SOME MECHANISMS OF CATALYTIC DIRECT AND OXIDATIVE CHLORINATION OF PROPYLENE

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The correlation between the reactions of direct and oxidative chlorination of propylene, which is apparently due to the general nature of catalysis by metal chlorides on carriers [1, 2], was previously demonstrated.

In this respect, a more detailed comparative study of direct and oxidative chlorination of propylene in the presence of the most characteristic catalysts of chlorination: chlorides of metals of variable and constant valence, and carriers consisting of the oxides of various elements, was conducted.

Due to the absence of systematic data on the catalytic activity of metal chlorides [3], we studied the dependence of their activity on the M-Cl binding energy in oxidative chlorination of propylene (Fig. 1). The activity of metal chlorides of variable valence in oxidative chlorination of propylene varies in the following order: $CuCl_2 > FeCl_3 > CoCl_3 > CrCl_3$.

The maximum value of the rate of transformation of propylene is observed for $CuCl_2$, the most active radical oxidant [4]. It is necessary to emphasize that the Cu-Cl bond is weakest $(\Delta H^0_{f,298} = -205,900, \Delta H^0_{f,763} = -163,512 \text{ J/mole})$ [5].

The chlorides of metals with a constant valence, LiCl for example, are significantly inferior to the chlorides of metals with a variable valence with respect to the activity. Carriers of an oxide character almost do not catalyze the complex process (conversion of HCl does not exceed 4-5% in the experimental conditions). The reaction of direct chlorination of propylene is relatively efficiently catalyzed by metal chlorides, regardless of their capacity to change valence, and by the carriers themselves (Table 1). Substitution of Cu²⁺ by cations of other metals has little effect on the activity of the catalyst [6, 7], while the selectivity of catalysts in the formation of allyl chloride varies in the following order: CuCl₂ > FeCl₃ > LiCl.

In the case of metal chlorides of variable valence, an order of activity similar to the complex process and the correlation between the rate of transformation of propylene into chlorinated products and the M-Cl binding energy are preserved for direct chlorination of propylene. We also found significant differences in the efficiency of the effect of addition of inhibitors on the process of direct chlorination of propylene as a function of the type of catalyst (Table 2).

It should be noted that the character of the effect of addition of inhibitors in reactions of direct chlorination of propylene catalyzed by metal chlorides of constant valence or oxide carriers on one hand, and metal chlorides of variable valence on the other hand, and metal chloride of variable valence on the other hand, can indicate a radical-chain mechanism of chlorination [8]. The length of the radical chlorination chain apparently varies as a function of the type of catalyst [9]. An analogous character of the effect of the same inhibitors has been found for oxidative chlorination of propylene in the presence of LiCl or $CuCl_2$.

The formation of $C_{3}H_{5}$ radicals in these reactions can take place in two ways [10]

$$Cl_2 \to 2Cl^* \tag{1}$$

(2)

$$C_3H_6 + CI \rightarrow C_3H_5 + HCI$$

 $C_{3}H_{6} + CuCl_{2} \rightarrow C_{3}H_{5} + HCl + CuCl$ (3)

The results of the thermodynamic analysis of different methods of generation C_3H_5 radicals (Table 3) indicates that reaction (3) is more probable than (2). The observed differences in

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Fig. 1. Dependence of the logarithm of the rate of transformation of propylene in the $HCl-O_2$ system on the heat of formation of the M-Cl bond: 1) 460, 2) 490°C. r: rate of transformation of C_3H_6 , mole/ liter kt·h; ΔH : heat of formation of the M-Cl bond.

TABLE 1. Effect of Catalysts on Indexes of Direct Chlorination of Propylene*

Catalyst (specific area of carrier 1 m ² /g)	Selectivity for allyl chloride	Rate of transforma- tion of C ₃ H ₆ , mole/liter kt•h
With no catalyst ($C_{9}H_{6}$:Cl ₂ molar	70.6	8.7
Carborundum	78.5	23.4
$\text{LiCl} - \alpha - \text{Al}_2 O_3$	80.2	24.0
$\operatorname{FeCl}_3 - \alpha - \operatorname{Al}_2 \operatorname{O}_3$	86.3	29.0
*Experimental conditions:	C ₃ H ₆ :Cl	molar ratio =

3:1; 490°C, 0.2 sec contact time.

the reactions of direct and oxidative chlorination of propylene in the presence of metal chlorides of constant and variable valence are in agreement with the results of the kinetic study of these reactions (Table 4).

In the case of LiCl, the same type of kinetic equations, which are identical in nature to thermal reactions of radical-chain chlorination of hydrocarbons in the vapor phase [11], is observed for direct and oxidative chlorination of propylene. For $CuCl_2$, the results appear more complex. In principle, both a radical and a nonradical mechanism of chlorination is possible in this case [12]. The same relatively low efficiency of inhibitors from different classes of compounds, together with the observed constant rate of their consumption, most probably indicate a radical-chain mechanism of chlorination of propylene with a small chain length. These processes of chlorination approach nonchain reactions.

