

Hydrogenation of Chlorinated Butenes

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Hydrogenation of several dichlorobutenes and 2,3,4-trichloro-1-butene was investigated. The most effective catalyst from the group of light and heavy platinum metals was found to be rhodium black adsorbed on alumina. This catalyst had the most selective effect on the hydrogenation of chlorinated alkenes. The hydrogenation proceeded with all the compounds under study, whereby also reductive dehalogenation took place and, consequently, the amount and the composition of hydrogenation products depended on the structure of alkene used.

The hydrogenation of chlorinated alkenes has not afforded in most cases chloroalkanes containing the original number of chlorine atoms in the molecule because the reductive dehalogenation predominantly occurred [1–5].

The communication of *Ham* and *Coker* [6] on the hydrogenation of 1,3-dichloropropene belongs to the small number of papers describing partially successful hydrogenation of chloroalkenes. Besides the hydrogenation yielding 1,3-dichloropropane also partial or total hydrogenolysis took place. The maximum yield of 1,3-dichloropropane was 50%.

In the present work we tried to find conditions and a selective catalyst for the hydrogenation of chlorinated alkenes. *trans*-1,3-Dichloro-2-butene, which is one of the starting substances for the production of 2,3-dichloro-1,3-butadiene (a comonomer for the preparation of chloroprene rubber), has been chosen as a model substance. The hydrogenation method was intended to be one of the identification procedures used in the analysis of raw materials and products in the 2,3-dichloro-1,3-butadiene production technology [7].

To prove the general use of rhodium as a selective hydrogenation catalyst we tested this reaction with different chlorinated C-4 alkenes:

- a) 3,4-dichloro-1-butene, where chlorine atoms are not linked to carbons joined together with double bond and where the double bond is located at the end of the molecule;
- b) *cis*-1,4-dichloro-2-butene, where the double bond is located in the middle of the molecule and the chlorine atoms are not directly linked to carbons bearing the double bond;
- c) 2,3,4-trichloro-1-butene containing in its molecule three C—Cl bonds and therefore affording a greater probability of cleavage of these bonds in the course of hydrogenation and thus yielding a greater variety of products.

Experimental

Materials

The values in the brackets are the reference data found in the literature.

trans-1,3-Dichloro-2-butene, prepared by addition of HCl to chloroprene [9] and subsequent

rectification. B.p. 128.2°C/760 Torr (127.9°C/745 Torr [8]); n_D^{20} 1.4719 (1.4719 [8]); ϵ_4^{20} 1.1590 (1.1585 [8]).

cis-1,3-Dichloro-2-butene, prepared according to [8] and isolated according to [7]. B.p. 50—51°C/40 Torr (129.9°C/745 Torr [8]); n_D^{20} 1.4740 (1.4731 [8]); ϵ_4^{20} 1.1610 (1.1605 [8]).

1-Chlorobutane, prepared by reaction of HCl and anhydrous ZnCl₂ with 1-butanol. B.p. 78.0—78.6°C/760 Torr (78.6°C/760 Torr [9]); n_D^{20} 1.4028 (1.4023 [9]); ϵ_4^{20} 0.8846 (0.8845 [9]).

2-Chlorobutane, prepared by reaction of HCl and anhydrous ZnCl₂ with 2-butanol. B.p. 67—68°C/760 Torr (68°C/760 Torr [10]); n_D^{20} 1.3976 (1.3970 [10]); ϵ_4^{20} 0.8712 (0.8740 [10]). Purity 98.5%, determined chromatographically.

1,1-Dichlorobutane, prepared by chlorination of butyraldehyde with PCl₅, rectified. B.p. 80.2°C/760 Torr (113—115°C/760 Torr [11]); n_D^{20} 1.4333 (1.4355 [11]); ϵ_4^{20} 1.0846 (1.0863 [11]). Purity 99%, determined chromatographically.

2,2-Dichlorobutane, prepared by chlorination of methyl ethyl ketone, with PCl₅, rectified. B.p. 40°C/140 Torr (102—104°C/760 Torr [12]); n_D^{20} 1.4301 (1.4306 [12]); ϵ_4^{20} 1.0694 (1.0665 [12]). Purity 96.3%, determined chromatographically.

1,2-Dichlorobutane, prepared by chlorination of 1-chlorobutane with elemental chlorine, rectified. B.p. 53.5°C/68 Torr (124°C/760 Torr [13]); n_D^{20} 1.4449 (1.4474 [13]); ϵ_4^{20} 1.1161 (1.1182 [13]). Purity 99%, determined chromatographically.

