Effect of chlorinated hydrocarbons on hydroformylation of propylene

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The effect of 1,2-dichloroethane, trichloroethylene, and tetrachloromethane on hydroformylation of propylene (0.596 mole) in toluene at 100 ± 1°C and initial pressure on an equilibrium mixture of carbon monoxide and hydrogen of approx. 13.8 MPa was investigated using *trans*-$RhCl(CO)(PPh_3)_2$ ($9.26 \times \times 10^{-6}$ mole) as a catalyst. These additives showed retardation and inhibitory effects on hydroformylation of propylene and their molar efficiency could be expressed by the following relative numbers: trichloroethylene : 1,2-dichloroethane : tetrachloromethane = 1 3.5 25. Trichloroethylene as well as allyl and vinyl chlorides were practically not hydroformylated even at threefold amount of the catalyst under the above-mentioned conditions.

При температуре 100 ± 1°C использованием в качестве катализатора *транс*-$RhCl(CO)(PPh_3)_2$ ($9,26\ \ 10^{-6}$ моля) при исходном давлении синтез-газа ($CO\ \ H_2 = 1\ \ 1$) приблизительно 13,8 MPa изучалось влияние примесей 1,2-дихлорэтана, трихлорэтилена и тетрахлорметана на гидроформилирование пропилена (0,596 моля). При этом толуол использовался как растворитель. Эти примеси обладают ингибиционным и ретардационным воздействием. Их молярное воздействие на ингибирование и ретардирование гидроформилирования пропилена можно выразить следующим отношением: трихлорэтилен 1,2-дихлорэтан тетрахлорметан = 1 3,5 25. При показанных условиях даже с трёхмерным количеством катализатора практически не происходит гидроформилирование трихлорэтилена, аллилхлорида и винилхлорида.

We have found earlier [1, 2] that vinyl and allyl chlorides were not hydroformylated even at 2—6% of octacarbonyldicobalt as a hydroformylating catalyst. On the other hand, fluoroolefins, 4-chlorophenyl allyl ether, and 2,4-dichlorophenyl allyl ether were readily hydroformylated, the reaction rate being comparable with that of the hydroformylation of higher olefins. It was shown [1] that hydroformylation was determined by the stability of carbon—halogen linkage and the ability to split off hydrogen halide, which decomposed octacarbonyldicobalt

$$Co_2(CO)_8 + 4HCl \rightarrow 2CoCl_2 + 8CO + 2H_2$$

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and tetracarbonylhydridocobalt

$$2CoH(CO)_4 + 4HCl \rightarrow 2CoCl_2 + 3H_2 + 8CO$$

thus making the hydroformylation impossible. Thus it is not surprising that the additives of dichloroethane into the solvent retarded the hydroformylation of propylene catalyzed by octacarbonyldicobalt and tetracarbonylhydridocobalt considerably [1].

However, it was interesting to determine the effect of chlorinated hydrocarbons on hydroformylation of propylene as well as the possibility of hydroformylation of chloroolefins under the catalytic action of *trans*-carbonylchlorobis(triphenylphosphine)rhodium(I) as the initial catalyst containing bound chlorine.

Experimental

Chemicals

trans-Carbonylchlorobis(triphenylphosphine)rhodium(I) $RhCl(CO)(PPh_3)_2$ — prepared from crystalline rhodium(III) chloride trihydrate and triphenylphosphine by treatment with carbon monoxide in ethanol [3, 4] in 81.3% yield, three times crystallized from methanol [5]; m.p. 188.5°C. For $RhCl(CO)(PPh_3)_2$ calculated: 64.41% C, 4.38% H; found: 64.45% C, 4.24% H.

1,2-Dichloroethane (Lachema, Brno) — freshly distilled before use, b.p. 83.5°C/101 kPa; $\varrho_{20°} = 1253 \text{ kg m}^{-3}$.

Trichloroethylene (Lachema, Brno) — freshly distilled, b.p. 87.2°C/101 kPa; $\varrho_{20°} = 1466 \text{ kg m}^{-3}$.

Tetrachloromethane (Lachema, Brno) — anal. grade.

Allyl chloride — purity 99%, freshly distilled, b.p. 45.1°C/101 kPa; $\varrho_{20°} = 935 \text{ kg m}^{-3}$; $n_D^{20} = 1.415$.

Propylene — purity 99.4% (wt); 0.4% (wt) ethylene, 0.1% (wt) propane, and traces of allene.

Toluene (Lachema, Brno) — anal. grade.

The equimolar mixture of carbon monoxide and hydrogen contained 0.3% (v) of carbon dioxide and 0.03% (v) of oxygen.

The other compounds used were of anal. grade.

Working procedure

The differentially weighed hydrocarbon in toluene (40 g) was poured into a rotating autoclave 0.5 l, stainless steel (82 rev./min) provided with electric heating. The catalyst (6.4×10^{-3} g: 9.26×10^{-6} mole) was dissolved in toluene (10 g) in a specially adapted test tube which was attached to the thermometer pocket inside the autoclave. After deaeration, propylene (25 g; 0.596 mole) was added and the equimolar mixture of carbon monoxide and hydrogen (13.8 MPa) was introduced. After the desired temperature (100 ± 1°C) was reached, the autoclave was put in motion and simultaneously, the solution of the catalyst was poured into the reaction mixture. The values of pressure were recorded in 5 min. intervals. One hour after the stabilization of decrease of pressure, the autoclave was allowed to cool down, degasified and the product was weighed.

