

# Mechanism of the Formation of Carbon Oxides under Conditions of the Oxidative Chlorination of Methane: IV. Kinetics of the Reaction of $\text{CCl}_4$ with Oxygen on Copper-Containing Salt Catalysts for Methane Oxychlorination at Reduced Partial Pressures of $\text{Cl}_2$ in the Reaction Mixture

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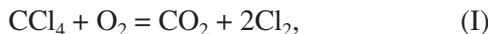
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**Abstract**—The kinetics of the oxidative dechlorination of  $\text{CCl}_4$  on two supported salt catalysts for methane oxychlorination ( $\text{CuCl}_2\text{--KCl}$  and  $\text{CuCl}_2\text{--KCl--LaCl}_3$ ) in the presence of methane at 350–450°C was studied using a gradientless method. It was found that, at  $P_{\text{Cl}_2} > 0.15$  kPa, the presence of methane in the reaction mixture had no effect on the kinetics of  $\text{CCl}_4$  oxidation but decreased the activation energy  $E$  to ~22 kcal/mol. At  $P_{\text{Cl}_2} < 0.15$  kPa, the kinetic orders with respect to oxygen and chlorine changed and  $E$  decreased to ~17 kcal/mol. The rate of formation of  $\text{CO}_2$  as a by-product of the reaction of methane oxychlorination was described by an exponential equation in combination with rate equations for the oxidation of other chloromethanes and methane. An equation consistent with the observed rate laws of this reaction in the presence of methane was derived from the previously proposed reaction scheme for the mechanism of the oxidative dechlorination of  $\text{CCl}_4$ .

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## INTRODUCTION

The reaction mixture formed under conditions of the direct interaction of  $\text{CCl}_4$  with oxygen in the presence of a catalyst

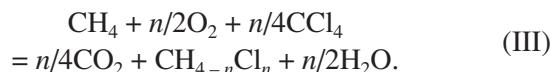


contained a much different amount of chlorine than that in the oxidative chlorination of methane



Reactions (I) and (II) performed under conditions of minimum chlorine partial pressure ( $P_{\text{Cl}_2}$ ) are of greatest interest. A natural way of producing these conditions is by performing reaction (I) in the presence of methane; this is equivalent to a combination of reactions (I) and (II). In this case, chlorine is formed by the oxidation of  $\text{CCl}_4$  and  $\text{HCl}$ , a product of the chain reaction of methane chlorination [1]. It was found experimentally that the degrees of conversion of chlorine and hydrogen chloride were higher than 95% under these conditions; that is, almost complete conversion occurred. Therefore, it is appropriate to represent

simultaneously occurring reactions (I) and (II) by the overall equation



A kinetic study of reaction (III) makes it possible to obtain information on the oxidation path of  $\text{CCl}_4$  in reaction (II). In addition, a study of reaction (III) is of interest because, in this reaction,  $\text{CCl}_4$  is a higher capacity source of chlorine than  $\text{HCl}$  in reaction (II).

## EXPERIMENTAL

The kinetics of reaction (III) in a fixed bed of supported catalysts with a particle size of 0.25–0.5 mm was studied using a gradientless flow circulation method. The  $\text{CuCl}_2\text{--KCl}$  and  $\text{CuCl}_2\text{--KCl--LaCl}_3$  salt systems with 1 : 1 and 1 : 1 : 0.33 molar ratios between the components, respectively, supported on KSK-2 silica gel ( $S_{\text{sp}} = 340 \text{ m}^2/\text{g}$ ). The use of a support with a large surface area increased the yield of carbon dioxide [3, 4] to facilitate the study of carbon dioxide formation. The copper contents of the copper–potassium catalysts

without and with an additive of  $\text{LaCl}_3$  were 4–7 and 1.5–2.8 wt %, respectively.

The procedures used for the purification of  $\text{CCl}_4$  and for the introduction of it into the reaction zone were described previously [2]. Methane and high-purity zero nitrogen containing 99.9% of the main substance were used in the experiments.

The procedure used for the analysis of the reaction mixture was also described previously [2]. It made it possible to monitor the reaction mixture composition, including possible chlorine derivatives of  $\text{C}_2$ , at the outlet of the circulation loop using gas chromatography. Chlorine and hydrogen chloride were determined by volumetric analysis; for this purpose, they were trapped in traps with an aqueous solution of potassium iodide. As found previously [2], the formation of phosgene can be ignored at high  $P_{\text{O}_2}/P_{\text{Cl}_2}$  ratios, which occurred under conditions of reaction (III). In the majority of the experiments, the partial pressure of carbon dioxide ( $P_{\text{CO}_2}$ ) in the reaction mixture was lower than 5 kPa, and it was no higher than 12 kPa in some experiments. This minimized the interfering effect of carbonic acid on the results of the titration of hydrogen chloride in a trap.