1,3-Dichlorobutane, prepared in the same way as 1,2-dichlorobutane, rectified. B.p. 61.5°C/68 Torr (131—133°C/760 Torr [14]); n_D^{20} 1.4452 (1.4443 [14]); ϵ_4^{20} 1.1143 (1.1174 [14]). Purity 98%, determined chromatographically.

1,4-Dichlorobutane, prepared in the same way as 1,2-dichlorobutane, rectified. B.p. 79.0—79.5°C/70 Torr (77—79°C/62 Torr [15]); n_D^{20} 1.4558 (1.4542 [15]); ϵ_4^{20} 1.1457 (1.1410 [15]). Purity 94%, determined chromatographically.

1,2,3-Trichlorobutane, prepared by chlorination of 1,2-dichlorobutane with elemental chlorine [16], rectified. B.p. 98.5°C/100 Torr (165—169°C/760 Torr [16]); n_D^{20} 1.4779 (1.4790 [16]); ϵ_4^{20} 1.3155 (1.3164 [16]). Purity 98.5%, determined chromatographically.

3,4-Dichloro-1-butene (Research Institute of Petrochemistry, Nováky), rectified. B.p. 115.5 ± 0.2°C/760 Torr (115°C/760 Torr [17]); n_D^{20} 1.4632 (1.4630 [17]).

cis-1,4-Dichloro-2-butene (Research Institute of Petrochemistry, Nováky), rectified. n_D^{20} 1.4891 (1.4882 [18]). Purity 96%, determined chromatographically. The main part of the residue consisted of *trans*-1,4-dichloro-2-butene.

2,3,4-Trichloro-1-butene, prepared by chlorination of 1,3-dichloro-2-butenes [19]. n_D^{20} 1.4936 (1.4944 [19]); ϵ_4^{20} 1.3421 (1.3430 [19]). Purity 94.6%, determined chromatographically. The main part of the residue consisted of *trans*-1,2,3-trichloro-2-butene.

Additional chemicals used were:

PdCl₂ in 10% (w/v) aqueous solution, RhCl₃, H₂PtCl₆, and RuCl₄, all reagent grade, were purchased from Safina (Czechoslovakia), OsO₄ (Johnson, Mathley and Co., Ltd., London), alumina for chromatography (Lachema, Brno), and electrolytically prepared hydrogen. Cyclohexane and 37% (w/v) aqueous solution of formaldehyde were of analytical purity. Mono-, di-, and trichlorobutanes were used as standards for gas chromatography.

Methods

Hydrogenation was carried out in a 250-ml rocking stainless steel autoclave built for pressures up to 300 kp cm⁻² with a double jacket equipped with a heater having an input of 250 W. The thermometer tube reached into the working space. The sample of chlo-

minated alkene was dissolved in cyclohexane at a molar ratio 1 : 9. After adding the catalyst adsorbed on a carrier (the amount used represented 30% of the weight of chloroalkene), the autoclave was heated to working temperature and the hydrogen was introduced up to the final pressure of 100 kPa cm⁻².

We tested all the highly effective hydrogenation catalysts, *i.e.* all the light and heavy platinum metals (except iridium), in our experiments. For comparison of their effectiveness the temperature of 20°C and 2 hours' reaction time were chosen.

All catalysts were prepared by reduction of the corresponding metal with formaldehyde from slightly alkaline aqueous solution of its salt in the presence of an insoluble carrier. The suspension was then filtered and the precipitate was dried.

The reaction courses were followed discontinuously in all cases. The hydrogenation products were analyzed by gas chromatography using the method of direct calibration.

Results and Discussion

The results of hydrogenation of *trans*-1,3-dichloro-2-butene summarized in Table 1 show that the best of all the catalysts used was rhodium. In the presence of this catalyst the hydrogenation predominated over the hydrogenolysis. Platinum was less effective and in the presence of palladium only partial or total hydrogenolysis occurred. Ruthenium and osmium were absolutely ineffective.

