

A Contribution to the Study of Hydroformylation of Halogenoolefins

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Vinyl chloride and allyl chloride were not hydroformylated even if dicobalt octacarbonyl concentration was as high as 2—6 %. After hydroformylation of allyl chloride from the reaction mixture were isolated cobaltous chloride, organic polymer and 1,5-hexadiene.

The attempts to hydroformylate halogenoolefins have been already reported [1—3], however, no positive results have been achieved. On the other hand, M. H. El-Makhzangi [4] succeeded in hydroformylation of some halogenoolefins viz. vinyl chloride to α -chloropropionaldehyde and identified also acrolein and propionaldehyde in the product. The preparation of fluoroaldehydes and fluoroalcohols via hydroformylation of fluoroolefins [5] and, in general, the synthesis of halogenoaldehydes, starting from substituted halogenoolefins with temperature being in the range 95—115 °C [6] has been patented. We succeeded in hydroformylation [7, 8] of fluoroarylallylethers and chloroarylallylethers to the corresponding fluoroarylalkoxyalkanes or chloroarylalkoxyalkanes in a high yield. On the other hand, the experiments on hydroformylation of 1,2-dichloroethane carried out under similar conditions, and, eventually at substantially higher concentration of dicobalt octacarbonyl [9] have failed. It was assumed [9] that it was because of high temperature (140—150 °C) under which hydrogen chloride can be split off, decomposing in turn dicobalt octacarbonyl giving rise to cobaltous chloride, hydrogen and carbon monoxide.

The aim of the presented work was to shed light on the mentioned contradictions.

Experimental

Materials

Allyl chloride, b. p. 44.5 °C/748 torr; bromine number 208.2 g Br₂/100 g; water contents 0.03 % (w).

4-Chlorophenylallylether, b. p. 106—107 °C/12 torr; $d_4^{20} = 1.1293$ g/cm³; iodine number 102.2 g I/100 g.

2,4-Dichlorophenylallylether, b. p. 121.6 °C/8 torr; hydroxyl number 0; bromine number 81.2 g Br₂/100 g; $d_4^{20} = 1.2602$ g/cm³; $n_D^{20} = 1.5536$.

Dichloroethane was of analytical grade.

Dicobalt octacarbonyl and an equimolar mixture of carbon monoxide and hydrogen have been specified already [10], the other, mostly auxiliary substances were of analytical grade.

Procedure

To half or one liter stainless steel autoclaves was added the needed amount of chloroolefin, a solvent if necessary other additives, dicobalt octacarbonyl and, in some experiments, after removing air was added propylene, and always an equimolar mixture of

carbon monoxide and hydrogen so that the pressure of ca 155 at was reached. The rotating autoclave was heated in order to reach the desired temperature. Both temperature and pressure were recorded in 5 min intervals. In the experiments when hydroformylation was performed at the temperature higher than 120 °C the catalyst i. e. dicobalt octacarbonyl was transferred into the reaction mixture from a special vessel attached inside of the autoclave only after the desired temperature was reached and at that moment also the rotation began. The time, when the temperature was reached was taken as the starting point for measurements. The experiments were continued until the decrease of pressure stopped. In the experiments in which hydroformylation did not work, they were interrupted only after 4–6 hours. The autoclave was cooled down, and the product weighted. The reaction rate was determined from the decrease of pressure and the reaction constants were calculated from the known kinetic equations [11].

The analysis of the product from hydroformylation of allyl chloride

The product was filtered in an atmosphere of nitrogen. A solid consisting, according the elemental analysis of cobalt, chlorine, carbon and hydrogen, was triturated and washed with light-petroleum and dried in an inert atmosphere. Infrared spectra (in KBr pellets) of the reaction product and dry CoCl_2 were measured using an UR-10 (VEB Carl Zeiss, Jena) infrared spectrometer.