Knowing the composition of the reaction mixture and the flow rate of light gases at the outlet of traps, we can determine the volume velocities ( $V_i$ ) of initial substances and reaction products (other than water) at the outlet of the loop. The value of  $V_{\text{H}_2\text{O}}$  was calculated with consideration for the stoichiometry of reaction (II) and the participation of water in the formation of chlorine and chloromethanes (CMs):

$$\begin{aligned} V_{\text{H}_2\text{O}} = & 1/2 V_{\text{CH}_3\text{Cl}} + V_{\text{CH}_2\text{Cl}_2} \\ & + 3/2 V_{\text{CHCl}_3} + 2 V_{\text{CCl}_4} + V_{\text{CO}_2}^{\text{CM}}. \end{aligned} \quad (1)$$

Here,  $V_{\text{CH}_3\text{Cl}}$ ,  $V_{\text{CH}_2\text{Cl}_2}$ ,  $V_{\text{CHCl}_3}$ , and  $V_{\text{CCl}_4}$  are the volume velocities of corresponding chloromethanes in the loop. The formation of a small portion of  $\text{H}_2\text{O}$  as a result of the oxidation of methane and the first three chloromethanes was taken into account by the term  $V_{\text{CO}_2}^{\text{CM}}$  in Eq. (1) with the stoichiometric coefficient that corresponds to the oxidation of  $\text{CH}_3\text{Cl}$ , which is the most reactive among them [3, 4]. As found experimentally, this simplification did not introduce any error into the determination of  $V_{\text{H}_2\text{O}}$ . The value of  $V_{\text{CO}_2}^{\text{CM}}$  was determined by difference between the rate of carbon dioxide formation in reaction (III) and the rate of oxidation of the initial  $\text{CCl}_4$  ( $V_{\text{CO}_2}$  and  $V_{\text{CCl}_4}^{\text{ox}}$ , respectively):

$$\begin{aligned} V_{\text{CO}_2}^{\text{CM}} = & V_{\text{CO}_2} - V_{\text{CCl}_4}^{\text{ox}} = V_{\text{CO}_2} \\ - \frac{V_{\text{CH}_3\text{Cl}} + 2 V_{\text{CH}_2\text{Cl}_2} + 3 V_{\text{CHCl}_3} + 4 V_{\text{CCl}_4} + 2 V_{\text{Cl}_2} + V_{\text{HCl}}}{4}. \end{aligned} \quad (2)$$

(The quantity  $V_{\text{CCl}_4}^{\text{ox}}$  includes the rates of formation of all of the chlorine-containing products of reaction (III).) Initially,  $V_{\text{H}_2\text{O}}$  was calculated from Eq. (1) without considering  $V_{\text{CCl}_4}$ , the volumetric rate of  $\text{CCl}_4$  formation in the course of the chain chlorination reaction of methane and chloromethanes. Then, with the use of the previously estimated partial pressures of reactants,  $V_{\text{CCl}_4}$  was calculated from the equation

$$\begin{aligned} V_{\text{CCl}_4} = & \omega k_4 \sqrt{K_c} [\text{CHCl}_3][\text{Cl}_2]^{0.5} \\ & \times 3600 \times 22.4 v_{\text{Cat}} \text{ (l/h)}, \end{aligned} \quad (3)$$

where  $\omega$  is the free volume between catalyst grains;  $v_{\text{Cat}}$  is the total catalyst volume;  $[\text{CHCl}_3]$  and  $[\text{Cl}_2]$  are the concentrations of chloroform and chlorine, respectively;  $k_4$  is the rate constant of the rate-limiting step of the chain reaction of chloroform chlorination ( $\dot{\text{C}}\text{l} + \text{CHCl}_3 = \dot{\text{C}}\text{Cl}_3 + \text{HCl}$ ); and  $K_c$  is the equilibrium constant of chlorine dissociation. Equation (3) takes into account the chain reaction paths of the chlorination of methane and chloromethanes in the free volume between catalyst grains under conditions of reaction (II) [1]. The numerical values and dimensionalities of concentrations, rates, and rate constants were taken from a handbook [5]. An averaged value from handbooks [6, 7] was taken as the equilibrium constant  $K_c$ . For the catalysts based on KSK-2 silica gel with a grain size of 0.25–0.5 mm,  $\omega = 0.6$  [1]. The value of  $V_{\text{CCl}_4}$  found in accordance with Eq. (3) makes it possible to refine the values of  $V_{\text{H}_2\text{O}}$  and  $P_i$ . Usually, the subsequent calculation of the values of  $V_{\text{CCl}_4}$ ,  $V_{\text{H}_2\text{O}}$ , and  $P_i$  resulted in only insignificant corrections.

To calculate the material balances for the initial substances in reaction (III), the following equations were used:

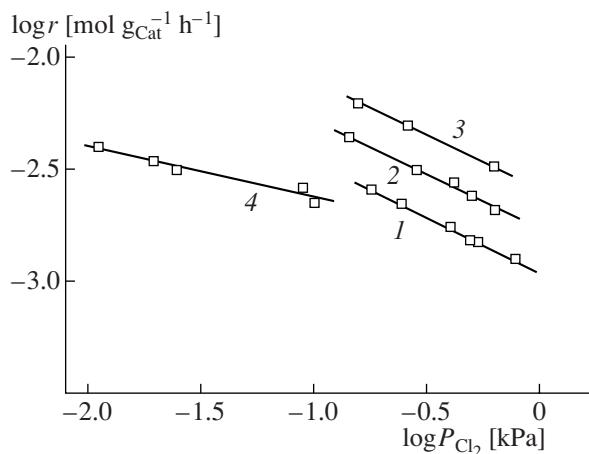
$$[\text{CCl}_4] = V_{\text{CCl}_4} + V_{\text{CCl}_4}^{\text{ox}}; \quad (4)$$

