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Reaction of Carbon Tetrachloride with Hydrogen Peroxide

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Abstract—Reaction of carbon tetrachloride with aqueous hydrogen peroxide in the presence of anhydrous iron(III) chloride was studied. Optimal conditions for the preparation of phosgene were found on the basis of analysis of the kinetic data and mechanism of the process. The reaction rate and yield (the latter reaching 95% in the stationary mode) are determined mainly by the amount of the heterogeneous catalyst. According to the experimental data, the reaction follows a radical mechanism.

Carbon tetrachloride is a large-scale product which is obtained mainly by treatment of waste products in the manufacture of organochlorine compounds. A large part of carbon tetrachloride was utilized in the manufacture of Freons 11 and 12 [1]. In keeping with the Montreal Convention, just these compounds are most hazardous for the ozone layer [2], so that their large-scale production was terminated. Another possible way for utilization of carbon tetrachloride is its conversion into phosgene. The latter is an important reagent for organic synthesis and is widely used in the preparation of medicines (as chloroformylating agent) [3], isocyanates, and polycarbonates [4–6].

In the worldwide industrial practice, carbon tetrachloride is processed at the same place where it is produced. However, the traditional procedure for the synthesis of phosgene from CO and Cl_2 [7] is hardly acceptable for factories utilizing relatively small amounts of carbon tetrachloride since the efficiency of such a plant is at least 10000 tons per annum.

According to published data [8, 9], hydrolysis of carbon tetrachloride in the presence of Friedel–Crafts catalysts, such as $SbCl_5$, $GaCl_3$, $FeCl_3$, and $FeCl_3 \cdot 4H_2O$, leads to formation of phosgene.

$$CCl_4 + H_2O \xrightarrow{FeCl_3} COCl_2 + 2HCl$$

On the other hand, this procedure cannot be applied on a large scale because of its low efficiency which is limited by the rate of water supply to prevent deactivation of the catalyst due to transformation into hexahydrate.

We have developed a procedure for the preparation of phosgene by oxidation of carbon tetrachloride with aqueous hydrogen peroxide in the presence of anhydrous iron(III) chloride. The reaction occurs at the boiling point of the mixture (72–73°C). Decomposition of carbon tetrachloride by the action of aqueous hydrogen peroxide may be described by the following general scheme:

$$2CCl_4 + 2H_2O_2 \xrightarrow{FeCl_3} 2COCl_2 + 4HCl + O_2$$

$$CCl_4 + H_2O \xrightarrow{FeCl_3} COCl_2 + 2HCl$$

In order to find optimal conditions of the process, we examined the relations between the yield of phosgene and the concentrations of hydrogen peroxide

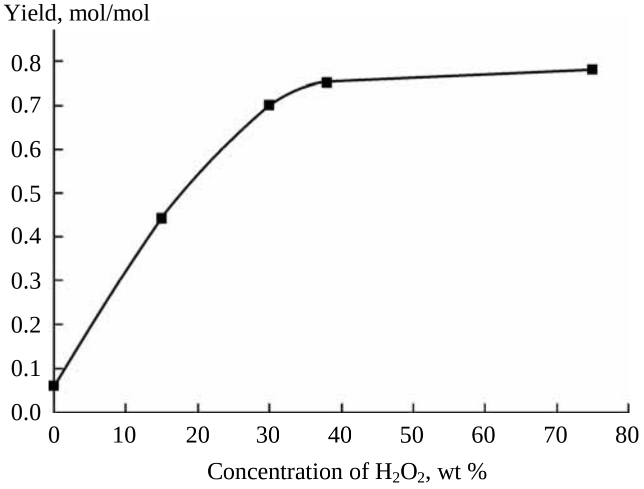

Fig. 1. Dependence of the yield of phosgene on the concentration of H_2O_2 (concentration of $FeCl_3$ 0.77 mol/l).