The kinetics of direct and oxidative chlorination of propylene on $CuCl_2$ are described by different equations, probably corresponding to different limiting stages of the processes. However, a common feature of all limiting stages is apparently the transformation of $CuCl_2$. For oxidative chlorination of propylene, the reaction of regeneration of $CuCl_2$ can be such a stage

$$2CuCl + 2HCl + 0.5O_2 \rightarrow 2CuCl_2 + H_2O \tag{4}$$

In the case of direct chlorination of propylene, reaction (3) can be considered the limiting stage in the region of pCl_2 up to 0.0125 MPa. For the region of pCl_2 equal to 0.0125-0.0250 MPa, these stages can be reactions (1) and (2).

Based on the results obtained, we proposed a scheme for describing the mechanism of direct and oxidative chlorination of propylene in the presence of $CuCl_2$ in which stages (2), (3), and (5)-(11) are general, and stages (4) and (12) only concern oxidative chlorination.

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		Rate of transformation of C_3H_6 , mole/liter kt h			
Catalyst	Type of inhibitor	with no additive	with ad- ditive		
α -Al ₂ O ₃	Nitrobenzene Hydroquinone	19.7	0.9 0.2		
LiCl	Ni trobenzene Hydroquinone	29,1	1.2 0.4		
CuCl ₂	Ni trobenzene Hydroquinone	31.2	14.7 15,6		

TABLE 2. Effect of Inhibitors on the Rate of Direct Chlorination of Propylene* (0.5% additive of the weight of C_3H_6)

*Experimental conditions: the amount of metal chloride was 1 wt. % for α -Al₂O₃, C₃H₆:Cl molar ratio = 3:1; 490°C, 0.2 sec contact time.

TABLE 3. Thermodynamic Parameters of Generation of Radicals in Reactions (1)-(3)

Elemen-	emen- ΔG , kJ/mole			Kp		
tary reac- tion	7 reac-298 K 643 K 763 K	763 K	298 K	643 K	763 K	
(1) (2) (3)	224.38 - 76.99 79.13	172.27 91.84 23.46	158,58 -97,01 3,89	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c} 1.01 \cdot 10^{-14} \\ 2.89 \cdot 10^7 \\ 0.012 \end{array}$	$\begin{array}{c} 1.39\cdot10^{-11} \\ 4.38\cdot10^6 \\ 0.54 \end{array}$

Formation of allyl chloride

$$C_{3}H_{6} + CuCl_{2} \rightarrow C_{3}H_{5} + HCl + CuCl$$
(2)

$$C_{3}H_{6} + Cl \rightarrow C_{3}H_{5} + HCl \qquad (2)$$

$$C_{8}H_{5} + Cl_{9} \rightarrow C_{9}H_{5}Cl + Cl \qquad (6)$$

(3)

(7)

$$C_{3}H_{5}^{*} + CuCl_{2} \rightarrow C_{3}H_{5}Cl + CuCl$$
(6)

Formation of 1,2-dichloropropane

 $C_{3}H_{6} + 2CuCl_{2} \rightarrow C_{3}H_{6}Cl_{2} + 2CuCl$ (8)
(9)

$$C_3H_6 + CI \rightarrow C_3H_6CI$$

$$C_3H_6CI + CI_2 \rightarrow C_3H_6CI_2 + CI$$
(10)

$$C_{3}H_{6}Cl + CuCl_{2} \rightarrow C_{3}H_{6}Cl_{2} + CuCl$$
(11)

Regeneration of Cu(II) chloride

$$2\operatorname{CuCl} + 2\operatorname{HCl} + 0,5\operatorname{O}_2 \to 2\operatorname{CuCl}_2 + \operatorname{H}_2\operatorname{O}$$

$$2\operatorname{CuCl} + \operatorname{Cl}_2 \to 2\operatorname{CuCl}_2$$
(4)
(12)

Oxidation

$$2\text{HCl} + 0.50_2 \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$$
 (13)

The reaction of propylene with chlorine on a catalyst of the LiCl type is a catalytic heterogeneous-homogeneous reaction in which adsorption of the reagents on the active sites of the catalyst plays the major role [13].

The mechanisms established thus open up new possibilities for increasing the selectivity of direct and oxidative chlorination of propylene.

EXPERIMENTAL

The method of vapor-phase halogenation of propylene and preparation of the catalysts is described in [1]. Conditions of oxidative chlorination of propylene (cf. Fig. 1): temperature of 490°C, 1 sec contact time, $C_{3}H_{6}$:HCl:O₂ molar ratio = 1:1:0.5. The chlorinated and gaseous products of the reactions were analyzed by GLC according to [1]. The enthalpy, Gibbs free