$$\begin{aligned} [\text{CH}_4] = & V_{\text{CH}_4} + V_{\text{CH}_3\text{Cl}} + V_{\text{CH}_2\text{Cl}_2} \\ & + V_{\text{CHCl}_3} + V_{\text{CCl}_4} + V_{\text{CO}_2}^{\text{CM}}; \end{aligned} \quad (5)$$

$$\begin{aligned} [\text{O}_2] = & V_{\text{O}_2} + V_{\text{CCl}_4}^{\text{ox}} + 1/4 V_{\text{CH}_3\text{Cl}} \\ & + 1/2 V_{\text{CH}_2\text{Cl}_2} + 3/4 V_{\text{CHCl}_3} + V_{\text{CCl}_4} + 3/2 V_{\text{CO}_2}^{\text{CM}}. \end{aligned} \quad (6)$$

Equation (6) suggested the equivalent participation of reactions (I) and (II) in the formation of chloromethanes. Difference between the calculated and experimental data was no higher than 6%.

To eliminate the distortion of the kinetic parameters of reaction (III) because of the volatility of copper chloride, the time of experiments for a single catalyst loading of volume 15–20  $\text{cm}^3$  was restricted to 30 or 12 h at



**Fig. 1.** Orders of reaction with respect to  $\text{Cl}_2$  in the presence of the  $\text{CuCl}_2\text{--KCl--LaCl}_3\text{/KSK-2}$  catalyst at (1) 375, (2, 4) 400, and (3) 425°C: (1)  $P_{\text{CCl}_4} = 15$  and  $P_{\text{O}_2} = 10$  kPa; (2)  $P_{\text{CCl}_4} = 9$  and  $P_{\text{O}_2} = 9.3$  kPa; (3)  $P_{\text{CCl}_4} = 8.5$  and  $P_{\text{O}_2} = 7$  kPa; and (4)  $P_{\text{CCl}_4} = 3.6$  and  $P_{\text{O}_2} = 5$  kPa.

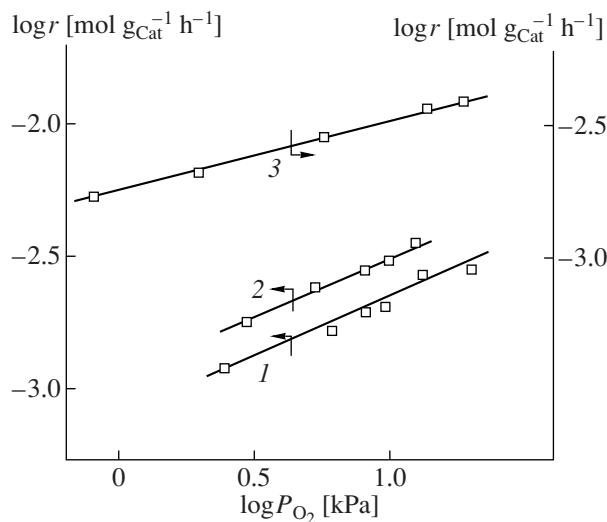
375 or 400°C, respectively. The catalyst operated for no longer than 4 or 2 h at 425 or 450°C, respectively.

The copper contents of the catalysts were monitored before and after the experiments. For this purpose, a ~0.5-g catalyst sample was dissolved in ~20 ml of a 20% NaOH solution on boiling. Then, 25 ml of nitric acid was added dropwise, and 20–25 ml of distilled water was added after evaporation. An ammonia solution was added dropwise to the cooled solution until the appearance of a blue color. Next, a 10% solution of sulfuric acid was added, and the concentration of copper was determined by iodometry after the dissolution of 6–8 g of crystalline potassium iodide. The error of analysis was  $\pm 4\%$ .

## RESULTS AND DISCUSSION

The kinetics of reaction (III) was studied in detail on the  $\text{CuCl}_2\text{--KCl--LaCl}_3$  catalyst (1 : 1 : 0.33) supported on KSK-2 with a copper content of 2.8 wt %. A part of experiments was performed on the  $\text{CuCl}_2\text{--KCl}$  catalyst (1 : 1) on KSK-2 with a copper content of ~7.0 wt %. The absence of diffusion limitations was due to the small size of catalyst grains (0.25–0.5 mm).

Reaction (III) was studied in the temperature range of 350–450°C. The rate of  $\text{CCl}_4$  conversion was converted to 1 g of the catalyst. The partial pressures of  $\text{CCl}_4$ ,  $\text{O}_2$ ,  $\text{CH}_4$ , and  $\text{Cl}_2$  were varied over the ranges of 1–20, 0.3–20, 3–52, and 0.005–1.3 kPa, respectively. The experiments performed with methane, nitrogen, and  $\text{CCl}_4$  mixtures at 400 and 425°C on the lanthanum-containing catalyst demonstrated the absence of chloromethanes and chlorine disproportionation products.