A sample of the product (0.5022 g) was then refluxed in 100 ml of distilled water for 40 minutes, filtered, the insoluble residue was again extracted with 50 ml of water for 30 minutes, filtered and dried. The resulting brown-yellowish product represented 5.2 % (0.0236 g) of the original sample. In a similar manner an additional amount of the insoluble residue was prepared. Its elemental analysis (79.21 % C, 12.6 % H, 3.74 % Cl) was performed and also was run its infrared spectrum (in KBr).

A pink filtrate was first concentrated in order to crystallize out $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. The crystalline product was identified by the analysis of cobalt and chlorine.

The analysis of the product after removal of solids was carried out employing gas-liquid chromatography. A column (3 × 200 mm) was packed with an adsorbent (grain-size 0.12–0.15 mm) treated with 5 % of a stationary phase consisting of Tridox (alkylpolyglycoether) and Slovafof (alkylphenolpolyglycoether) in the ratio 1 : 1. As a carrier gas was used hydrogen at a flow rate 60 ml/hr, column temperature 82.7 °C. Retention times for *n*-hexane, 1,5-hexadiene, allyl chloride and toluene were 1 min 18 s; 1 min 30 s; 2 min 15 s; and 11 min 36 sec, respectively.

Results and discussion

The results of the experiments on hydroformylation of propylene in the presence of allyl chloride, vinyl chloride and dichloroethane along with the results of hydroformylation of allyl chloride, vinyl chloride and 4-chlorophenylallyl ether alone, as well as the reaction conditions are listed in Tab. 1. The course of some experiments is demonstrated on Fig. 1.

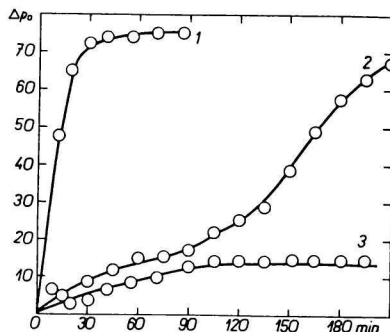
From the presented results it can be seen that allyl chloride in not hydroformylated even at 4–6 % concentration of dicobalt octacarbonyl at 100–140 °C. In its presence or in the presence of vinyl chloride neither hydroformylation of propylene can take place. The retardation effect of dichloroethane and namely allyl chloride on hydro-

Table 1
Hydroformylation of propylene in the presence of chlorinated hydrocarbons or chloroolefins alone

| Volume of autoclave [l] | Batch consisted of [g] | | | | | | Temperature [°C] | Overall time of experiment [hr] | Conversion of hydroformylation [%] | Rate constant $k \cdot 10^3$ [min ⁻¹] | Remarks |
|-------------------------|------------------------|------------------------------|--------|----------|--------|-----------------------------------|------------------|---------------------------------|------------------------------------|---|--|
| | Propylene | Chlorinated hydrocarbon | | Solvent | | Co ₂ (CO) ₈ | | | | | |
| | | compound | amount | compound | amount | | | | | | |
| 0.7 | — | allyl chloride | 38 | toluene | 50 | 1.7 | 75 | 6 | 0 | — | with addition of 0.3 g of pyridine |
| 1 | — | allyl chloride | 76.5 | — | — | 1.7 | 100 | 7 | 0 | — | |
| 0.7 | — | allyl chloride | 38 | butanol | 50 | 0.86 | 100 | 6 | 0 | — | |
| 1 | — | allyl chloride | 76.5 | butanol | 50 | 1.7 | 120 | 6 | 0 | — | |
| 1 | — | allyl chloride | 76.5 | toluene | 50 | 1.7 | 140 | 4 | 0 | — | reference experiment 0.5 g of hydroquinone added 0.5 g of hydroquinone added |
| 1 | 50 | dichloroethane | 25 | toluene | 25 | 0.58 | 143 | 4 1/2 | 91 | — | |
| 1 | 50 | dichloroethane | 26 | toluene | — | 0.58 | 140 | 4 | 89 | — | |
| 1 | 50 | allyl chloride | 17 | toluene | 34 | 0.58 | 140 | 3 1/2 | 24 | — | |
| 1 | 50 | — | — | toluene | 50 | 0.58 | 140 | 2 1/2 | 99.5 | 9.7 | |
| 1 | 50 | vinyl chloride | 14 | toluene | 50 | 0.58 | 140 | 3 | 14.5 | — | |
| 1 | 50 | vinyl chloride | 14 | toluene | 50 | 0.58 | 140 | 4 1/2 | 0 | — | |
| 1 | — | vinyl chloride | 31 | toluene | 50 | 1.0 | 140 | 4 | 0 | — | |
| 1 | — | allyl chloride | 76.5 | toluene | 50 | 3.0 | 100 | 5 | 0 | — | |
| 1 | — | allyl chloride | 76.5 | toluene | 50 | 5.0 | 140 | 4 | 0 | — | |
| 1 | — | 4-chlorophenylallylether | 70 | — | — | 1.0 | 150 | 1 1/2 | 99 | 5.0 | |
| 1 | — | 2,4-dichlorophenylallylether | 100 | — | — | 0.58 | 140 | 1 | 99 | 6.5 | |

