Low-temperature hydrodechlorination of 2,3-dichlorodibenzo-*p*-dioxin and chlorobenzene with hydrides catalyzed by transition metal compounds

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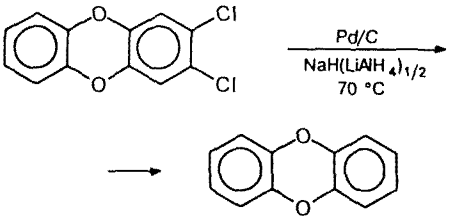
Hydrodechlorination of chlorobenzene by chemically bound hydrogen in the presence of transition metal compounds was studied. Alkali and alkaline earth metal hydrides (NaH, MgH_2, $LiAlH_4$, $NaH(LiAlH_4)_{1/2}$) were used as the sources of the chemically bound hydrogen. The effect of the natures of the hydride and of the transition metal on the activity was studied under comparable conditions. The Pd/C—$NaH(LiAlH_4)_{1/2}$ catalytic system was found to be the most active. This system made it possible to perform the quantitative dechlorination of 2,3-dichlorodibenzo-*p*-dioxin at 70 °C.

Key words: hydrodechlorination, hydrides, supported catalysts, chlorobenzene, chlorinated dioxins.

Hydrodechlorination of chloroaromatic compounds has aroused considerable interest, since investigation of this reaction is needed in order to develop methods for the detoxification of polychloroaromatic compounds, which constitute a serious environmental hazard.[1–2] In addition, hydrogenolysis of the C—Cl bond is important for synthetic organic chemistry.[3]

Hydrides of nontransition metals (NaH, MgH_2, and $LiAlH_4$) are known to be relatively inactive in the reductive dechlorination of nonactivated chloroaromatic compounds.[4] However, the reactivity of these hydrides toward the hydrogenolysis of carbon—halogen bonds sharply increases when a transition metal salt or complex is added to them.[5–7]

In the present work we have studied the catalytic properties of a series of compositions including transition metal compounds (Pd/C, $NiCl_2$, $TiCl_3$, $CoCl_2$, $CuCl_2$) and nontransition metal hydrides (NaH, MgH_2, $LiAlH_4$, $NaH(LiAlH_4)_{1/2}$) in order to find efficient systems for dechlorination of relatively unreactive 2,3-dichlorodibenzo-*p*-dioxin with a high degree of conversion under mild conditions, the transition metal being present in a catalytic amount.



To increase the reaction rate, we used new carbon materials (Sibunit and catalytic fibrous carbon KVU-53) as supports for the active component.

Experimental

Chlorobenzene of the "pure for analysis" grade was purified by vacuum distillation (99.5 % purity); 2,3-dichlorodibebnzo-*p*-dioxin was prepared by heating 1,2,4,5-tetrachlorobenzene with dipotassium salt of pyrocatechol (the latter was obtained using metallic potassium; see Ref. 8). The yield of dioxin after recrystallization from a CCl_4—EtOH mixture (4 : 1 v/v) repeated twice was 76 %. According to GLC, this compound contained no more than 1 % impurities.

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Toluene of the "extrapure" grade was used as the solvent. 4 % Pd and 8 % Ni on Sibunit[9] and KVU-53[10] were used as supported catalysts.

Magnesium hydride was obtained by the known procedure.[11] The rest of the hydrides and transition metal salts were used as commercial reagents of the "pure for analysis" grade, metal salts were dried before use by treating them with thionyl chloride. Samples for GLC and NMR analyses were withdrawn from the reaction mixture during the process.

The reaction mixtures were analyzed on an LKhM-80 chromatograph (a 2 m×3 mm stainless-steel column filled with 5 % 8E 30 on Chromaton N-AW-DMCS using a flame ionization detector and argon as carrier gas, 60 mL min^{-1}). The products were identified and the degrees of conversion were determined by GLC by comparing the retention times for the products with those for reference compounds (internal standard). NMR spectra were recorded on a Bruker CXP-300 spectrometer. The specific surface areas of samples were determined by the method of low-temperature adsorption of nitrogen on a Didicsorb-2600 automatic setup.

The catalytic experiments were carried out in a flask equipped with a magnetic stirrer. The required amount of a transition metal compound was placed into a flask in an argon atmosphere, and then the solvent and the appropriate amount of hydride were added. After that, the mixture was cooled to 0—5 °C and vigorously stirred until gas evolution ceased. When the temperature of the reaction mixture reached ~20 °C, the calculated amount of the organochlorine compound was added. The flask was brought to the required temperature and the reaction was carried out with temperature control. The activities of the catalysts were characterized by the initial specific rate of the formation of benzene from chlorobenzene (W_0, mol g-at. of M min^{-1}, where M = Pd, Ni).