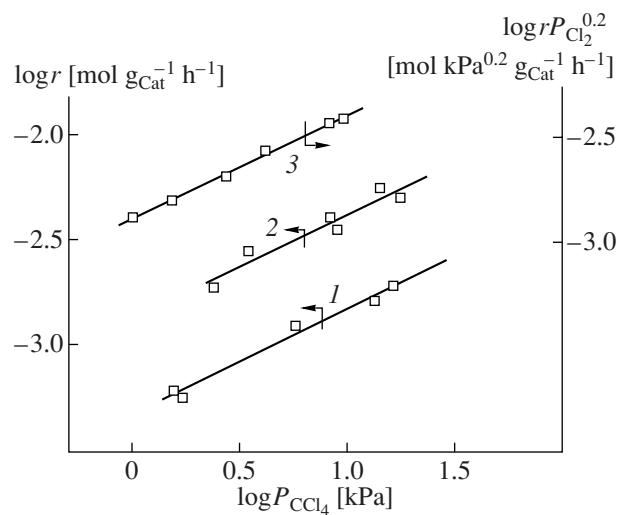
**Fig. 2.** Orders of reaction with respect to  $\text{O}_2$  in the presence of the  $\text{CuCl}_2\text{--KCl--LaCl}_3\text{/KSK-2}$  catalyst at (1) 375 and (2, 3) 400°C: (1)  $P_{\text{CCl}_4} = 12.5$  and  $P_{\text{Cl}_2} = 0.25$  kPa; (2)  $P_{\text{CCl}_4} = 9$  and  $P_{\text{Cl}_2} = 0.3$  kPa; and (3)  $P_{\text{CCl}_4} = 2$  and  $P_{\text{Cl}_2} = 0.02$  kPa.

Rozanov et al. [8] reported on the occurrence of such a reaction in a gas phase at temperatures higher than 450°C, although at low rates. Tetrachloroethylene, which is formed in the mixtures of methane and  $\text{CCl}_4$  at high temperatures in a gas phase [9] and in the presence of copper-containing catalysts [10], was not detected among the products of reaction (III).

In a number of the experiments on the determination of the kinetic orders of reaction with respect to  $\text{CCl}_4$  and oxygen ( $n_{\text{CCl}_4}$  and  $n_{\text{O}_2}$ ), the partial pressures of chlorine were maintained at an approximately constant level by appropriately changing the partial pressure of methane (an acceptor of chlorine). This technique was also used to extend the range of varying  $P_{\text{Cl}_2}$  in the evaluation of  $n_{\text{Cl}_2}$ .

It was found experimentally that the presence of methane in the reaction mixture and a dramatic decrease in  $P_{\text{Cl}_2}$  in the reaction mixture to ~0.15 kPa, as compared with that in reaction (I), had almost no effect on the reaction kinetics of  $\text{CCl}_4$  with oxygen, which was found previously [2]. Over wide concentration and temperature ranges at  $P_{\text{Cl}_2} > 0.15$  kPa, the following kinetic orders were found for reaction (III):  $n_{\text{Cl}_2} \approx -0.5$ ,  $n_{\text{O}_2} \approx 0.5$ , and  $n_{\text{CCl}_4} \approx 0.5$  (Figs. 1–3). They were independent of temperature and the partial pressures of reactants. The observed kinetics was described by the exponential equation

$$r = k_1 (P_{\text{CCl}_4} P_{\text{O}_2})^{0.5} P_{\text{Cl}_2}^{-0.5}, \quad (7)$$



**Fig. 3.** Orders of reaction with respect to  $\text{CCl}_4$  in the presence of the  $\text{CuCl}_2\text{--KCl--LaCl}_3\text{/KSK-2}$  catalyst at (1) 375, (2) 400, and (3) 425°C: (1)  $P_{\text{O}_2} = 10$  and  $P_{\text{Cl}_2} = 0.45$  kPa; (2)  $P_{\text{O}_2} = 10$  and  $P_{\text{Cl}_2} = 0.3$  kPa; and (3)  $P_{\text{O}_2} = 3$  kPa.

which is applicable to reactions on the copper–potassium catalyst both in the presence of  $\text{LaCl}_3$  (Table 1) and in its absence (Table 2). In both cases, the activation energy was  $E \approx 22$  kcal/mol. A comparison between the rate constants of reactions (I) and (II) on both of the catalysts (Tables 1, 2 and Tables 4, 5 from [2]) indicated that, in the presence of methane, the rate of  $\text{CCl}_4$  oxidation decreased by about 40%. However, at  $P_{\text{CH}_4} < 4$  kPa, the rate constants of reactions (I) and (III) approached each other (Table 1, experiment nos. 5 and 6).

