products become not polymeric compounds but dichloroacetyl chloride and phosgene, i.e., oxidation products.

Along with peroxides, the cause of chain initiation may also be the photoinitiated decomposition of dichloroacetyl chloride, whose long-wavelength absorption boundary lies in the region of 370 (established by us on an SF-4 spectrophotometer). The energy of the C–Cl bond in the chlorocarbonyl group was determined as 79.8 kcal (8), which corresponds to a quantum of light with $\lambda = 358$ mμ, transmitted by the filters used.

As a result of the investigations carried out, it has been shown that direct liquid-phase photooxidation of trichloroethylene to dichloroacetyl chloride proceeds as a radical-chain process. The primary act of the reaction may be the photoinitiated decomposition of peroxide compounds formed also in the dark process, as well as the decomposition of dichloroacetyl chloride. Owing to the latter, the reaction obeys the regularities of autocatalytic processes. Contrary to the data available in the literature (2), this leads to the conclusion that, in the practical use of the photooxidation of trichloroethylene, there is no need to employ halides as sensitizers.

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