Photocatalytic Conversion of a FeCl₃–CCl₄–ROH System

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Abstract—The photocatalytic transformations of carbon tetrachloride and aliphatic primary alcohols in the presence of iron trichloride and a molar ratio of components $FeCl_3 : CCl_4 : ROH = 1 : 300 : 2550$ were studied. CCl_4 is transformed into chloroform and hexachloroethane after exposure to a mercury lamp (250 W) to the $FeCl_3$ — CCl_4 —ROH system at 20°C, whereas the primary ROH alcohols are selectively oxidized into acetals (1,1-dialkoxyalkanes). The maximum conversion of CCl_4 reaches 80%. The kinetics and mechanism of the photocatalytic conversion of the $FeCl_3$ — CCl_4 —ROH system are considered.

Keywords: carbon tetrachloride, primary aliphatic alcohols, iron trichloride, photocatalysis, 1,1-dialkoxyal-kanes, chloroform, hexachloroethane

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INTRODUCTION

Interest in photochemical and photocatalytic processes has increased in the past few decades. This is primarily due to the prospects of creating effective artificial systems to use solar energy [1]. An important advantage of the photoactivation of molecules, in contrast to their thermal activation, is that the chemical transformations occur under relatively mild conditions, significantly decreasing the contribution of undesirable side reactions. The photocatalytic approach is also applicable to the selective conversion of carbon tetrachloride in the presence of aliphatic alcohols to obtain compounds that are more in demand.

Thermal halogenation processes of alcohols with carbon tetrachloride under the action of complex manganese, vanadium, and molybdenum compounds as catalysts are not selective. As a rule, the products contain complex substances (aldehydes, ethers, esters, acetals, and various chloroalkanes) [2, 3].

Photocatalytic conversions of CCl_4 in the presence of aliphatic primary alcohols and iron trichloride (FeCl₃-CCl₄-ROH system) proceed selectively to form three main products: chloroform, hexachloroethane, and acetals (1,1-dialkoxyalkanes).

The products of photocatalytic conversion are more in demand than the original CCl_4 . Chloroform, for example, is used as a solvent and extractant; it is also used in the production of certain dyes, pesticides, refrigerants, etc. Detailed information on the use of chloroform can be found in [4]. Hexachloroethane is used to obtain HFC-113 and degassing tablets in aluminum production, it replaces in camphor nitrocellulose plastics, and it serves as a smoke generator and intensifier of luminescence. Hexachloroethane is used in medicine to control helminths of the liver [5]. Acetals (1,1-dialkoxyalkanes) are solvents and fragrances in the perfumery and food industries and they are used as additives to medicaments in medicine. The use of 1,1-diethoxyethane as an oxygenate additive to motor fuels is considered promising [6].

Iron trichloride is used as a photocatalyst due to two main reasons. Firstly, it easily oxidizes ethyl alcohol during irradiation by visible light [7]. Secondly, efficiency in the Fenton reaction significantly increases under UV irradiation ($\lambda_{max} = 240$ nm) in its presence due to the activation of the following stage: Fe(H₂O)³⁺ + *h*v \rightarrow Fe²⁺ + 'OH + H⁺ [8, 9]. In addition, FeCl₃ possesses photocatalytic activity in the aerobic oxidation processes of alkanes into alcohols and ketones [10].

EXPERIMENTAL

The chemically pure initial reagents carbon tetrachloride, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, and isoamyl alcohols, pyridine, and aniline produced by EKOS-1 were preliminarily distilled according to the methods in [11, 12].

Chemically pure crystalline hydrates $FeCl_3 \cdot 6H_2O$ (Brom, Russia) and $CoSO_4 \cdot 7H_2O$ (Splav, Russia) did not undergo additional purification.

The photocatalytic processes were carried out on a Photo Catalytic Reactor (Lelesil Innovative Systems, India) with a quartz reactor of 500 mL (Stromeyer type photoreactor with a magnetic stirrer) [13].

A GCMS-QP2010S Ultra gas chromatographymass spectrometer (SHIMADZU, Japan) equipped with a Restek Rtx-5MS column (Restek, United States) having a length of 30 m and internal diameter of 0.25 mm (the thickness of a liquid film was 0.25μ m) was used to identify the conversion products. The quantitative amount of 1,1-diethoxyethane was found on a hardware-software complex based on Kristall 5000.1 and 5000.2 chromatographs (Khromatek, Russia) equipped with 19091F-413 HP-FFAP (Agilent Technologies, United States, 30 m × 0.32 mm, 0.25 μ m) and Analytical Science (SGE, Australia, 30 m × 0.32 mm, 0.5 μ m) columns, respectively. Spectrophotometric and kinetic analysis was performed on a UV-1800 scanning spectrophotometer (SHIMADZU, Japan).