Reaction and catalyst	Kinetic equation	Dependences of reaction rate constants on the temperature
Oxidative chlorina- tion of C ₃ H ₆ 1% CuCl ₂ on α-Al ₂ O ₃	$r = k p_{O_2}^{0,8}$	$k=1,1\cdot10^{9}\exp\left(-102016/RT\right).$ mole/liter kt • h • MPa
The same	$r = k p_{\mathrm{Cl}_2} p_{\mathrm{C}_3} \mathrm{H}_{6}$	$k = 2,2 \cdot 10^{11} \exp(-81\ 200/RT).$ mole/liter kt • h • (MPa) ²
Direct chlorination of C ₃ H ₆ : a) 1% LiCl on α-Al ₂ O ₃	$r = k p_{Cl_2} p_{C_s} H.$ ($p_{Cl_2} = 0 - 0.0250 \text{ MPa}$)	$k=2.95 \cdot 10^{11} \exp(-97.515/RT)$. mole/liter kt·h·(MPa) ²
b) 1% CuCl ₂ on α-Al ₂ O ₃	$r_{1} = k_{1} p_{Cl_{2}} p_{C,H}^{0,95}$ $(p_{Cl_{2}}=0-0,0125 \text{MPa})$ $r_{2} = k_{2} p_{C,H_{5}}^{0,95}$ $(p_{Cl_{2}}=0,0125-0,0250 \text{ MPa})$	$ \begin{array}{c} k_1 = 1.82 \cdot 10^{41} \exp(-90.649/RT) \\ \text{mole/liter kt} \cdot \mathbf{h} \cdot (\text{MPa})^2 \\ k_2 = 2.09 \cdot 10^{41} \exp(-90.649/RT) \\ \text{mole/liter kt} \cdot \mathbf{h} \cdot (\text{MPa})^2 \end{array} $

TABLE 4. Kinetics of Direct and Oxidative Chlorination of Propylene*

*Experimental conditions of the kinetic experiments on oxidative chlorination of propylene: C_3H_6 :HCl:O₂ molar ratio = 1: 1:0.5, 370-490°C, 0.4-0.6 sec contact time. Experimental conditions in direct chlorination of propylene: C₃H₆:Cl₂ molar ratio = 2:1, 430-490°C, 0.1-0.2 sec contact time.

energy, and equilibrium constants were calculated according to [4]. The thermodynamic properties of the radicals were taken from [14] for C1 and from [15] for C_3H_5 .

The kinetic measurements were performed in gradient-free reactors of the Korneichuk system [16] and with a vibrating fluidized bed [17].

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CONCLUSIONS

1. The order of activity of the catalysts was found: $CuCl_2 > FeCl_3 > CoCl_3 > CrCl_3$, which is in agreement with the similar dependence of their activity on the M-Cl binding energies for the reactions of direct and oxidative chlorination of propylene.

2. Differences were established in the character of the effect of inhibitors on the rate of the reactions of direct and oxidative chlorination of propylene on metal chlorides of constant and variable valence.

3. The kinetic parameters of the reactions of direct and oxidative chlorination of propylene on metal chlorides were found. The kinetic equations for the processes on LiC1 are identical to the reaction of free radical chlorination of propylene. For CuCl2, a radical mechanism with a small chain length is most probable.

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OXIDATION OF METHYLCYCLOHEXANOLS BY THE Pb(OAc)₄-LiC1 SYSTEM

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Secondary five- and six-member cyclic alcohols are oxidized with ring opening into ω chloroalkenals and ω -alkenals under the effect of oxidizing systems based on lead tetraacetate (LTA) such as LTA-LiCl and LTA-Cu(OAc)₂. Aliphatic aldehydes are primarily obtained from cyclopentanol, while in addition to aldehydes, a significant amount of cyclohexanone is formed from cyclohexanol [1]. The information on the reaction of monosubstituted cycloalkanols is very limited. It is known that oxidation of 2-methylcyclohexanol by LTA alone (without Li and Cu salts) take place with an insignificant degree of ring opening. Cyclic ketone is the basic product in this reaction. An addition of an alkyl substituent in position 3 or 4 of the ring, the products of β -fragmentation are virtually not obtained, i.e., oxidation take place as in the case of unsubstituted cyclohexanol [2].

The reaction of 2-, 3-, and 4-methylcyclohexanols (Ia-c) under the effect of the Pb- $(OAc)_4$ -LiCl system was investigated in the present study to study the effect of the structure of the alcohol on the oxidation process. The reaction was conducted in benzene at 70-80°C. The results obtained are reported in Table 1.

The reaction included a number of successive stages. In the first stage, methylcyclohexylalkoxyl radicals (IIa-c) are generated from alcohols (I), and their formation was confirmed by EPR. In oxidation of (Ia-c) with LTA in C_6H_6 at ~20°C in the presence of a C_6H_5CH- N(O)C(CH₃)₃ (PBN) spin trip, the EPR spectrum of adducts of PBN with radicals (II) was observed



The EPR spectrum of nitroxyl radicals (III) is a triplet of doublets (cleavage on N and β -H atoms) with the following HFS constants: $a_n = 14.4$, 14.2, and 14.4 Oe; $a_{\beta}^{H} = 1.9$, 1.8, and 1.8 Oe for (IIIa-c), respectively. The parameters of the spectra correspond to the data in [3, 4].

In the general case, radicals (II) can be rearranged into methylcycloalkanones (IVa-c) and fragmented with ring opening, yielding formalylalkyl radicals (V), (VIII), (IX), and (XI). The latter are quantitatively oxidized with transfer of the Cl atom into chloro-alkanals (VI), (VIII), (X), and (XII)

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