At a partial pressure of chlorine lower than 0.15 kPa, the kinetic orders with respect to chlorine and oxygen decreased to -0.2 (Fig. 1) and 0.25 (Fig. 2), respectively, on both of the catalysts, whereas the order with respect  $\text{CCl}_4$  remained unchanged, that is, 0.5 (Fig. 3). Under these conditions, the kinetics of reaction (III) on both of the catalysts is described by the exponential equation

$$r = k_2 P_{\text{CCl}_4}^{0.5} P_{\text{O}_2}^{0.25} P_{\text{Cl}_2}^{-0.2} \quad (8)$$

at  $E \approx 17$  kcal/mol (Tables 1, 2). The numerical values of reaction rate constants on the copper–potassium catalyst without additives (~7.0 wt % copper) and with an additive of  $\text{LaCl}_3$  (2.8 wt % copper) were

$$k_2 = 102.5 e^{-\frac{17000}{RT}} \quad (9)$$

and  $k_2 = 189 e^{-\frac{17000}{RT}} \text{ mol g}_{\text{Cat}}^{-1} \text{ h}^{-1} \text{ kPa}^{-0.55}$ , respectively

At the same copper content of both of the catalysts, the ratio between the rate constants of  $\text{CCl}_4$  oxidation in

reaction (III), as well as in reaction (I) [2], was ~4.5. Thus, lanthanum chloride also retained its promoting effect at minimum partial pressures of chlorine.

Equation (8) in combination with rate equations for the oxidation of the other chloromethanes and methane [4] describes the kinetics of formation of carbon dioxide in the oxidative chlorination of methane in the most interesting region of reaction conditions. These conditions are characterized by not only the exhaustive use of intermediate chlorine (minimum  $P_{\text{Cl}_2}$ ) but also the possibility of catalyst stabilization due to the conversion of copper chloride into an oxide–oxychloride species [4]. By combining Eq. (8) with Eq. (1) from [4], we obtain the following expression for the rate of  $\text{CO}_2$  formation in reaction (II):

$$\begin{aligned} r = & (0.1\text{--}0.15)k P_{\text{CH}_4} P_{\text{O}_2}^{0.25} P_{\text{Cl}_2}^{-0.2} \\ & + k P_{\text{CH}_3\text{Cl}} P_{\text{O}_2}^{0.25} P_{\text{Cl}_2}^{-0.2} + 0.5k P_{\text{CH}_2\text{Cl}_2} P_{\text{O}_2}^{0.25} P_{\text{Cl}_2}^{-0.2} \\ & + 0.3k P_{\text{CHCl}_3} P_{\text{Cl}_2}^{-0.2} + k_2 P_{\text{CCl}_4}^{0.5} P_{\text{O}_2}^{0.25} P_{\text{Cl}_2}^{-0.2}. \end{aligned} \quad (10)$$

The 1 : 0.5 : 0.3 : (0.1–0.15) ratio between the rate constants of oxidation of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and methane [3, 4] was used in Eq. (10). Qualitatively, differences in the oxidation rates of chloromethanes and methane can be explained by the fact that these reactions are limited by the steps of C–Cl and C–H bond cleavage [11]. Taking into account a much lower C–Cl bond energy in adsorbed compounds [12], the higher activity of methyl chloride can be related to the polarity of its molecule.

Because kinetic parameters of the side paths of reaction (II) are similar, Eq. (10) can be written in the more compact form

$$r = (k P_{\Sigma} + k_2 P_{\text{CCl}_4}^{0.5}) P_{\text{O}_2}^{0.25} P_{\text{Cl}_2}^{-0.2}, \quad (11)$$

where  $k$  is the rate constant of oxidation of methyl chloride, and  $P_{\Sigma} = (0.1\text{--}0.15)P_{\text{CH}_4} + P_{\text{CH}_3\text{Cl}} + 0.5P_{\text{CH}_2\text{Cl}_2} + 0.3P_{\text{CHCl}_3}$ .

According to previous estimations [4], the rate constants of oxidation of methyl chloride on analogous  $\text{CuCl}_2\text{--KCl--LaCl}_3\text{/KSK-2}$  (2.2 wt % copper) and  $\text{CuCl}_2\text{--KCl/KSK-2}$  (7.5 wt % copper) catalysts are

$$k = 2.79 e^{-\frac{16000}{RT}} \quad (12)$$

and  $k = 11.22 e^{-\frac{16000}{RT}} \text{ mol g}_{\text{Cat}}^{-1} \text{ h}^{-1} \text{ kPa}^{-1.05}$ , respectively

A comparison between these values demonstrated [3, 4] that the rate constant of oxidation of methyl chloride depends on only the copper content of the catalyst, whereas lanthanum chloride has almost no effect on the rates of oxidation of the chloromethanes  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ , and  $\text{CHCl}_3$ . The rate of carbon dioxide forma-

**Table 1.** Rates and rate constants of the oxidative dechlorination of  $\text{CCl}_4$  in the presence of methane at various  $P_{\text{Cl}_2}$  on the  $\text{CuCl}_2\text{--KCl--LaCl}_3$  catalyst (1 : 1 : 0.33) supported on KSK-2 with a copper content of 2.8 wt %