For a photocatalytic conversion, 1.40 mmol (378 mg) of crystalline hydrate $FeCl_3 \cdot 6H_2O$ and 3.40 moles of alcohol were placed into a flask-reactor. After the complete dissolution of the crystal hydrate, 0.40 moles (40 mL) of CCl₄ was added during stirring. The loaded reactor was connected to a photocatalytic unit as indicated in the manufacturer's instructions [13]. A mercurv lamp of medium pressure with a power of 250 W was used as the radiation source. The spectral composition of the radiation was as follows (in terms of energy): UV (48%), visible (43%), and IR (9%). The range of lengths was 222-1368 nm. A light flux reached the reaction system passing through an aqueous layer thermostated at 20°C. Photocatalytic conversion was performed within 240 min. The liquid phase was fractionated and analyzed after the reaction.

RESULTS AND DISCUSSION

Photocatalytic Conversion of the $FeCl_3$ - Ccl_4 - C_2H_5OH Model System

The reaction mixture $FeCl_3-CCl_4-C_2H_5OH$ obtained after the dissolution of all the initial compo-

nents appeared as a homogeneous brown solution. The dissolution of crystalline hydrate $FeCl_3 \cdot 6H_2O$ in ethyl alcohol leads to the displacement of the crystallization water by alcohol molecules from the coordination sphere of the iron ions to form iron trichloride solvate complexes. The solvate complex has the $FeCl_3 \cdot 2C_2H_5OH$ composition [14]. Water molecules form a $C_2H_5OH \cdot H_2O$ aqua complex in excess of ethyl alcohol [15]. The process proceeds according to the following general scheme (Scheme 1):

$$FeCl_{3} \cdot 6H_{2}O + 8C_{2}H_{5}OH$$

$$\xrightarrow{excess \ C_{2}H_{5}OH} FeCl_{3} \cdot 2C_{2}H_{5}OH + 6C_{2}H_{5}OH \cdot H_{2}O.$$

Scheme 1

Thus, the role is fulfilled by a $\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$ photocatalyst iron trichloride solvate complex.

The addition of CCl_4 does not damage the homogeneity of the $FeCl_3 \cdot 2C_2H_5OH$ solution in ethanol. The molar ratio of the starting components in the reaction mixture was $FeCl_3 : CCl_4 : C_2H_5OH = 1 : 300 :$ 2550. The irradiation of the reaction mixture for 240 min at 20°C gave a homogeneous yellow solution.

Analysis of the reaction products shows that CCl_4 (1) transforms into chloroform (3) and hexachloroethane (4) during irradiation, whereas ethyl alcohol (2) is selectively converted to 1,1-diethoxyethane (5) (Scheme 2):



The molar ratio of the reaction products 3:4:5=2:1:3. The conversion of CCl₄ reaches 56%.

Kinetics of Photocatalytic Conversion for a FeCl₃-CCl₄-ROH System

According to Scheme 2, HCl is released into the reaction medium after the conversion of CCl_4 . To detect it, the FeCl₃ : CCl_4 : C_2H_5OH system was irradiated in the

presence of 3.5 mmol (1.0 g) of crystalline hydrate cobalt sulfate $CoSO_4 \cdot 7H_2O$. In addition, the solution acquired an intense blue color, which indicated the exchange reaction between HCl and a pink $CoSO_4 \cdot 7H_2O$ compound that is insoluble in ethanol (Scheme 3):



Fig. 1. Kinetic curves of photocatalytic conversion of $FeCl_3-CCl_4-ROH$ system in presence of various alcohols.

Cobalt chloride complexes CoCl⁺, CoCl₂, CoCl₃,

and CoCl_4^{2-} are formed according to Scheme 3; they are readily soluble in ethanol and have an intense blue color with an absorption maximum at 670 nm [16].

The colored cobalt complexes made it possible to clearly study the kinetics of the process with the pho-

tometry method in the Kinetics mode at 670 nm. For this purpose, the samples were selected from the reactor during the experiment every 30 min to measure their optical density, which is correlated with the degree of conversion of CCl₄. Figure 1 shows the kinetic curves of the photocatalytic conversion of CCl₄ in the presence of various alcohols. These curves have an S shape and are located on a plateau after 270 min of the reaction. Further irradiation has no effect on the kinetics of the reaction and the yield of the products. Conversion depth weakly depends on the nature of the alcohol: it slightly decreases in series CH₃OH > $C_2H_5OH > C_3H_7OH > C_4H_9OH \approx i-C_4H_9OH >$ $C_5H_{11}OH \approx i-C_5H_{11}OH$. This is due to an increase in the length of the hydrocarbon fragment in aliphatic alcohols, which affect the polarity of the reaction medium.

