NOTES

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Formation of Acetals from Vinyl Chloride and Alcohols Catalyzed by Transition Metal Chlorides

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Recently, the formation of acetaldehyde dialkyl acetal from vinyl chloride and alcohol catalyzed by palladium chloride and a base was reported.[1,2]

In an attempt to oligomerize vinyl chloride by transition metal chlorides in alcohol, we have observed the formation of acetaldehyde dialkyl acetals instead of the oligomerization by ruthenium, rhodium and palladium chlorides. This reaction did not take place by iron, cobalt, chromium, zirconium and hafnium chlorides.

Results and Discussion

In a preliminary experiment, vinyl chloride and rhodium trichloride trihydrate (molar ratio; 150) were dissolved in methanol and the mixture was kept at 50°C for 48 hr. The only product isolated was acetaldehyde dimethyl acetal, no product corresponding to a dimer of vinyl chloride being detected on gaschromatography.

More detailed studies on the acetal formation reaction by rhodium trichloride trihydrate were carried out using ethanol. The time dependence of the formation of acetaldehyde diethyl acetal at 60°C is shown in Fig. 1. The selectivity for acetaldehyde diethyl acetal was about 70% and it decreased when the reaction time exceeded 25 hr. In the reaction at 80°C, vinyl chloride was consumed completely in 24 hr but the selectivity for acetaldehyde diethyl acetal was only 20.3%. Small amounts of vinyl ethyl ether and acetaldehyde were detected on gas chromatography (identified by comparing retention times with those of authentic samples), and the rest was higher boiling products. The formation of acetaldehyde is likely to be due to the reaction of vinyl chloride with water[3] and/or the oxidation of ethanol by rhodium(III). Higher boiling products were not studied further.

Ruthenium and palladium chlorides also catalyzed the formation of acetaldehyde diethyl acetal but iron, cobalt, chromium, zirconium and hafnium chlorides did not (Table 1). In the reaction using palladium dichloride as a catalyst, partial reduction to palladium metal was observed.

Recently, the formation of acetal from vinyl chloride and alcohol catalyzed by palladium chloride was reported, but those reactions require the presence of a strong base[1] or an alkoxide anion.[2]

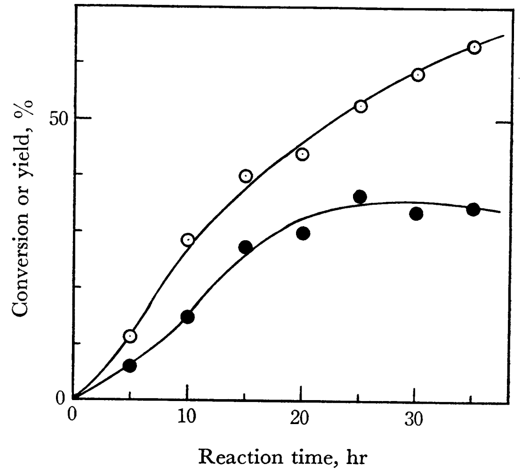

Fig. 1. Time dependence of the acetal formation.
—⊙—: Conversion of vinyl chloride, %
—●—: Yield of acetaldehyde diethyl acetal, %
Reaction conditions:
Vinyl chloride, 43 mmol; $RhCl_3.3H_2O$, 0.22 mmol; EtOH, 160 mmol; Reaction temperature, 60°C

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[1] E. W. Stern, M. L. Spector and H. P. Leftin, *J. Catal.*, **6**, 152 (1966).

[2] C. F. Kohll and R. van Helden, *Rec. Trav. Chim. Pays-Bas*, **87**, 481 (1968).

[3] J. Smidt, W. Hafner, R. Jira, J. Sedlmeier, R. Sieber, R. Ruttinger and H. Kojer, *Angew. Chem.*, **71**, 176 (1959).

Table 1. Reaction of vinyl chloride and ethanol

Catalyst	Reaction temp. (°C)	Reaction time (hr)	Conv.*	Yield**
$RhCl_3 \cdot 3H_2O$	60	5	12.3	6.3
	60	25	52.5	36.6
	80	24	100	20.3
$RhCl(PPh_3)_3$	60	6	5.3	3.2
$RuCl_3 \cdot 3H_2O$	80	24	41.5	21.9
$PdCl_2$	80	24	26.5	14.0
$FeCl_3$	60	48	no reaction	
$CoCl_2 \cdot 6H_2O$	60	48	no reaction	
$CrCl_3 \cdot 6H_2O$	80	24	no reaction	
$ZrCl_4$	80	24	no reaction	
$HfCl_4$	80	24	no reaction	

Reaction conditions: Vinyl chloride, 43 mmol; Catalyst, 0.2—0.4 mmol; Ethanol, 160 mmol

* Conversion of vinyl chloride, %

** Yield of acetaldehyde diethyl acetal based on vinyl chloride supplied, %

The reaction intermediate was considered to be vinyl ether which is formed by the nucleophilic attack of an alkoxide anion onto vinyl chloride coordinating to a palladium ion.

We believe that the coordination of vinyl chloride to ruthenium, rhodium or palladium is significant in the acetal formation reaction.

Experimental

Reagents. Vinyl chloride was passed through columns packed with calcium chloride and phosphorus pentoxide and then condensed into a pressure glass tube held at −78°C.

Methanol and ethanol were purified by conventional methods, and were distilled under a nitrogen stream.

Tris(triphenylphosphine)chlororhodium(I) was synthesized according to the reported method.[4]

Commercial metal chlorides were used without further purification.

Reaction Procedure. In a typical reaction, vinyl chloride (43 mmol) was charged into a glass ampule (20 m*l*) containing rhodium trichloride trihydrate (0.22 mmol) by a trap-to-trap distillation and then ethanol (160 mmol) was charged with a syringe under nitrogen stream. Then the solution was freezed with liquid nitrogen, and the ampoule was evacuated and was sealed. It was then kept at 60°C for 20 hr.

Analysis. The gas chromatography was carried out for the detection and the quantitative analysis of products using a 2 m stainless steel column, 4 mm in diameter, packed with bis(2-cyanoethyl) ether on Diasolid M. Operation conditions: column temperature, 68°C; flash evaporator, 200°C; carrier gas (helium) speed, 40 m*l*/min. Ethyl formate was used as the internal standard.

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4) J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc., A*, **1966**, 1711.