Experiment no.	$T, ^\circ\text{C}$	$P_i, \text{kPa}$									$r \times 10^6, \text{mol g}^{-1}\text{h}^{-1}$	$k_1 \times 10^6, \text{mol g}^{-1}\text{h}^{-1}\text{kPa}^{-0.5}$	$k_2 \times 10^6, \text{mol g}^{-1}\text{h}^{-1}\text{kPa}^{-0.5}$	
		$\text{O}_2$	$\text{CH}_4$	$\text{CCl}_4$	$\text{Cl}_2$	$\text{CO}_2$	$\text{CH}_3\text{Cl}$	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{HCl}$				
1	350	18.1	35.8	12.7	0.36	2.4	4.2	1.3	0.22	0.9	3.9	1308	51.7	—
2	375	9.7	36.3	16.1	0.40	3.0	3.8	1.7	0.40	1.2	4.6	1935	98.0	—
3	375	19.8	28.3	10.3	0.31	4.3	5.7	2.8	0.93	1.0	7.6	2500	97.5	—
4	375	12.5	6.4	14.8	1.15	2.1	1.0	0.65	0.33	2.0	1.85	1400	110	—
5	375	11.7	2.6	14.4	1.86	1.95	0.46	0.39	0.24	2.75	0.81	1467	154	—
6	375	14.5	1.62	14.4	2.30	1.86	0.34	0.29	0.19	1.9	0.70	1660	174	—
7	400	5.2	33.5	12.5	0.31	5.2	4.6	3.0	1.1	1.4	8.5	2900	200	—
8	400	11.9	6.0	8.95	0.65	6.0	2.1	2.35	2.2	1.6	9.5	2470	193	—
9	425	3.7	5.8	8.8	0.26	11.9	2.4	3.4	4.1	4.2	19.3	3580	320	—
10	350	2.3	30.8	12.2	0.08	2.5	4.3	1.6	0.36	0.8	4.4	1395	—	197
11	350	5.5	67.1	4.8	0.04	1.95	5.0	0.65	0.04	0.50	3.4	1290	—	201
12	375	3.6	49.2	9.1	0.11	2.7	4.5	1.6	0.31	1.1	4.6	2192	—	340
13	400	7.9	25.3	8.2	0.12	8.0	6.55	5.3	2.5	1.6	14.1	4020	—	550
14	400	3.8	27.9	3.8	0.025	7.3	6.6	4.8	1.85	1.0	12.7	3246	—	576
15	425	3.4	17.8	9.1	0.065	9.0	7.5	6.1	3.6	1.0	17.1	6305	—	895
16	450	2.15	20.0	7.2	0.018	11.7	7.8	7.2	4.1	1.65	21.3	9955	—	1374

Note: The constants  $k_1$  and  $k_2$  were determined using Eqs. (7) and (8), respectively.

tion in reaction (II) at  $P_{\text{Cl}_2} < 0.15 \text{ kPa}$  can be described by Eq. (11) using the rate constants of oxidation of methyl chloride (12) and  $\text{CCl}_4$  (9) with consideration for the copper contents of the catalysts (Tables 3, 4). Evidently, the oxidation of  $\text{CCl}_4$ , especially, on the lanthanum-containing catalyst, considerably contributes to the overall rate of a side reaction. The higher rate of oxidation of  $\text{CCl}_4$ , as compared with those of other chloromethanes, and the dependence of this rate on the presence of lanthanum chloride as a catalyst constituent suggest another mechanism of this reaction. The similarity of the rate laws of reactions (I) and (III) over a wide range of  $P_{\text{Cl}_2}$  (from 0.15 to 9 kPa), in spite of differences between their rates, allows one to use the previously formulated mechanism [2] of  $\text{CCl}_4$  oxidation in this case. The hypothesized nature of sites Z as coordinatively unsaturated complexes of bivalent copper makes it possible to explain not only the acceleration of

reaction upon the introduction of lanthanum chloride as a catalyst constituent [2] but also the lower rate of reaction (III), as compared with that of reaction (I). In my opinion, this is due to a decrease in the steady-state concentration of the coordinatively unsaturated ions of bivalent copper because of the reaction of methane with copper chloride, which can occur under the specified conditions [13, 14]. However, at low  $P_{\text{CH}_4}$ , an increase in the steady-state concentration of sites Z would be expected; this is supported by an increase in the rate constant of reaction (III) at  $P_{\text{CH}_4} < 4 \text{ kPa}$  (Table 1, experiment nos. 5 and 6).

As applied to reaction (III), the reaction scheme becomes single-path because the high values of  $P_{\text{O}_2}/P_{\text{Cl}_2}$  under conditions of this reaction exclude the formation of phosgene [2]. The combination of steps 4

**Table 2.** Rates and rate constants of the oxidative dechlorination of  $\text{CCl}_4$  in the presence of methane at various  $P_{\text{Cl}_2}$  on the  $\text{CuCl}_2\text{--KCl}$  catalyst (1 : 1) supported on KSK-2 with a copper content of ~7 wt %