*Effect of Reaction Conditions on Photocatalytic Conversion of the FeCl*₃–*CCl*₄–*ROH System*

Chloroform (3) and hexachloroethane (4) are products of the photocatalytic conversion of the FeCl₃-CCl₄-ROH system in methyl (6), propyl (7), butyl (8), isobutyl (9), amyl (10), and isoamyl (11) alcohols, whereas 1,1-dialkoskialcanes 12-17 conform to the initial alcohols (Scheme 4):

$$CCl_{4} + ROH \xrightarrow{FeCl_{3}, UV, 20^{\circ}C} CHCl_{3} + CCl_{3} - CCl_{3} + R' \xrightarrow{O} \xrightarrow{R'} O^{-1}$$

$$6-11 \xrightarrow{I2-17} R'$$

$$(R = CH_{3} - (6), C_{3}H_{7} - (7), C_{4}H_{9} - (8), i - C_{4}H_{9} - (9), C_{5}H_{11} - (10), i - C_{5}H_{11} - (11);$$

$$R' = H - (12), C_{2}H_{5} - (13), C_{3}H_{7} - (14), i - C_{3}H_{7} - (15), C_{4}H_{9} - (16), i - C_{4}H_{9} - (17))$$

Scheme 4

The molar ratio of the reaction products 3:4:12-17 is 2:1:3. The conversion of CCl₄ slightly decreases as the hydrocarbon moiety of alcohol increases from 64% for methanol to 49% for amyl alcohol. Chlorination products of the oxidized alcohols (aldehydes, acids, and ethers) formed together with the main products of photocatalytic conversion in systems with alcohols **8**, **9**, **10**, and **11**, whose total yield was 5-8%. When the length of hydrocarbon fragments increases, the probability of chlorination also increases.

The temperature effect on the photocatalytic conversion of the FeCl₃–CCl₄–ROH system was studied on the FeCl₃–CCl₄–C₂H₅OH model system in the presence of CoSO₄ · 7H₂O (Fig. 2). The shape of the kinetic curves remains significantly unchanged at $10-40^{\circ}$ C. However, the increase in temperature up to 70°C changes both the rate of the process and the nature of the dependence, which is due to the increased effect of thermal processes on the conversion of CCl₄. Analysis of the reaction mass under the conditions on thermal conversion of the FeCl₃– CCl₄–C₂H₅OH system (70°C, 240 min, and without irradiation) showed that the chlorination products of ethyl alcohol, acetaldehyde, ethyl acetate, acetic acid, and acetal, as well as compounds **3** and **4** and pentachloroethane (products of the CCl₄ transformation), are formed. Thus, the simple thermal conversion of the FeCl₃–CCl₄–C₂H₅OH system proceeds as an unselective process to form complex reaction products.

The effect of pyridine and distilled water on the photocatalytic conversion of CCl_4 and the yield of the



Fig. 2. Effect of temperature on photocatalytic conversion of $FeCl_3-Ccl_4-C_2H_5OH$ system.

products is given in Table 1. As can be seen, the addition of 0.12 mol (10 mL) of pyridine to the reaction medium increases the conversion of CCl_4 with the methanol system to 80% (Table 1, experiment 2). As a result, the yield of the reaction products also increases. The molar ratio of the products 3:4:5, 12, 14, 16 remains unchanged at 2:1:3. In systems with alcohols 8 and 10 (Table 1, experiments 9 and 11), the addition of pyridine decreases the yield of the chlori-

nation products of oxidized forms of alcohol (aldehydes, acids, and ethers). The fact that pyridine is used as an additive is due to its basic nature, because it binds the acids formed after the photocatalytic process (HCl, etc.) and thereby prevents the formation of a complex between the acids and iron ions. There are data which confirm the inhibitory effect of acids on the photocatalytic activity of iron ions in the Fenton photoreaction [17]. Other bases (for example, alkalis) disrupt the homogeneity of the system to form a precipitate of iron hydroxides, so that photocatalytic conversion does not occur in this case.

The addition of distilled water of up to 30% to the FeCl₃-CCl₄-C₂H₅OH system (experiments 5, 6, and 7) does not disrupt their homogeneity and slightly increases the conversion of CCl₄, which makes it possible to use the more easily available aqueous alcohol mixtures in the photocatalytic conversion process.