The total amount of aldehydes was determined by oximation method, *n*-butyraldehyde and isobutyraldehyde were determined by gas—liquid chromatography with thermal conductivity detection. A column (3 m × 3 mm) packed with Chezasorb containing 5% of the liquid alkyl poly(glycol ether) (Tridox) was used. The column temperature was kept constant at 60°C. Hydrogen was used as a carrier gas at a flow rate of 28 ml/min. The retention times for isobutyraldehyde, *n*-butyraldehyde, and toluene were 1.5, 2.2, and 7.1 min., respectively.

The kinetics of hydroformylation was calculated from the decrease of pressure using the kinetic equation for the first order reaction [6, 7]

$$k = \frac{2.303}{t} \log \frac{p_0 - p_f}{p_t - p_f},$$

where k — rate constant,
p_0 — initial pressure,
p_t — pressure at time t,
p_f — final pressure.

Results and discussion

The effect of 1,2-dichloroethane, trichloroethylene, and tetrachloromethane on hydroformylation of propylene at 100 ± 1°C using *trans*-$RhCl(CO)(PPh_3)_2$ as a catalyst has been examined in a series of discontinuous experiments.

The increasing amount of 1,2-dichloroethane decreased the rate constant of propylene hydroformylation and prolonged the inhibition time (Table 1; Fig. 1), however, it did not affect the total conversion of propylene. Thus, dichloroethane acted mainly as inhibitor and retardant of hydroformylation. This can be explained by splitting off of hydrogen chloride from dichloroethane which slowed down the formation of catalyst by shifting the equilibrium to the left side of equation

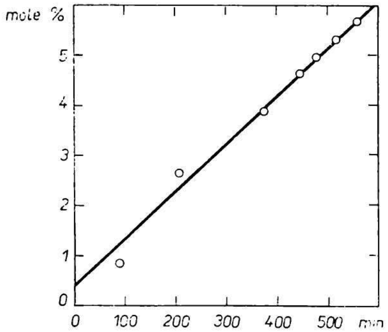
$$RhCl(CO)(PPh_3)_2 + H_2 \rightleftarrows RhH(CO)(PPh_3)_2 + HCl.$$

Table 1

Effect of dichloroethane on hydroformylation of propylene

The overall time of experiment (min)	Inhibition time (min)	Additives of 1,2-dichloroethane		Conversion of propylene (%)	*n*-Butyraldehyde : isobutyraldehyde in the product (wt)	Rate constant of hydroformylation $k \cdot 10^3\ \mathrm{min}^{-}$
		mol 10^2	mole % in the batch			
175	0	0.00	0.00	99.9	1.11	23.0
125	40	0.19	0.35	98.9	1.05	22.2
335	80	0.38	0.71	98.6	1.03	18.1
365	120	0.57	1.06	99.1	1.03	13.4
380	160	0.76	1.43	98.8	1.05	13.2
620	225	1.14	2.18	97.9	1.01	9.8
785	390	1.90	3.36	98.1	1.053	8.8
755	510	2.66	5.19	98.0	0.988	4.2

Fig. 1. Inhibition time of propylene hydroformylation *vs.* the molar concentration of dichloroethane.



However, the amount of hydrogen chloride thus formed (moreover, it could be consumed in the reaction with propylene), similarly as the small amount of the formed vinyl chloride were not so high that they could preclude the hydroformylation.

Under the above conditions, the dependence of the inhibition time J (min) on the amount of dichloroethane c_D (mole %) in the batch can be expressed by the following empirical equation

$$J = \frac{c_D}{8.25 \times 10^{-3}}\,.$$

1,2-Dichloroethane did not influence the ratio of the formed *n*-butyraldehyde and isobutyraldehyde (Table 1).

Trichloroethylene (Table 2) exhibited a significantly lower inhibitory effect than dichloroethane (probably a smaller amount of hydrogen chloride was split off in this case). Higher amounts than 5×10^{-2} mole of trichloroethylene practically stopped the hydroformylation of propylene before reaching a total conversion.

Table 2

Effect of trichloroethylene on hydroformylation of propylene

The overall time of experiment (min)	Inhibition time (min)	Additives of trichloroethylene		Conversion of propylene (%)	*n*-Butyraldehyde : isobutyraldehyde in the product (wt)	Rate constant of hydroformylation $k \cdot 10^3$ min^{-1}
		mol 10^2	mole % in the batch			
175	0	0.00	0.00	99.9	1.11	23.0
175	7	0.38	0.71	99.8	1.08	23.1
180	10	0.76	1.43	99.2	1.03	18.4
175	10	1.90	3.68	98.0	1.11	10.5
280	30	3.80	7.77	94.5	1.10	9.1
400	40	5.70	12.38	82.9	1.23	7.0
380	75	7.62	17.52	85.3	1.20	7.1
470	110	11.43	30.10	33.8	1.10	2.1
60	—	19.05	70.20	0	—	—

Probably the double bond in trichloroethylene made possible the formation of stable (*e.g.* by substitution of phosphines or by a formation π complexes) and consequently catalytically ineffective complexes with the catalyst (equilibrium was shifted significantly to the side of the catalytically ineffective complex). Our conception on the deactivation of the rhodium catalyst by trichloroethylene was supported also by the fact that we failed to hydroformylate trichloroethylene (see later).