Experiment no.	$T, ^\circ\text{C}$	$P_i, \text{kPa}$									$r \times 10^6, \text{mol g}^{-1} \text{h}^{-1}$	$k_1 \times 10^6, \text{mol g}^{-1} \text{h}^{-1} \text{kPa}^{-0.5}$	$k_2 \times 10^6, \text{mol g}^{-1} \text{h}^{-1} \text{kPa}^{-0.55}$
		$\text{O}_2$	$\text{CH}_4$	$\text{CCl}_4$	$\text{Cl}_2$	$\text{CO}_2$	$\text{CH}_3\text{Cl}$	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{HCl}$			
1	350	14.0	36.8	19.4	0.38	1.2	1.91	0.36	0.04	0.67	1.5	750	27.9
2	375	11.3	36.3	17.2	0.34	2.5	2.32	0.98	0.20	0.60	3.5	1132	47
3	400	8.4	32.5	11.9	0.23	3.2	2.95	1.45	0.33	1.05	4.6	2144	103
4	425	3.3	36.5	14.5	0.16	5.6	4.35	2.75	0.87	1.85	8.4	3695	212
5	375	1.3	48.9	18.2	0.074	1.8	2.75	0.58	0.18	0.84	2.65	1405	—
6	400	5.9	22.7	10.9	0.055	8.2	5.4	4.0	1.9	0.8	13.0	2883	—
7	400	0.2	40.0	13.0	0.019	4.4	5.0	2.4	0.6	0.9	7.2	1670	—
8	425	1.0	24.0	10.7	0.025	9.3	5.3	4.4	2.3	1.7	14.7	3165	—
9	425	2.9	11.3	12.9	0.056	11.0	3.7	4.1	3.7	2.3	17.8	3790	—
10	450	0.67	23.0	8.3	0.017	12.4	5.9	5.5	3.1	3.0	19.6	4420	—

Note: The constants  $k_1$  and  $k_2$  were determined using Eqs. (7) and (8), respectively.

**Table 3.** Comparison between the experimental and calculated rates of  $\text{CO}_2$  formation and the evaluation of the contribution of  $\text{CCl}_4$  oxidation to the reaction of methane oxychlorination on the  $\text{CuCl}_2\text{--KCl--LaCl}_3$  catalyst (1 : 1 : 0.33) supported on KSK-2

No.	$T, ^\circ\text{C}$	[Cu], wt %	$P_i, \text{kPa}$							$r_{\text{CO}_2} \times 10^6, \text{mol g}^{-1} \text{h}^{-1}$ (expt.)	$r \times 10^6, \text{mol g}^{-1} \text{h}^{-1}$ (calculated)			
			$\text{CH}_4$	$\text{O}_2$	$\text{HCl}$	$\text{Cl}_2$	$\text{CH}_3\text{Cl}$	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$		$\text{CCl}_4$	$\text{CH}_4$ and $\text{CH}_x\text{Cl}_{4-x}$	$\Sigma$	
1	400	1.6	32.9	13.8	1.3	0.10	8.7	6.1	2.9	0.35	1150	630	590	1120
2	400	1.7	15.1	18.7	0.68	0.07	4.1	3.2	1.5	0.13	829	442	375	817
3	425	2.2	47.6	5.7	0.92	0.006	6.7	2.94	0.38	0.03	2080	526	1531	2057
4	425	2.2	50.3	17.7	1.5	0.007	6.5	2.9	0.35	0.02	2502	554	1972	2526
5	425	2.0	34.5	15.9	0.57	0.054	9.0	5.7	2.4	0.16	2300	906	1431	2337
6	425	2.0	29.3	12.7	1.03	0.106	7.7	6.8	3.6	0.45	2453	1275	1116	2391
7	450	1.60	29.0	4.9	1.6	0.033	9.2	7.4	3.9	0.59	3030	1750	1470	3220
8	450	1.60	20.2	2.75	2.9	0.07	7.85	8.0	5.7	1.3	2840	1950	1010	2960
9	450	1.55	41.1	5.1	0.92	0.01	11.1	6.05	1.61	0.20	3162	1280	2020	3300

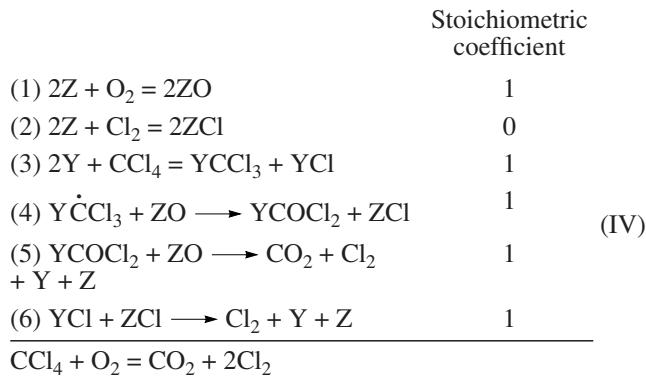
Note: The formation of CO via a side reaction can be ignored.

**Table 4.** Comparison between the experimental and calculated rates of  $\text{CO}_2$  formation and the evaluation of the contribution of  $\text{CCl}_4$  oxidation to the reaction of methane oxychlorination on the  $\text{CuCl}_2\text{-KCl}$  catalyst (1 : 1) supported on KSK-2

