Radical-Chain Reactions of CCl₄ with Hydrocarbons in the Presence of Silica-Immobilized Copper-Containing Catalysts

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Abstract—The activities of two catalytic systems toward the exchange reaction of CCl₄ with hydrocarbons are compared: a copper chloride complex with DMF and polycopperphenylsiloxane (PCPS). PCPS is a very stable catalyst. It completely preserves its catalytic activity after six catalytic cycles. Competitive reactions with the pairs of hydrocarbons suggested a radical-chain mechanism for the title reaction for both catalysts.

INTRODUCTION

Carbon tetrachloride exchange with alkanes (C–Cl bond metathesis)

$$CCl_4 + RH \longrightarrow CHCl_3 + RCl \qquad (I)$$
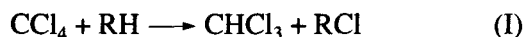
is an interesting promising method for efficient CCl₄ processing. The reaction is thermodynamically favorable: it is exothermic and the entropy is close to zero. However, acceptable yields were obtained only recently. For instance, in the presence of radical initiators (light or peroxides), reaction (I) with cumene led to large amount of coupling products, HCl, and unidentified heavy products along with the product of α-chlorination [1]. The use of palladium [2, 3] and copper [4, 5] complexes was more efficient. Acceptable product yields can be obtained in the presence of triphenylphosphine complexes of palladium halides in donor solvents (e.g., acetonitrile) and a solid alkali. A copper complex with DMF supported on silica enables high conversions of hydrocarbons (up to 80%) and a selectivity of at least 97% without additional reagents.

Reaction (I) on the above catalyst was studied in detail [5]. The reaction most likely occurs in the film of excess DMF adsorbed on the support surface and containing catalytically active complexes. Gradual loss of DMF deactivates the catalyst. Therefore, a search for a catalyst free of this limitation is a topical problem. In principle, candidate catalysts are organocopper compounds. In this work, we studied reaction (I) in the presence of oligomeric polycopperphenylsiloxane (PCPS) immobilized on Silochrome S-80. Earlier, this catalyst was shown to be rather active in dichlorobutene isomerization [6]. The structure of PCPS was discussed in [7]. Another problem solved in this study is the determination of relative reactivities of n-decane, cyclohexane, and toluene on the proposed catalyst and on the old cat-

alyst (silica-immobilized copper chloride complex with DMF). The relative reactivity of various C–H bonds suggest the nature of intermediates in this process and its mechanism.

EXPERIMENTAL

The procedures for PCPS-based catalyst preparation and reaction were analogous to those described earlier [6–8]. A copper–siloxane catalyst was prepared by the immobilization of PCPS (18.1 wt % of copper) on Silochrome S-80 surface (a specific surface area of 80 m²/g). Samples were heated for an hour at 180°C upon solvent removal to ensure PCPS immobilization. The overall concentration of copper in the heterogeneous catalyst was 2.3%. Silochrome-immobilized DMF–Cu complex was prepared as described in [4, 5]. The process was carried out at 160–180°C according to the method described in [5]. The CCl₄ : decane molar ratio was varied from 1 : 1 to 4 : 1. The overall catalyst amount in a sample was 14% (including the active phase and support). Experiments were carried out at a stirring intensity that eliminated diffusion control of the reaction. The reaction rate was independent of stirring intensity when the latter changed by an order of magnitude. It was shown earlier [5] that, under the conditions chosen, the reaction rate does not change when linear dimensions of support grains are varied several-fold. This excludes the possibility of internal diffusion control.

RESULTS AND DISCUSSION

PCPS is catalytically active in reaction (I). That is, we found a catalyst of the second type for this reaction in addition to immobilized copper complexes with low-molecular donor ligands which represent catalysts of

Relative reactivities of hydrogen atoms in hydrocarbons in reaction (I)

Hydrocarbon pair R^1H/R^2H*	Catalyst			
	PCPS		DMF–copper chloride complex	
	160°C	180°C	160°C	180°C
Decane/cyclohexane	1.0	0.98	0.92	0.97
Decane/toluene	0.64	0.60	0.63	0.67
Cyclohexane/toluene	0.62	0.60	0.71	0.72

* The activity of hydrogen in R^2H is set to unity.

the first type. However, the reaction behavior is noticeably different from those observed earlier [4, 5] for DMF complexes. The kinetic curves of the process in the presence of PCPS do not show induction periods, but the catalytic activity is much lower than in the case of DMF complexes. In the presence of DMF complexes in the concentrations used in this work at 160°C, the conversion of decane is 60% for 6 h. In the presence of PCPS on Silochrome at 180°C, the conversion is lower than 12% for the same period. However, PCPS has some advantages over DMF complexes. The activity of the latter decreases during one 6- to 10-h run [4] and cannot be restored without additional treatment. In contrast to this, the activity of PCPS is stable as seen from the data presented below on decane conversion on the same immobilized PCPS sample. Between the cycles, the products were removed and new portions of reagents were added. The contact time for each catalytic cycle was 6 h at 180°C. The CCl_4 : decane ratio was 4 : 1.

