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Abstract

Full Text

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ON THE MECHANISM OF THE PHOTOCHEMICAL CHLORINATION OF CHLOROACETALDEHYDE

(Presented by Academician N. N. Semenov, April 22, 1963)

Chlorination of aldehydes usually leads to the formation of acid chlorides (^{1}). G. A. Razuvaev and co-workers (^{2}), in the photochemical chlorination of monochloroacetaldehyde, succeeded in isolating a small amount of dichloroethyl chloride.

We have developed a method for the photochemical chlorination of chloroacetaldehyde in which the yield of monochloroacetyl chloride is 96–98% of theory. Since reactions of this type, judging from the available literature, have not been studied, it was of interest to investigate the mechanism of this process.

Fig. 1. Formation of chloroacetyl chloride (CAC) during the photochemical chlorination of a 40% solution of chloroacetaldehyde in CCl_4 at 30°: 1 –without additives, 2 –in the presence of 0.1% benzoyl peroxide.

Experiments were carried out by bubbling chlorine gas through a solution of anhydrous chloroacetaldehyde in carbon tetrachloride under irradiation with ultraviolet radiation. The kinetic curves for the formation of chloroacetyl chloride at constant rates of chlorine feed and irradiation intensity are presented in Figs. 1 and 2. At high concentrations of chloroacetaldehyde (Fig. 1), after a short initial period the process develops at a constant rate independent of concentration. At low concentrations (Fig. 2), the rate of the process depends to a considerable extent on the concentration of chloroacetaldehyde. Increasing the reaction temperature leads to a decrease in the yield of chloroacetyl chloride owing to its photochemical decomposition (cf. curves 1, 2, and 3).

The quantum yield of the reaction, determined by us with the aid of a uranyl oxalate actinometer under conditions of a chlorine feed rate sufficient for complete absorption of the incident radiation, proved to be 20. On the basis of the known principles of photochemical chlorination and the experimental data, it may be considered most probable that the process under study proceeds by a radical-chain mechanism according to a scheme in which chain initiation occurs through formation of the chloroacetyl radical and propagation through its interaction with molecular chlorine.

$$\mathrm{Cl_2} + \mathrm{h}\ \rightarrow \mathrm{Cl}^{\times} + \mathrm{Cl}^{\cdot} \quad (\text{abs. } h\nu), \tag{1}$$

$$\mathrm{ClCH_2{-}C}\left(\frac{\mathrm{O}}{\mathrm{H}}\right) + \mathrm{Cl}^{\cdot} \rightarrow \mathrm{ClCH_2{-}C}^{\cdot}\left(\frac{\mathrm{O}}{}\right) + \mathrm{HCl} \quad (\text{slow}), \tag{2}$$

$$\mathrm{ClCH_2{-}C}^{\cdot}\left(\frac{\mathrm{O}}{}\right) + \mathrm{Cl_2} \rightarrow \mathrm{ClCH_2{-}C}\left(\frac{\mathrm{O}}{\mathrm{Cl}}\right) + \mathrm{Cl}^{\cdot} \quad (\text{fast}), \tag{3}$$

$$\mathrm{ClCH_2{-}C}^{\cdot}\left(\frac{\mathrm{O}}{}\right) + \mathrm{Cl}^{\cdot} \rightarrow \mathrm{ClCH_2{-}C}\left(\frac{\mathrm{O}}{\mathrm{Cl}}\right) \quad (\text{fast}). \tag{4}$$

When the reaction is carried out in carbon tetrachloride medium, participation of the solvent in chain propagation is possible; this was confirmed by us by isolating chloroform from the reaction mixture.

$$\mathrm{ClCH_2{-}C\cdot{=}O} + \mathrm{CCl_4} \rightarrow \mathrm{ClCH_2{-}C({=}\,O)Cl} + \mathrm{CCl_3\cdot}, \tag{5}$$

$$\mathrm{ClCH_2{-}C({=}\,O)H} + \mathrm{CCl_3\cdot} \rightarrow \mathrm{ClCH_2{-}C\cdot{=}O} + \mathrm{CHCl_3}, \quad \text{etc.} \tag{6}$$

The probability that the reaction proceeds by this mechanism is confirmed by the dependence of the reaction rate on the irradiation intensity, by the value of the quantum yield of the reaction, by the increase in the rate of the process in the presence of radical-forming additives, for example peroxides (see Fig. 1), by the high yield of chloroacetyl chloride, and by the formation of chloroform. The fact that chloroacetyl chloride is formed in the direct photochemical chlorination of chloroacetaldehyde with a yield close to quantitative indicates the possible existence of a chloroacetyl radical.

