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Homogeneous catalytic hydrogenolysis of chlorodifluoromethane

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ABSTRACT

CHF_2Cl has been converted to CHF_3 and CH_4 as main products when hydrogenolyzed in the presence of $RhCl_3(py)_3$ and other homogeneous catalysts modified with bases (amines and fluoride ion). Pyridine additive was partly hydrogenated and then alkylated to *N*-alkylpiperidines. Nucleophilic attack of fluoride ion on the substrate as well as difluorocarbene formation and hydrogenolysis in the coordination sphere of rhodium are the possible crucial steps leading to the gaseous products.

1. Introduction

Chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) compounds destroy the stratospheric ozone as it was recognized in the seventies and eighties. The ozone depleting potential of CFC-*s* is in general an order of magnitude greater than that of HCFC-*s*. In accordance with The Montreal Protocol on Substances that Deplete the Ozone Layer and its amendments, the production of CFC-*s* (e.g. $CFCl_3$, CFC-11) was prohibited. The use of HCFC-*s* (e.g. CHF_2Cl, HCFC-22) was controlled as well, thus they may not be consumed after 2030 [1].

The transformation of CFC-*s* and HCFC-*s* to valuable chemicals seemed to be reasonable to avoid the costly storage of their stocks or the waste management. Catalytic hydrodechlorination proved to be a promising method to convert these harmful materials into environmentally friendly ones. Heterogeneous catalysts (Pd, Rh, and Ru; see e.g. ref. [2]) have been used generally for these purposes, however, some homogeneous methods have been published recently as well [3–6]. We have shown that rhodium and palladium complexes are effective catalysts in hydrodechlorination of some CFC and HCFC compounds. $RhCl_3(py)_3$ and in situ generated $Pd(P^iPr_3)_3$ surpassed Pd/Al_2O_3, the most active heterogeneous catalyst tested in the transformation of CF_3CHFCl to CF_3CH_2F. The substrate CF_3CHFCl was one of the three components of a gas mixture (named R401) which contained CHF_2Cl and CHF_2CH_3 as well. Actually, we investigated the co-hydrogenation of CF_3CHFCl and CHF_2Cl [6].

In the present work, we report on the hydrogenolysis of pure CHF_2Cl with various homogeneous catalytic systems.

2. Experimental

2.1. General

All manipulations involving air-sensitive compounds employed Schlenk techniques using deoxygenated, dry solvents and gases.

$RhCl_3{\cdot}xH_2O$, $Pd(OAc)_2$, and Pd/Al_2O_3 (5%) were the products of Pressure Chemical Co. Benzyltrimethylammonium fluoride hydrate and triisopropylphosphine were purchased from Fluka and the latter was distilled freshly. Pyridine and primary, secondary, and tertiary amines (Reanal and Fluka) were purified and dried according standard methods. CHF_2Cl and the gas mixture R401 were purchased from EVIRT (Hungary). The components of R401 were CHF_2Cl (53% (w/w)), CH_3CHF_2 (13% (w/w)), and CF_3CHFCl (34% (w/w)).

Homogeneous catalysts $[RhCl(COD)]_2$ [7], $RhCl_3(py)_3$ [8], $RuCl_2(CO)_2(PPh_3)_2$ [9], and $RuCl(H)(CO)(P^iPr_3)_2$ [10] were prepared according literature methods. $Pd(P^iPr_3)_3$ was obtained in situ from $Pd(OAc)_2$ and P^iPr_3 (molar ratio: 1:4) [11].

Gas chromatograms were recorded on Hewlett-Packard model 5830 A and 5890 Series II chromatographs (both with flame ionization detector), while GC–MS analyses were performed on

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Table 1
Identification of typical products and byproducts by comparison of their mass spectral data with reported ones

Compound	Fragmentation found *m/z* (relative intensity)	Fragmentation reported *m/z* (relative intensity)
Difluoromethane	52 (5); 51 (75); 33 (100); 31 (30)	52 (M^+, 10); 51 (90); 33 (100); 31 (25) [12a]
Trifluoromethane	69 (80); 51 (100); 50 (20); 31 (75)	69 (100); 51 (90); 50 (15); 31 (50) [12a]
Ethane	30 (15); 29 (15); 28 (100); 27 (15)	30 (M^+, 25); 29 (20); 28 (100); 27 (25) [12a]
Chloroethane	66 (15); 64 (45); 49 (20); 29 (75); 28 (100)	66 (20); 64 (M^+, 60); 49 (25); 29 (90); 28 (100) [12a]
N-Methylpiperidine	99 (30); 98 (100); 84 (15); 70 (35); 58 (10)	99 (M^+, 35); 98 (100); 84 (10); 70 (30); 58 (10) [12d]
N-Ethylpiperidine	113 (15); 112 (20); 98 (100); 84 (10)	113 (M^+, 25); 112 (20); 98 (100); 84 (10) [12d]
N-Pentylpiperidine	155 (5); 99 (10); 98 (100)	155 (M^+, 10); 154 (5); 99 (5); 98 (100) [12b]
N-Octylpiperidine	197 (1); 99 (3); 98 (100)	197 (M^+, 1); 98 (100) [12b]
N-Formylpiperidine	113 (100); 112 (40) 103 (10); 98 (50)	113 (M^+, 100); 112 (50); 103 98 (50) [12a]
N-Propylbutylamine	115 (10); 114 (10); 86 (35); 72 (100)	115 (M^+, 18); 114 (7); 86 (43); 72 (100) [12c]
N-Butylformamide	101 (3); 100 (5); 72 (25); 59 (60); 58 (100)	101 (M^+, 5); 100 (3); 72 (30); 59 (50); 58 (100) [12a]
N-Methyl-dibutylamine	143 (10); 100 (80); 58 (100)	143 (M^+, 10); 100 (100); 58 (80) [12e]
N,N-Dibutylformamide	157 (3);114 (40); 72 (100); 58 (15)	157 (M^+, 3);114 (60); 72 (100); 58 (15) [12e]