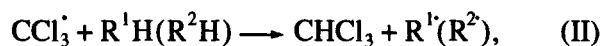| Catalytic cycle	1	2	3	4	5
Conversion, %	10.9	10.0	11.5	8.9	11.0

Stable catalyst activity is accompanied by changes in the selectivity. In the first two cycles (for 12 h), the selectivity is high, which is usual for copper-containing catalysts: 100% to chlorodecanes, including a selectivity of 97% to monochlorodecanes, and 97–98% to chloroform. In subsequent cycles, the selectivity to chloroform decreases. After 24 h, methylene chloride is formed in substantial amounts: the ratio between the yields of $CHCl_3$ and CH_2Cl_2 is about 2 : 1, and up to 1% of a lighter product is formed (probably, methyl chloride). The selectivity to chlorodecanes is preserved.

The difference in the behavior of supported complexes and PCPS can be explained by the earlier idea on the role of DMF, which is in the composition of complexes, in catalysis. Golubeva *et al.* [5] assumed that the film of a polar component on the support surface plays an important role. The reaction probably occurs in this film. DMF may also participate in Cu(II) reduction to Cu(I). In the case of PCPS, such a film is absent. The role of a reducing agent belongs to an unreactive alkane or the phenyl groups of PCPS. This leads to the loss of catalytic activity. An additional factor is the relatively

rigid structure of PCPS, which hinders the interaction of copper ions with the reactants in the solution. On the other hand, the absence of the labile surface film stabilizes the catalyst work in time.

PCPS and the immobilized copper chloride complexes with DMF catalyze the reactions of CCl_4 with cyclohexane and toluene along with *n*-decane.

Golubeva *et al.* [4] assumed that reaction (I) occurs via a radical-chain mechanism, and copper complexes play the role of a renewable initiator. This mechanism is not the only one possible. Reactions are known where CCl_4 is activated by the oxidative addition to a metal complex [9]. The processes with trichloromethyl radical stabilized in the metal coordination sphere are also possible [10]. If the process occurs via a classical radical-chain mechanism (as suggested by the regioselectivity of side-chain toluene chlorination), the product ratio in the competitive chlorination of hydrocarbons should correspond to the ratio of elementary step rate constants of hydrogen abstraction by a trichloromethyl radical (reaction (II)):

$$CCl_3^\cdot + R^1H(R^2H) \longrightarrow CHCl_3 + R^{1\cdot}(R^{2\cdot}), \quad (II)$$

$$R^{1\cdot}(R^{2\cdot}) + CCl_4 \longrightarrow R^1Cl(R^2Cl) + CCl_3^\cdot. \quad (III)$$

In this case, the reactivity series for hydrocarbons should correspond to the literature data on the attack of a C–H bond by a trichloromethyl radical. In this case, the relative reactivities should be independent of a metal complex. Conversely, if the process occurs in the coordination sphere of a metal complex, it should substantially affect the reactivity pattern and the ratio of reactivities toward different positions in hydrocarbons should differ from that known for the $CCl_3^\cdot$ radical. The table specifies the data on relative reactivities of hydrocarbons. They were corrected taking into account the number of active hydrogen atoms in the molecules (the activity per one atom). Hydrogen atoms at the aromatic ring in toluene that do not participate in the reaction, as well as hydrogen atoms belonging to the methyl group in decane, were not taken into account. These atoms do not participate in the reaction with CCl_4 because their activity is ~40 times lower than the activity of secondary hydrogen atoms in decane and cyclohexane. Note

that the ratio between the activities of primary and secondary hydrogen atoms in alkanes is characteristic of hydrogen abstraction by the $CCl_3^.$ radical [11, 12].

The table shows the values obtained directly in the experiment. The activity for one pair may also be calculated from the activities of other pairs. For example, the activity of hydrogen in decane versus hydrogen activity in cyclohexane can be calculated from the values for decane/toluene and cyclohexane/toluene pairs. However, this calculation gives similar values and the error is lower than the experimental error. This table shows that the nature of the copper-containing complex does not affect the selectivity in the pairs of hydrocarbons. It is also seen that the results of measurements do not depend on temperature. That is, the activation energies of steps determining the product composition are close. Finally, the values for the cyclohexane/toluene pair are close to the published value on the ratio of reactivities in hydrogen abstraction by the trichloromethyl radical, which is 0.56 [13]. A small difference is explainable by the difference in the experimental temperatures: Dneprovskii et al. [13] carried out their experiments at 90°C. Thus, our data suggest that reaction (I) occurs via a radical-chain mechanism both in the presence of PCPS and immobilized copper chloride complexes with DMF. The ratio of hydrogen reactivities in alkanes and toluene obtained under similar conditions in [3] for the homogeneous palladium-containing catalyst differs substantially from that observed in this work. To be more specific, the reactivity of cyclohexane was unusually high. The mechanisms of reaction (I) over copper and palladium catalysts are probably different. In the latter case, we can exclude the radical-chain mechanism with chain transfer via a trichloromethyl radical.

The results obtained in this work suggest further directions in the development of an efficient catalyst for reaction (I). The catalyst should contain copper in a bound state similar to that in PCPS and it should have a rigid structure. One of the variants is a metal-containing chain aggregates grafted on the surface of a support.

The presence of heteroatoms (nitrogen, phosphorus, or sulfur) bound to copper is also desirable because they stabilize copper in the Cu(I) state. Currently, research is underway on the development of such catalytic systems for the reactions of CCl₄ with alkanes.

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