Fig. 1. The course of hydroformylation of propylene alone and in the presence of dichloroethane and allyl chloride at $141 \pm 2^\circ\text{C}$ and 1.16 % (w) of dicobalt octacarbonyl.

1. propylene in absence of chlorinated hydrocarbon (reference experiment); 2. in the presence of 0.22 mol. of dichloroethane; 3. in the presence of 0.22 mol. of allyl chloride.



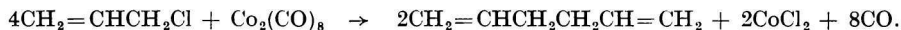
formylation of propylene is evident (Fig. 1). The obtained products do not contain cobalt carbonyls presenting thus an evidence that hydroformylation was retarded or completely stopped by decomposition of hydroformylation catalyst. This effect was more pronounced in the attempts to hydroformylate vinyl chloride and allyl chloride, respectively, when, even at low temperatures ($75\text{--}140^\circ\text{C}$) and a high concentration of dicobalt octacarbonyl hydroformylation, as the matter of fact, has not been started. On the other hand, hydroformylation of 4-chlorophenylallyl ether and 2,4-dichlorophenylallyl ether proceeds at a similar rate as hydroformylation of higher olefins [12] and the reaction rates check with the first-order kinetic equation. It follows that the deciding fact for hydroformylation is the stability of C—halogen linkage in organic halogen-containing compounds and the possibility to split off hydrogen halogenide or hydrogenolysis. The C—F linkage is stronger than C—Cl one (bond energy of C—F is 107 kcal, of C—Cl 66.5 kcal). Consequently, fluoroolefins are easily hydroformylated to fluoroaldehydes [5]. Allyl chloride readily forms complexes with cobalt carbonyls facilitating thus the removal of halogen, the process favoured by stabilising effect of π -electrons of the double bond. However, this is not the case with dichloroethane, even if hydrogen chloride can be split off readily; in its presence hydroformylation of olefins still can be carried out. If chlorine is attached to an aromatic nucleus neither the removal of hydrogen chloride can be considered.

From the reaction mixtures resulting from our attempts to hydroformylate allyl chloride was isolated a compound resulting from reaction or decomposition of cobalt carbonyls with allyl chloride. Comparing the infrared spectra of this compound and that of pure cobaltous chloride they were shown to be almost superimposable. So, under the conditions of hydroformylation dicobalt octacarbonyl is decomposed by allyl chloride and vinyl chloride giving rise to cobaltous chloride. As it was found [13, 14] the latter, being the salt of a very strong acid, stronger than cobalt hydro-tetracarbonyl, cannot under the given conditions form cobalt tetrahydrocarbonyl, the catalyst of hydroformylation.