Fig. 2. Consumption of chloroacetaldehyde and formation of chloroacetyl chloride at 60° (1, 2), and the same at 30° (3), during photochemical chlorination of 6% chloroacetaldehyde in CCl_4 (*a*–CAA, *b*–CACC)

In the photochemical chlorination of chloroacetaldehyde in an aqueous medium, monochloroacetic acid is formed in 90-98% yield ([3]). As can be seen from Fig.

3, ultraviolet irradiation increases the rate manyfold in comparison with the dark reaction. The quantum yield is 16.

Fig. 3. Formation of monochloroacetic acid during chlorination of a 6% aqueous solution of chloroacetaldehyde at 30°: 1—in the dark, 2—under ultraviolet irradiation. *a*—HCl, *b*—CAA, *c*—MCAA

Despite the fact that propagation of a radical chain in a polar medium is less probable than in a nonpolar one, the same order of quantum yield and the closeness of the kinetic curves for the processes in different media (Fig. 4) make it probable that, in the presence of water, the process also develops by a radical-chain mechanism through the stage of formation of the chloroacetyl radical. The somewhat higher reaction rate and quantum yield in carbon tetrachloride medium (curve 1) are a consequence of participation of the solvent in chain transfer.

Of the three possible pathways of interaction of the chloroacetyl radical—with $Cl\cdot$ or Cl_2 to form chloroacetyl chloride, which is then hydrolyzed to monochloroacetic acid, or with H_2O to form monochloroacetic acid directly —the first two are energetically more favorable. Therefore, under kinetically equal conditions, apparently, they are preferentially realized.

Experimental Part

The starting material for the study was chloroacetaldehyde dimer hydrate, prepared according to (4). Dehydration of chloroacetaldehyde for the preparation of solutions in carbon tetrachloride was carried out by passing vapors of chloroacetaldehyde dimer hydrate (100 g, i.e., 90 g of 100%) through ignited calcium chloride (100 g) and absorbing the vapors of anhydrous chloroacetaldehyde (68 g) in carbon tetrachloride. The yield in the dehydration was 75% of theory. Aqueous solutions were prepared by dissolving the dimer hydrate.

Chlorination of chloroacetaldehyde solutions of various concentrations, both in aqueous medium and in carbon tetrachloride, was carried out in a quartz vessel under irradiation (or without it) with a PRK-2 mercury-quartz lamp, without catalysts or in the presence of peroxides (0.1% of the chloroacetaldehyde charged), at various temperatures and with chlorine passed through at a constant specified rate. In samples withdrawn at definite time intervals, the concentration of chloroacetaldehyde was determined by the method described earlier (5), and chloroacetyl chloride and monochloroacetic acid were determined alkalimetrically. The most characteristic results of the experiments are presented in Figs. 1—4.

Fig. 4. Formation of chloroacetyl chloride (1) and monochloroacetic acid (2) during chlorination of chloroacetaldehyde in CCl_4 (1) and H_2O (2) under otherwise identical conditions

Under optimum conditions, chloroacetyl chloride was obtained in a yield of 97% of theory by passing chlorine at a rate of 700 mg/min through a solution of 68 g

Fig. 4. Formation of chloroacetyl chloride (1) and monochloroacetic acid (2) during chlorination of chloroacetaldehyde in CCl_4 (1) and H_2O (2) under otherwise identical conditions

Figure 2: Fig. 4. Formation of chloroacetyl chloride (1) and monochloroacetic acid (2) during chlorination of chloroacetaldehyde in CCl_4 (1) and H_2O (2) under otherwise identical conditions

of chloroacetaldehyde in 242 g of carbon tetrachloride at 30° for two hours and irradiating with ultraviolet radiation. The quantum yield of the reaction was determined by the uranyl oxalate method (6), and it was 20. On distillation of the chlorination products, 2 g of chloroform were isolated, identified by color reactions (7), and 95 g of chloroacetyl chloride, identified as the amide—m.p. 118.5° (lit. 119°); as esters: methyl—b.p. 129° (lit. 130°), ethyl—b.p. 144° (lit. 144°); and as monochloroacetic acid—m.p. 62.5° (lit. 62—63°). Di- and trichloro derivatives were not detected.

Under optimum conditions, monochloroacetic acid was obtained in a yield of 98% of theory by chlorinating 200 g of a 35% aqueous solution of chloroacetaldehyde (70 g of 100%) while passing chlorine at a rate of 700 mg/min at 30° for two hours and irradiating with ultraviolet radiation. The quantum yield of the reaction was 16. From the reaction products, by rectification under vacuum, monochloroacetic acid was isolated in an amount of 82 g with m.p. 62° (lit. 62 —63°).

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Note: Figure translations are in progress. See original paper for figures.