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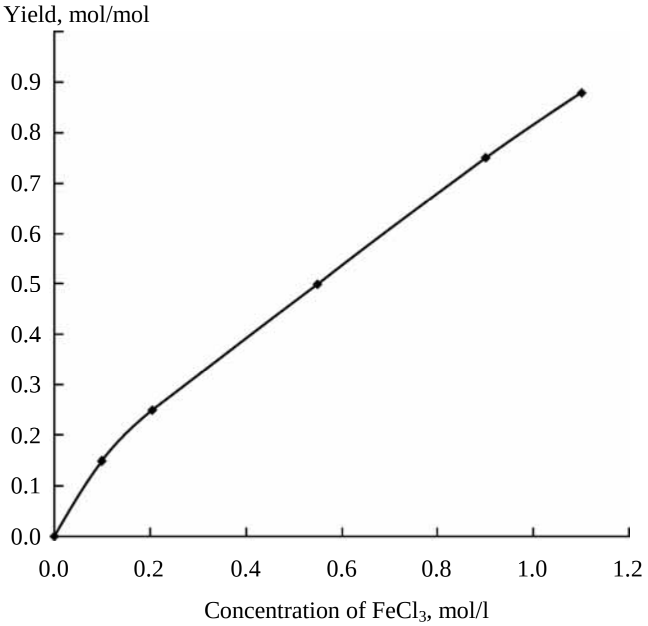

Fig. 2. Dependence of the yield of phosgene on the concentration of $FeCl_3$; molar ratio (H_2O + H_2O_2)–CCl_4 0.347.

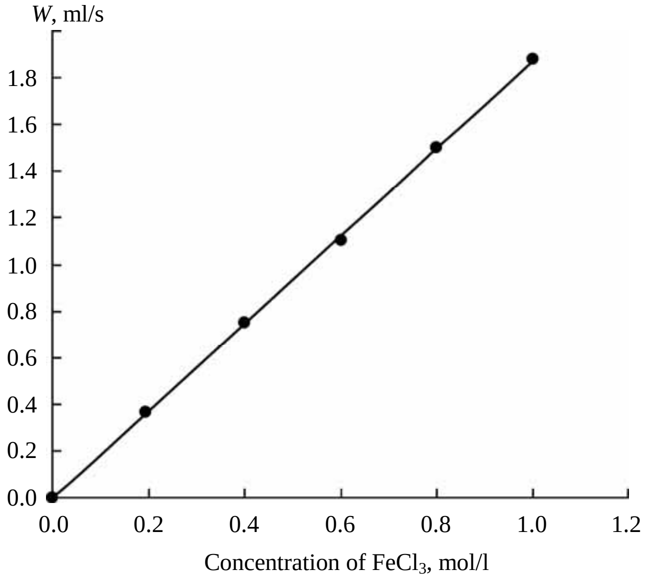

Fig. 3. Dependence of the rate of formation of phosgene (*W*) on the concentration of $FeCl_3$ (stationary mode).

(Fig. 1) and $FeCl_3$ (Fig. 2). The yield of $COCl_2$ linearly increases as the hydrogen peroxide concentration rises up to 35 wt % (Fig. 1). Further raising the H_2O_2 concentration (to 75 wt %) leads to only slight increase in the yield of phosgene. Simultaneously, the amount of chlorine formed by oxidation of hydrogen chloride increases. The intercept on the *y* axis corresponds to the yield of phosgene in the hydrolysis of CCl_4 in the absence of hydrogen peroxide. Figure 2 shows that the yield of $COCl_2$ increases up to quantitative with rise in the concentration of $FeCl_3$.

Taking into account that a solution of hydrogen peroxide in water with a concentration of 30 to 35 wt % is commercially available, in our further experiments on studying the reaction kinetics and mechanism we used a 35% solution of H_2O_2. The reaction was carried out at the boiling point of the mixture (i.e., at a constant temperature) with a large excess of CCl_4; the reactant concentrations were maintained constant. Insofar as hydrogen peroxide is poorly soluble in CCl_4, the reaction rate depends only on the amount of the catalyst ($FeCl_3$). The rate of formation of phosgene linearly increases as the amount of the catalyst rises.

The scheme of decomposition of CCl_4 can be represented as follows:

H_2O_2 + H_2O ⟶ Solution of H_2O_2 + H_2O in CCl_4
⟶ Diffusion of the reactants to the catalyst surface
⟶ Adsorption of the reactants on the catalyst surface
⟶ Synthesis of $COCl_2$ ⟶ Desorption of the products
⟶ Diffusion of the products

Taking into account that the viscosity of the mixture is low and that the mixture is vigorously stirred due to boiling, the reaction rate should be determined mainly by the chemisorption and desorption processes, i.e., it should depend only on the amount of $FeCl_3$. This means that the kinetics of the process in the stationary mode with respect to the yield of phosgene should fit pseudozero order in the reactants, for the reaction occurs only on the catalyst surface.