Extraction and crystallisation of the given compound afforded pure cobaltous chloride, in addition to the rest of water-insoluble organic compound, which formed 5.24 % of the original sample. From the elemental analysis (79.21 % C, 12.62 % H, 3.75 % Cl) and the infrared spectrum with the absorption bands at $\tilde{\nu}$ (cm^{-1}) 3040—2800, maxima 2930 (s) and 2870 (m), 1800—1690 with maxima at 1760—1710 (m), 1490—1420 with maxima at 1460 (m) and 1390—1375 (w) it was evident that we were dealing with an organic compound. It originated probably from polymerisation

of the reaction products of dicobalt octacarbonyl with allyl chloride, or also by copolymerisation with allyl chloride.

Finally, in the liquid product after separating the compound resulting from decomposition of dicobalt octacarbonyl with allyl chloride, by gas-liquid chromatography was identified 1,5-hexadiene which on hydrogenation on palladium was converted to *n*-hexane. 1,5-Hexadiene originated probably from allyl chloride by the action of cobalt carbonyls e. g. dicobalt octacarbonyl:



The situation is presumably analogous to that reported [15—18] on action of nickel tetracarbonyl on allyl chloride.

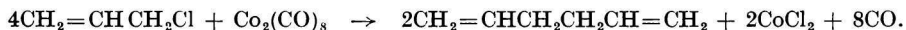
PRÍSPEVOK K ŠTÚDIU HYDROFORMYLÁCIE HALOGÉNOLEFÍNŮV

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Pri hydroformylácii propylénu pri teplote okolo 140 °C a koncentrácii 1,16 % hm. oktokarbonylu dvojkobaltu má dichlóretán retardačný účinok, avšak v prípade vinylchloridu a alylchloridu hydroformylácia už takmer neprebíha. Samotný vinylchlorid a alylchlorid sa dokonca ani pri koncentrácii 2—6 % oktokarbonylu dvojkobaltu (na hmotu alylchloridu) nehydroformylujú. Naproti tomu 4-chlórfenylalyléter i 2,4-dichlórfenylalyléter sa ľahko hydroformylujú a rýchlosť je porovnateľná s rýchlosťou hydroformylácie vyšších olefinov.

Rozhodujúca pre hydroformyláciu halogénolefinov alebo olefinov za prítomnosti halogénuhlovodíkov je predovšetkým pevnosť väzby uhlík—halogén, ako aj schopnosť odštiepovať halogénvodík. V prípade alylchloridu sa z produktu izolovala tuhá látka, pozostávajúca z 94,8 % chloridu kobaltnatého a 5,2 % organického polyméru. V kvapalnom produkte sa zistil 1,5-hexadién. Jednou z reakcií bol zrejme rozklad oktokarbonylu dvojkobaltu alylchloridom:



ИЗУЧЕНИЕ ГИДРОФОРМИРОВАНИЯ ГАЛОГЕНОЛЕФИНОВ

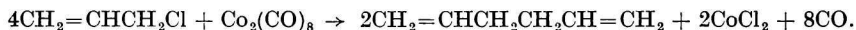
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При гидроформилировании пропилена при температуре 140° и концентрации 1,16 % вес. дикобальтоктокарбонила дихлорэтан действует как замедлитель, однако в случае винилхлорида и аллилхлорида гидроформилирование уже почти не протекает. Винилхлорид и аллилхлорид даже при концентрации 2—6 % дикобальтоктокарбонила (на вес аллилхлорида) не гидроформилируются. В противоположность этому 4-хлорфенилаллилэфир и 2,4-дихлорфенилаллилэфир легко гидроформилируются, причем

скорость их гидроформилирования сравнительна со скоростью гидроформилирования высших олефинов.

Решающим при гидроформилировании галогенолефинов или олефинов в присутствии галогенуглеводородов является сила связи углерод—галоген, а также способность отщеплять галогенводород. В случае аллилхлорида из продукта выделили твердое вещество, состоящее из 94,8 % хлористого кобальта и 5,2 % органического полимера. В жидком продукте нашли 1,5-гексадиен. Одной из реакций было, очевидно, разложение дикобальтоктокарбонила аллилхлоридом:



Перевела Т Диллингерова.

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