Results and Discussion

Our experiments have shown that chlorobenzene (CB) dissolved in a diethyl ether—toluene mixture (1 : 4 v/v) is dechlorinated to benzene to only a small extent (~6 %) over a period of 4 h at 70 °C in the presence of NaH, MgH_2, or $LiAlH_4$, at a hydride : chlorobenzene ratio of 2 : 1. When a mixed hydride of the composition $NaH(LiAlH_4)_{1/2}$ is used, the degree of conversion of CB under the same conditions is 40 %.

Previously[12] it has been shown that when alkyl halides are reduced with $LiAlH_4$, the addition of lithium hydride makes it possible to accelerate the transformation of alkyl halides. The increase in the reactivity is apparently due to the fact that in the reaction of lithium hydride with alkyl halides (RX), lithium tetrahydroaluminate acts as a proton transferring agent.

In our case, when CB is reduced, the use of the mixed hydride $NaH(LiAlH_4)_{1/2}$ made it possible to attain high degrees of dechlorination of the substrate. The specific surface areas measured for the samples of lithium and sodium hydrides were 1—1.5 m^2 g^{-1}, and that for the hydride $NaH(LiAlH_4)_{1/2}$ was 20—25 m^2 g^{-1}. Since LiH, NaH, MgH_2, and $NaH(LiAlH_4)_{1/2}$ react as suspensions, an increase in the specific surface area of the hydride may account for the increase in its reactivity.

Table 1. Hydrodechlorination of CB in the presence of catalytic compositions

Run	Hydride	W_0 /mol g-at. of Pd min^{-1} (4 % Pd/C)	W_0 mol g-at. of Ni min^{-1} (8 % Ni/C)
1	$(LiAlH_4)_{1/2}NaH$	1.42	0.09
2	$LiAlH_4$	0.56	—
3	MgH_2	0.09*	—
4	NaH	0.12	—

Note. T = 20 °C, toluene as the solvent, hydride : chlorobenzene = 2 : 1. * In THF.

The results of the study of the dechlorination of CB at 22 °C under argon in the presence of catalytic compositions consisting of 4 % Pd/C or 8 % Ni/C and a nontransition metal hydride are presented in Table 1. The reaction yields benzene and the corresponding alkali or alkaline earth metal chloride. The Pd/C—$NaH(LiAlH_4)_{1/2}$ system proved to be the most efficient.

We also studied the efficiency of the catalytic compositions MCl_n—$NaH(LiAlH_4)_{1/2}$ (where M = Ni, Ti, Fe, Cu, Co; n = 2, 3) in the hydrodechlorination of CB. For each catalytic composition, the variation of the CB concentration as a function of time was studied. The ratio of the reactants was chosen in such a way that the reaction was pseudo-first order with respect to CB. We determined the effective rate constants (k_{eff}) for the hydrodechlorination of CB in the presence of catalytic compositions (transition metal compound — $NaH(LiAlH_4)_{1/2}$, T = 70 °C, toluene as the solvent):

MCl_n	$NiCl_2$	$CoCl_2$	$FeCl_2$	$TiCl_3$	$CuCl_2$
$k_{\text{eff}}\cdot 10^5$/s^{-1}	27.4	14.31	2.25	3.75	0.97

On the basis of the k_{eff} values, the compounds studied can be arranged in the following sequence in terms of their activity in the hydrodechlorination of CB:

$$NiCl_2 > CoCl_2 > TiCl_3 > FeCl_2 > CuCl_2.$$

This sequence is similar to that obtained by Ashbi *et al.*[6] for dechlorination of CB to benzene in the presence of MCl_n—$LiAlH_4$ catalytic systems. However, in a more recent paper,[7] stoichiometric amounts of the reactants were used (transition metal salt : chlorobenzene = 1 : 1), and in this case, a decrease in the amount of transition metal salts resulted in sharp retardation of the reaction or even in its termination. In the present work, the use of mixed hydride, which is highly reactive, made it possible to attain high degrees of conversion of CB in this reaction under the same conditions but at the molar ratio metal chloride : chlorobenzene ≤ 1 : 5.

We also studied the efficiency of the Ni/C and Pd/C catalysts under comparable conditions. It follows from the data of Table 1 that in the presence of palladium