Shimadzu GC 17-A, QP-5000MSD or Hewlett-Packard 5890 Series II GC-MSD spectrometers. Analyses of gaseous samples were made using a Poraplott Q (30 m, Chrompack) capillary column at 50 °C constant temperature. Fluid samples were analyzed using SPB1 (30 m, Supelco) or CP-Sil 5CB (25 m, Chrompack) capillary columns (initial temperature: 50 °C; temperature gradient: 10 K min^{-1}).

Infrared spectra were recorded by using a 0.06-mm CaF_2 cuvette on Specord IR 75 (Carl Zeiss, Jena) or Avatar 330 FT-IR (Thermo Nicolet, USA) spectrometers, the former one of them was calibrated with benzene (1959.6 cm^{-1}) or polystyrene (1601.4 cm^{-1}). The NMR measurements were performed on Varian UNITY 300 and Bruker Avance 400 spectrometers.

The identities of the majority of the products were confirmed by comparison of their MS (see Table 1) and/or ^1H NMR data (see Fig. 1) with those of compounds published in the literature [12]. The structures of other products were assigned by comparison of their MS fragmentation patterns with related spectra (e.g. with spectra of homologs). The conversion of CHF_2Cl was calculated by internal standard method (see also later).

2.2. Hydrogenation in a shaking autoclave (Method A)

Into a 20-mL stainless steel shaking autoclave equipped with manometer and valve, the catalyst (with 0.2–0.8 mmol metal content), solvent, additive(s), and isopentane as the internal standard were added under argon. The autoclave was cooled slowly to −78 °C while flowing argon continuously. From a Schlenk tube equipped with septum, a measured amount of the liquid CHF_2Cl (40 mmol) was added through a stainless steel capillary by a slight argon pressure. The autoclave was closed and pressurized to 2–10 MPa with H_2, and shaken in a heating mantle thermostatted at the desired temperature for 6 h. The autoclave was then immersed in an oil bath, heated to the same temperature, and connected to a gas chromatograph or a GC–MS apparatus through a pressure regulator of the type A-982000-32 (Cole-Parmer) to analyze the gas phase. After cooling and releasing the pressure, the condensed materials were transferred into a Schlenk tube under argon and the autoclave was rinsed with 2 × 3 mL of dichloromethane. The combined mixture was filtered, the solvent evaporated, and the residue analyzed by IR, NMR, GC or GC–MS methods (see above).

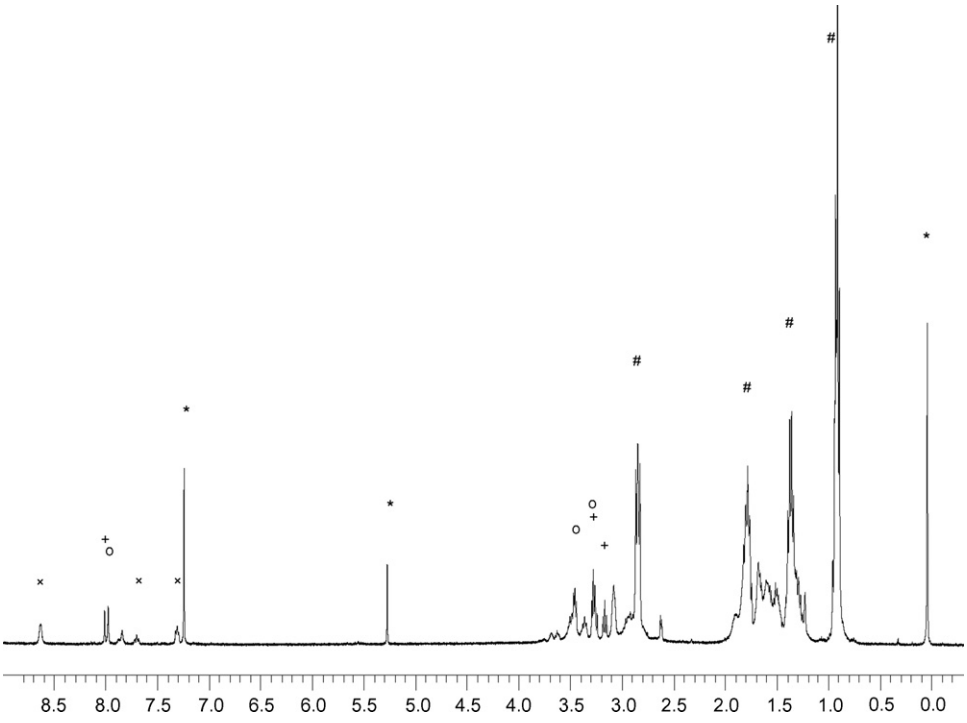

Fig. 1. ^1H NMR spectrum of a mixture of fluid byproducts formed during the hydrogenation of CHF_2Cl by the system $RhCl_3(py)_3$/pyridine/$HNBu_2$ at 150 °C and 10 MPa H_2 pressure (further reaction conditions as at Entry 18 in Table 1). Identified components: py (×); $HNBu_2$·HX (X = F, Cl) (#); $C_5H_{10}NCHO$ (○); NBu_2CHO (+); solvent, standard (*).