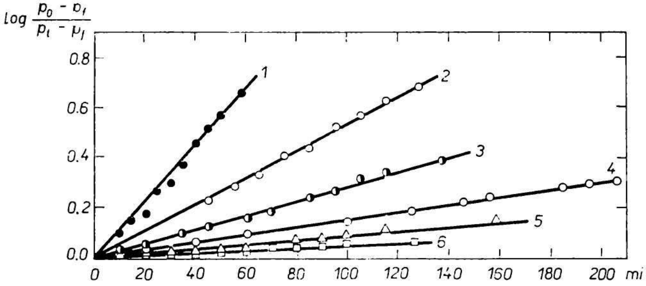


Fig. 2. Reaction rate *vs.* the amounts of tetrachloromethane.
1. Reference experiment (without CCl_4); *2.* 0.0584 g (0.0702 × 10^{-2} mole %) CCl_4; *3.* 0.1169 g (0.139 × 10^{-2} mole %) CCl_4; *4.* 0.292 g (0.354 × 10^{-2} mole %) CCl_4; *5.* 0.494 g (0.597 × 10^{-2} mole %) CCl_4; *6.* 0.584 g (0.71 × 10^{-2} mole %) CCl_4.

Tetrachloromethane affected the decrease of the hydroformylation rate more significantly (Fig. 2). This is evidently connected with a greater ability to split off chlorine (*e.g.* under the formation of trichloromethyl radical or ion) since the energy of $Cl_3C—Cl$ bond is only 284.7 kJ mol^{-1} [8, 9] while that of C—Cl bond in dichloroethane is 351.7 kJ mol^{-1}. Then it is not surprising that tetrachloromethane had a higher inhibitory and a significant retardation effects on hydroformylation of propylene (Table 3).

For the relation of the degree of conversion x with the concentration of tetrachloromethane C_{CCl_4} (mole %), under the above conditions, the following empirical equation is valid

$$= (0.985 \pm 0.0429) - (85.208 \pm 7.73)\, C_{CCl_4}.$$

Hydroformylation of allyl chloride was not successful even with a threefold amount of the catalyst (19.5 × 10^{-6} mole). Allyl chloride (14.5 g) hindered also the hydroformylation of propylene (25 g). Experiments using pyridine as a solvent were also unsuccessful though pyridine could shift the reaction course to the formation of the catalytically active hydridocarbonylrhodium by binding the possibly formed hydrogen chloride.

The results can be explained by the fact that allyl chloride, due to the double bond, can easily split off chlorine and form a relatively stable radical (stabilized by π electrons of the double bond) and subsequently a relatively stable and thus catalytically ineffective π complex with the catalyst.

Similarly, trichloroethylene and vinyl chloride were not hydroformylated even at the presence of a threefold amount of the catalyst.

Table 3

Effect of tetrachloromethane on hydroformylation of propylene

The overall time of experiment (min)	Inhibition time (min)	Additives of tetrachloromethane		Conversion of propylene (%)	n-Butyraldehyde : isobutyraldehyde in the product (wt)	Rate constant of hydroformylation $k \cdot 10^3$ min^{-1}
		mol 10^2	mole % 10^2 in the batch			
175	0	0.00	0.00	99.9	1.11	23.0
655	235	0.038	0.070	99.2	1.00	11.5
435	300	0.075	0.139	94.5	1.00	6.6
545	200	0.19	0.354	58.5	0.99	3.6
810	245	0.32	0.597	53.0	1.04	2.1
455	280	0.38	0.71	30.0	0.93	1.3
180	—	0.57	1.07	12.5	0.97	—
385	—	0.76	1.42	9.0	0.92	—

Hereby we have shown that the additives of chlorinated hydrocarbons had inhibitory and retardation effects on hydroformylation of olefins catalyzed by both carbonylcobalt [1] and carbonylrhodium, the differences being only quantitative. According to their effects on prolongation of the inhibition time and to the increase of retardation of propylene hydroformylation (under the above-mentioned conditions) the studied chlorinated hydrocarbons can be ranged as follows: trichloroethylene $<$ 1,2-dichloroethane $<$ tetrachloromethane with an approximate numerical expression 1 : 2.3 : 21 (wt) and 1 3.5 : 25 (mole), respectively.

From these results it also follows that chlorinated hydrocarbons are not suitable as solvents for this process and that the reaction mechanism of hydroformylation of olefins catalyzed by both carbonylcobalt and carbonylrhodium is similar.

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