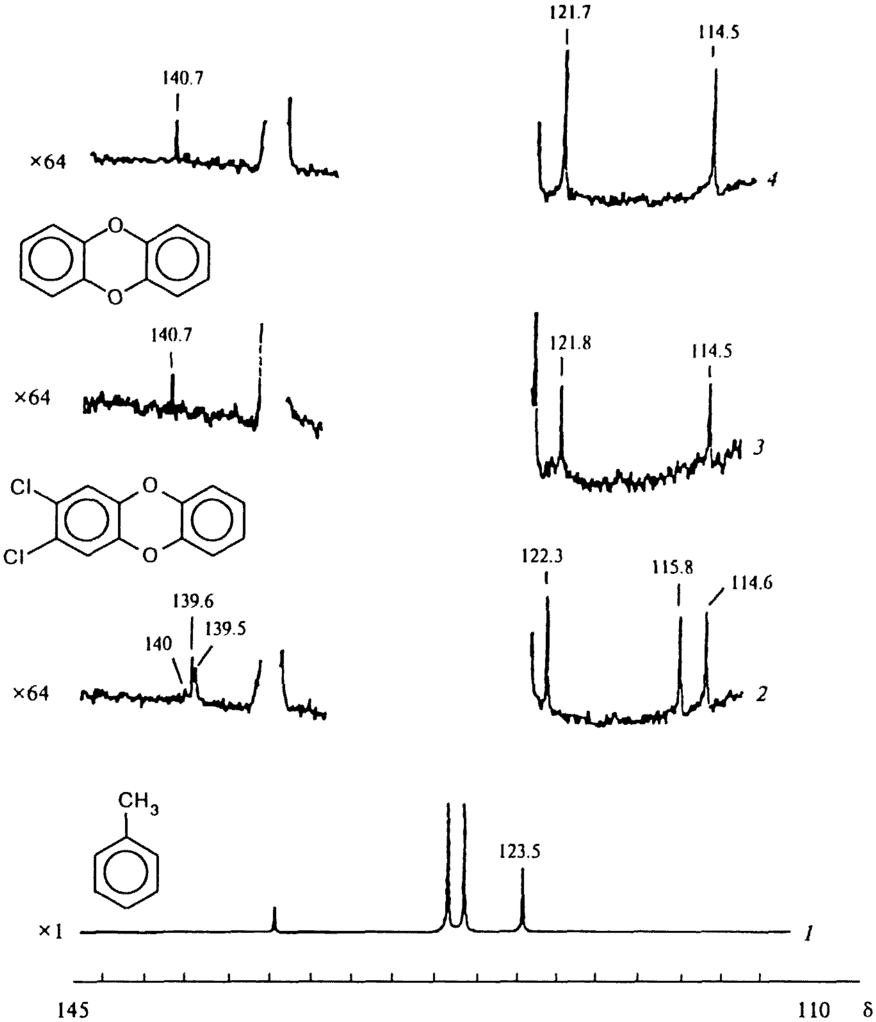

Fig. 1. ^{13}C NMR spectra of 2,3-dichlorodibenzo-*p*-dioxin before and after dechlorination in the presence of the Pd/C—NaH(LiAlH$_4$)$_{1/2}$ catalytic composition: solvent (*1*); solution of 2,3-dichlorodibenzo-*p*-dioxin before the reaction (*2*); solution of dibenzo-*p*-dioxin (reference solution) (*3*); solution of 2,3-dichlorodibenzo-*p*-dioxin after the reaction (*4*). Reaction conditions: $1.9 \cdot 10^{-4}$ g-at. of Pd, $4.97 \cdot 10^{-3}$ mol of NaH(LiAlH$_4$)$_{1/2}$, $5.1 \cdot 10^{-4}$ mol of $C_{12}H_6O_2Cl_2$, KVU-53 as the carbon support, 1 mL of toluene, 70 °C, 10 h.

catalyst, this reaction occurs at a high rate. We obtained the following results in the study of hydrodechlorination of CB in the presence of the Pd/C—NaH(LiAlH$_4$)$_{1/2}$ catalytic systems on various carbon supports (T = 20 °C; toluene as the solvent) with a surface Pd concentration of $0.6 \cdot 10^{-7}$ g-at. of Pd m^{-2}:

Carbon	S /m^2 g^{-1}	W_0 /mol g-at. of Pd min^{-1}
Sibunit	260	1.42
KVU-53	220	2.40

Thus, the use of KVU-53 as the support leads to an increase in the rate of dechlorination. This fact can be explained by characteristic features of the structure of the surface of this support. For example, most of the accessible surface of Sibunit is formed by the basal planes of graphite-like crystallites, whereas in the case of KVU-53, the surface is made of the side faces of these crystallites.

The catalytic composition found was tested in the reductive dechlorination of 2,3-dichlorodibenzo-*p*-dioxin under mild conditions. The removal of chlorine atoms from the lateral positions of dioxins is known[1] to be the most difficult task; however, the presence of halogen atoms in exactly these positions accounts for the high toxicity of xenobiotics of the dioxin type.

The data of ^{13}C NMR spectroscopy (Fig. 1) confirm the results of chromatographic analysis, which indicate that 2,3-dichlorodibenzo-*p*-dioxin is quantitatively dechlorinated to dibenzo-*p*-dioxin in the presence of the Pd/KVU—NaH(LiAlH$_4$)$_{1/2}$ catalytic composition.

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