No.	$T, ^\circ\text{C}$	[Cu], wt %	$P_i, \text{kPa}$							$r_{\text{CO}_2} \times 10^6,$ mol $\text{g}^{-1} \text{h}^{-1}$ (expt)	$r \times 10^6, \text{mol g}^{-1} \text{h}^{-1}$ (calculated)			
			$\text{CH}_4$	$\text{O}_2$	$\text{HCl}$	$\text{Cl}_2$	$\text{CH}_3\text{Cl}$	$\text{CH}_2\text{Cl}_2$	$\text{CHCl}_3$	$\text{CCl}_4$	$\text{CCl}_4$	$\text{CH}_4$ and $\text{CH}_x\text{Cl}_{4-x}$	$\Sigma$	
1	375	4.5	38.3	11.9	2.1	0.14	8.4	5.5	2.13	0.25	1287	167	1133	1300
2	400	4.5	25.0	1.4	5.8	0.077	7.3	7.6	4.75	1.14	1550	385	1180	1565
3	400	4.0	43.3	9.1	1.5	0.023	8.2	5.0	1.5	0.19	2290	237	2168	2405
4	400	4.5	39.4	4.4	2.3	0.044	8.3	6.1	2.4	0.39	2050	330	1820	2150
5	400	4.5	32.0	5.8	2.7	0.06	7.6	6.6	3.4	0.67	2075	440	1760	2200
6	400	4.0	45.3	3.4	1.8	0.12	7.0	3.4	0.85	0.10	1155	115	1065	1180
7	425	4.5	20.0	0.95	3.8	0.06	7.4	7.5	5.0	1.9	2340	755	1690	2445
8	425	3.3	49.9	1.73	3.35	0.067	9.3	5.0	1.7	0.26	1817	233	1647	1880
9	450	3.3	30.6	1.35	7.7	0.061	8.45	6.9	3.71	0.59	2585	508	2174	2682
10	450	4.1	39.4	1.0	3.4	0.007	7.53	5.5	1.82	0.41	4520	755	3565	4320

Note: The formation of CO via a side reaction can be ignored.

and 5 in scheme (IV) [2] results in the following tentative mechanistic scheme of this reaction:



Here, Z is a coordinatively unsaturated divalent copper ion and Y is a univalent copper ion. Note that equilibrium steps 1–3 also participate in the  $\text{Cl}^-/\text{O}_2^{2-}$  exchange [15] and in the formation of a steady-state catalyst composition.

On the assumption that step 4 is a rate-limiting step of the reaction, the following rate equation can be obtained:

$$r = \frac{k_4(K_1 K_3)^{0.5} P_{\text{CCl}_4}^{0.5} P_{\text{O}_2}^{0.5}}{(1 + K_3^{0.5} P_{\text{CCl}_4}^{0.5})(1 + K_1^{0.5} P_{\text{O}_2}^{0.5} + K_2^{0.5} P_{\text{Cl}_2}^{0.5})}. \quad (13)$$

According to published data [16], the chlorine adsorption constant  $K_2$  on copper-containing salt catalysts for

methane oxychlorination is much greater than the oxygen adsorption constant  $K_1$ . At  $K_2 \gg K_1 > K_3$ , Eq. (13) adequately describes the kinetics of  $\text{CCl}_4$  oxidation in reactions (I) and (III). The constancy of  $n_{\text{CCl}_4}$  is explained by the fact that  $(K_3 P_{\text{CCl}_4})^{0.5} \ll 1$  in the denominator of Eq. (13). Under conditions of reactions (I) and (II) at  $P_{\text{Cl}_2} > 0.15 \text{ kPa}$ , the term  $(K_2 P_{\text{Cl}_2})^{0.5} \gg 1$  and Eq. (13) is transformed to exponential equation (7). The absolute values of the kinetic orders with respect to oxygen and chlorine can decrease at minimum values of  $P_{\text{Cl}_2}$  ( $< 0.15 \text{ kPa}$ ) in the reaction mixture and the commensurability of the terms  $(K_1 P_{\text{O}_2})^{0.5}$  and  $(K_2 P_{\text{Cl}_2})^{0.5}$ ; this is reflected in exponential equation (8). The arrangement of adsorption constants in the order  $K_2 \gg K_1 > K_3$  and the adequacy of the proposed reaction mechanism are also supported by a decrease in the apparent activation energy from  $\sim 26 \text{ kcal/mol}$  for reaction (I) to  $\sim 17 \text{ kcal/mol}$  for reaction (III). Thus, Eq. (13) adequately describes the oxidation of  $\text{CCl}_4$  in the absence and presence of methane in spite of changes in the chemical and phase compositions of catalysts at low  $P_{\text{Cl}_2}$  [4]. It is likely that the reaction also occurs in accordance with the proposed mechanism at trace concentrations of chlorine in the reaction mixture. Under these conditions, the retention of the coordinatively unsaturated ions of bivalent copper (Z-type sites) on the catalyst surface with the partial replacement of chloride anion ligands by oxygen ions would be expected under

these conditions. It is well known [17, 18] that even transition metal oxides are characterized by a wide range of nonstoichiometry.

The results of this work and previous studies [3, 4] can be used to describe the formation of carbon oxides as by-products in the reaction of methane oxychlorination on any copper-containing salt catalysts. With the kinetics of a chain reaction of methane chlorination [1], they can form the basis for the physicochemical simulation of reaction (II).

This study suggests that reaction (III) can be considered as an analogue of the oxidative chlorination of methane but with the use of a potentially higher capacity chlorine source than hydrogen chloride. In the future, this reaction can supplement currently available processes for  $\text{CCl}_4$  utilization by hydrodechlorination [19, 20], interaction with methanol [21], exchange interaction with hydrocarbons [22], etc. [23]. For well-known reasons [22, 23],  $\text{CCl}_4$  is a large-scale waste of the chlorine industry. It is likely that its utilization will remain an urgent problem in the near future because the processing of halogenated organic wastes by chlorolysis remains irreplaceable [23, 24].

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