Unlike aqueous hydrolysis of carbon tetrachloride, which follows a ionic mechanism, the reaction with hydrogen peroxide is a radical process where H_2O_2 is the primary source of radical species:

$$H_2O_2 \rightleftharpoons 2\,HO^{\bullet} \qquad (1)$$

Hydroxyl radical reacts with carbon tetrachloride to form hypochlorous acid and trichloromethyl radical [reaction (2)]. Combination of the latter with hydroxyl radical gives unstable trichloromethanol which decomposes to $COCl_2$ and HCl [reaction (3)].

$$HO^{\bullet} + CCl_4 \longrightarrow \dot{C}Cl_3 + HOCl \qquad (2)$$

$$HO^{\bullet} + {}^{\bullet}CCl_3 \longrightarrow [Cl_3COH] \longrightarrow COCl_2 + HCl \qquad (3)$$

Hypochlorous acid is also unstable; it decomposes with liberation of atomic oxygen [reaction (4)] which reacts with trichloromethyl radical to give phosgene and atomic chlorine [reaction (5)].

$$\mathrm{HOCl} \longrightarrow \mathrm{HCl} + \mathrm{O}^{\bullet} \qquad (4)$$

$$\mathrm{O}^{\bullet} + {}^{\bullet}\mathrm{CCl_3} \longrightarrow \mathrm{COCl_2} + \mathrm{Cl}^{\bullet} \qquad (5)$$

The most probable further process is the reaction of atomic chlorine with water, leading to regeneration of hydroxyl radical [reaction (6)]; $\mathrm{HO}^{\bullet}$ species can also be formed by reaction of water with trichloromethyl radical according to reaction (7).

$$\mathrm{H_2O} + \mathrm{Cl}^{\bullet} \longrightarrow \mathrm{HO}^{\bullet} + \mathrm{HCl} \qquad (6)$$

$$\mathrm{H_2O} + {}^{\bullet}\mathrm{CCl_3} \longrightarrow \mathrm{CHCl_3} + {}^{\bullet}\mathrm{OH} \qquad (7)$$

Intermediate trichloromethanol can react with $\mathrm{FeCl_3}$ to give $\mathrm{COCl_2}$ and $\mathrm{FeCl_2}$ [reaction (8)]. Oxidation of iron(II) chloride thus formed with atomic chlorine [reaction (9)] or hypochlorous acid [reaction (10)] ensures regeneration of the catalyst.

$$\mathrm{FeCl_3} + \mathrm{Cl_3COH} \longrightarrow \mathrm{COCl_2} + \mathrm{FeCl_2} \qquad (8)$$

$$\mathrm{FeCl_2} + \mathrm{Cl}^{\bullet} \longrightarrow \mathrm{FeCl_3} \qquad (9)$$

$$\mathrm{FeCl_2} + \mathrm{HOCl} \longrightarrow \mathrm{FeCl_3} + \mathrm{HO}^{\bullet} \qquad (10)$$

Reactions (11)–(14) lead to chain termination as a result of radical combination.

$$\mathrm{O}^{\bullet} + {}^{\bullet}\mathrm{O} \longrightarrow \mathrm{O_2} \qquad (11)$$

$${}^{\bullet}\mathrm{CCl_3} + {}^{\bullet}\mathrm{CCl_3} \longrightarrow \mathrm{C_2Cl_6} \qquad (12)$$

$$\mathrm{Cl}^{\bullet} + \mathrm{Cl}^{\bullet} \longrightarrow \mathrm{Cl_2} \qquad (13)$$

$$\mathrm{Cl}^{\bullet} + {}^{\bullet}\mathrm{CCl_3} \longrightarrow \mathrm{CCl_4} \qquad (14)$$

The above combination processes require almost zero energy of activation, and their rates can be determined on the basis of the gas kinetic theory from the number of double collisions. Insofar as the mobility of oxygen atoms is much greater than that of heavier chlorine atoms, the number of collisions (reactivity) of atomic oxygen is much higher. Therefore, the formation of neutral oxygen molecules is more probable than the formation of chlorine molecules. In fact, the resulting phosgene contains only traces of chlorine. The low concentration of chlorine, as compared with the other recombination products, may also be due to its reaction with primary hydroxyl radicals, which leads to hypochlorous acid and atomic chlorine [reaction (15)].