Mechanism of Photocatalytic Conversion of the $FeCl_3$ - Ccl_4 - C_2H_5OH System

As mentioned above, the solvate complex of iron trichloride $\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$ fulfills the role of a photocatalyst in the $\text{FeCl}_3-\text{CCl}_4-\text{C}_2\text{H}_5\text{OH}$ system. Absorbing a UV radiation quantum, it passes into the electronexcited state [FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}]^* and easily oxidizes ethyl alcohol into acetal **5** (Scheme 5, stage 2):

No. exp	Alcohol	Mole ratio of components $FeCl_3 : CCl_4 : ROH : C_6H_5N : H_2O$	Conversion of CCl ₄ , %	Composition of products, mol %			
				CHCl ₃	C_2Cl_6	acetal	chlorination products
1	CH ₃ OH	1:300:2550:0:0	64	34	18	48	_
2	CH ₃ OH	1:300:2550:85:0	80	32	17	51	—
3	C ₂ H ₅ OH	1:300:2550:0:0	56	31	20	49	—
4	C ₂ H ₅ OH	1:300:2550:85:0	66	30	17	53	—
5	C ₂ H ₅ OH	1:300:2550:0:500	57	29	19	52	—
6	C ₂ H ₅ OH	1:300:2550:0:2000	59	37	15	48	—
7	C ₂ H ₅ OH	1:300:2550:0:3500	60	33	16	51	—
8	C ₄ H ₉ OH	1:300:2550:0:0	52	24	16	55	5
9	C ₄ H ₉ OH	1:300:2550:85:0	59	32	16	52	—
10	C ₅ H ₁₁ OH	1:300:2550:0:0	49	30	14	48	8
11	C ₅ H ₁₁ OH	1:300:2550:85:0	56	33	16	51	_

Table 1. Effect of pyridine and water on photocatalytic conversion of FeCl₃–CCl₄–ROH system

Dashes mean that there are no chlorination products.



Scheme 5

It is well known that acetals are obtained by the interaction between alcohols and aldehydes [18].

Acetaldehyde is formed during the oxidation of ethyl alcohol with iron trichloride [7]. To detect free acetaldehyde as a stable intermediate of the photocatalytic reaction, aniline was added to the FeCl₃– $CCl_4-C_2H_5OH$ system. Analysis of the reaction products in this model system showed that the presence of chloroform (3), hexachloroethane (4), and 1,1-diethoxyethane (5); however, Schiff bases and condensation products obtained after the interaction between acetaldehyde and aniline were not observed. Thus, it can be assumed that free acetaldehyde is not formed in the system studied.

The photooxidation of ethanol was carried out with iron trichloride at a ratio of FeCl₃: C₂H₅OH = 1 : 2550 without CCl₄. The quantitative chromatographic analysis of the solution after the reaction showed that the amount of 1,1-diethoxyethane is 3.3×10^{-3} mol/L, whereas the concentration of iron trichloride decreases from 7.0×10^{-3} to 4.4×10^{-4} mol/L according to the photometric data. Consequently, two moles of iron trichloride is reduced to form a mole of acetal (Scheme 5, step 2).

The oxidation of the intermediate two-valence iron complex $FeCl_2 \cdot C_2H_5OH$ proceeds under the action of CCl_4 (Scheme 5, step 3). The whole complex is oxidized, i.e., the two-valence iron ion and ethanol molecule are in it. As a result, iron trichloride returns to the reaction medium, whereas oxidized ethanol reacts with the $FeCl_3 \cdot 2C_2H_5OH$ complex to form acetal **5**. Chloroform **3** and hexachloroethane **4** are reduction products of CCl_4 .

Iron trichloride FeCl_3 coordinates new ethanol molecules in the reaction medium, so that the catalytically active form of the $\text{FeCl}_3 \cdot 2\text{C}_2\text{H}_5\text{OH}$ (Scheme 5, step 4) solvate complex is reduced.

CONCLUSIONS

In summary, studying the photocatalytic conversion of the $\text{FeCl}_3-\text{CCl}_4-\text{ROH}$ system showed that CCl_4 is transformed into chloroform and hexachloroethane under the action of medium-pressure mercury lamp radiation at 20°C, whereas the primary ROH alcohols are selectively oxidized to 1,1-dialkoxyalkanes. The addition of pyridine and water affects the conversion of CCl₄, so that the maximum conversion of CCl₄ reaches 80%. The kinetics of the process were studied in the presence of colored cobalt complexes and a probable mechanism of the photocatalytic conversion of the FeCl₃-CCl₄-ROH system was proposed.

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