$$\mathrm{HO}^{\bullet} + \mathrm{Cl_2} \longrightarrow \mathrm{HOCl} + \mathrm{Cl}^{\bullet} \qquad (15)$$

Hydrogen peroxide is capable of acting as both oxidant and reducing agent, and it can decompose along two pathways:

$$\mathrm{H_2O_2} \longrightarrow \mathrm{HO}\!\mid\!\mathrm{OH} \longrightarrow 2\,\mathrm{HO}^{\bullet} \qquad (1)$$

$$\mathrm{H_2O_2} \longrightarrow \mathrm{HO:OH} + \mathrm{Fe^{2+}} \longrightarrow \mathrm{Fe^{3+}} + \mathrm{HO}^{\bullet} + \mathrm{HO^{-}} \qquad (16)$$

Depending on the reaction conditions, one of the above pathways may prevail. In our case, reaction (1) predominates, for alternative process (16) requires the presence of an electron donor (reducing agent) in the system [10]. Iron(II) chloride formed by reaction (8) instantaneously undergoes oxidation to $\mathrm{FeCl_3}$ via reactions (10) and (13); therefore, the concentration of $\mathrm{FeCl_2}$ is so small that reaction (16) seems to be improbable. Thus the formation of $\mathrm{COCl_2}$ in the presence of $\mathrm{H_2O_2}$ is a radical process, and it cannot be regarded as a purely hydrolytic reaction.

In order to obtain additional proofs for the radical mechanism of the reaction under study, we examined the effect of UV irradiation. Irradiation of the system $\mathrm{CCl_4}$–$\mathrm{FeCl_3}$–$\mathrm{H_2O_2}$ with UV light at room temperature resulted in an appreciable increase of the reaction rate, which is typical of radical processes. Another support for the radical mechanism is a sharp decrease in the yield of phosgene on addition of molecular iodine or bromine. These compounds react with radical species to give long-lived $\mathrm{I}^{\bullet}$ and $\mathrm{Br}^{\bullet}$ radicals. The process is completely inhibited in the presence of atomic oxygen (ozone). The subsequent irradiation of the $\mathrm{CCl_4}$–$\mathrm{FeCl_3}$–$\mathrm{H_2O_2}$ system in the absence of other inhibitors leads to equilibrium between the formation of phosgene and its decomposition.

Partial reduction of $\mathrm{Fe^{3+}}$ to $\mathrm{Fe^{2+}}$ and oxidation of the latter maintains a constant concentration of radical species on the $\mathrm{FeCl_3}$ surface, which determines the pseudozero order of the reaction; i.e., the reaction rate is proportional to the surface area of the catalyst.

Atomic chlorine and hypochlorous acid molecules are also trapped by $\mathrm{Fe^{2+}}$. Therefore, the rate of phosgene formation is determined by two factors: the rate of formation of the $\mathrm{Fe^{3+}/Fe^{2+}}$ redox system (which quickly comes to equilibrium) and the solubility of hydrogen peroxide in carbon tetrachloride.

EXPERIMENTAL

Decomposition of carbon tetrachloride (I). A mixture of 1–5 g (0.01–0.05 mol) of anhydrous iron(II) chloride and 40 ml of carbon tetrachloride was heated to the boiling point (72–73°C) on a water bath, and 3–10 ml of a 35% aqueous solution of hydrogen peroxide was slowly added. The evolved phosgene and concomitant gases passed through a reflux condenser, an empty gas-washing bottle, and a gas-washing bottle charged with concentrated sulfuric acid into a trap cooled to –20°C, where liquid phosgene was collected. Gaseous hydrogen chloride was trapped in a gas-washing bottle filled with aqueous ammonia. The yield of phosgene was determined by iodometric titration [11]; it was purified by distillation according to a standard procedure. The yield of $COCl_2$ reached 95% (calculated on CCl_4), bp 7.56°C (760 mm) [4].

Decomposition of carbon tetrachloride under UV irradiation. The reaction was performed at room temperature in a quartz flask which was irradiated with a UV lamp (λ 254 nm, 250 W).

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