Table 2 shows that the composition of the reaction product practically did not vary with temperature at the temperatures above 36°C. The temperature of 20°C was chosen

Table 1

Effect of different catalysts on hydrogenation of *trans*-1,3-dichloro-2-butene

Catalyst	Composition of hydrogenation product [mole %]			
	<i>n</i> -butane	monochlorobutanes	<i>trans</i> -1,3-dichloro-2-butene	1,3-dichlorobutane
Ru	0.0	0.0	100.0	0.0
Rh	11.8	35.7	0.0	52.5
Pd	11.9	6.9	81.2	0.0
Os	0.0	0.0	100.0	0.0
Pt	72.6	8.0	0.0	19.4

Table 2

Effect of temperature on hydrogenation of *trans*-1,3-dichloro-2-butene

Temperature [°C]	Composition of hydrogenation product [mole %]				
	<i>n</i> -butane	2-chlorobutane	1-chlorobutane	<i>trans</i> -1,3-dichloro-2-butene	1,3-dichlorobutane
20	6.6	0.8	12.6	40.4	39.6
36	11.0	8.3	31.8	0.0	48.9
43	11.4	7.0	33.3	0.0	48.3
58	12.6	5.6	33.0	0.0	48.8

for the hydrogenation experiments because at this temperature the reaction courses could be easily followed.

From Table 3 it follows that the hydrogenation of *trans*-1,3-dichloro-2-butene was completed after 75 minutes under the given conditions and that after this time no unsaturated hydrocarbons could be found in the reaction mixture. No changes in the composition of the reaction product could be found even when extending the reaction time up to 3 hours.

Tables 4–7 indicate that rhodium can be used as a catalyst in the hydrogenation of all chlorinated dichloro- and trichlorobutenes tested.

Table 3

Time course of hydrogenation of *trans*-1,3-dichloro-2-butene

Time [min]	Composition of hydrogenation product [mole %]				
	<i>n</i> -butane	2-chlorobutane	1-chlorobutane	<i>trans</i> -1,3-dichloro-2-butene	1,3-dichlorobutane
15	2.9	1.5	4.9	90.6	0.0
30	6.6	2.5	12.5	65.4	13.0
45	7.2	3.0	15.0	38.5	36.3
60	11.2	5.9	27.6	4.4	49.7
75	11.6	7.4	27.9	0.0	50.9

Table 4

Hydrogenation of *cis*-1,3-dichloro-2-butene

Time [min]	Composition of hydrogenation product [mole %]			
	<i>n</i> -butane	monochlorobutenes	1,3-dichlorobutane	<i>cis</i> -1,3-dichloro-2-butene
15	0.0	0.0	0.0	100.0
30	15.0	15.3	7.3	62.4
45	17.2	21.9	17.2	43.7
60	21.8	25.5	43.5	9.0
75	23.8	27.7	45.8	1.7
90	24.5	28.4	46.1	0.0

Table 5

Hydrogenation of 3,4-dichloro-1-butene

Time [min]	Composition of hydrogenation product [mole %]				
	<i>n</i> -butane	2-chlorobutane	1-chlorobutane	3,4-dichloro-1-butene	1,2-dichlorobutane
0	0.0	0.0	0.0	100.0	0.0
30	17.2	6.2	5.8	0.0	70.8

Table 6
Hydrogenation of *cis*-1,4-dichloro-2-butene

Time [min]	Composition of hydrogenation product [mole %]			
	<i>n</i> -butane	1-chlorobutane	1,4-dichlorobutane	<i>cis</i> -1,4-dichloro- -2-butene
60	12.4	28.7	7.1	51.8
120	15.6	47.8	7.6	29.0
180	26.7	46.8	9.3	17.2
240	28.6	49.4	12.3	9.7

Table 7
Hydrogenation of 2,3,4-trichloro-1-butene

Time [min]	Composition of hydrogenation product [mole %]							
	<i>n</i> -butane	mono- chloro- butanes	1,2-di- chloro- butane	<i>trans</i> -1,3- -dichloro- -2-butene	1,3-di- chloro- butane	<i>trans</i> - -1,2,3-tri- chloro- -2-butene	2,3,4-tri- chloro- -1-butene	1,2,3-trichlo- robutane
0	0.0	0.0	0.0	0.2	0.0	5.2	94.6	0.0
60	5.7	1.1	11.9	27.7	0.0	4.6	29.5	19.5
90	8.3	1.3	12.5	19.4	6.2	5.2	16.9	30.2
120	10.7	1.5	14.3	8.3	15.0	5.2	1.2	43.7
150	12.1	1.6	18.8	0.8	17.5	2.7	0.0	44.9

The hydrogenation of *cis*-1,3-dichloro-2-butene (Table 4) proceeded little slower and with lower yield than the hydrogenation of *trans*-1,3-dichloro-2-butene.

The hydrogenation of 3,4-dichloro-1-butene (Table 5) gave the totally hydrogenated product (1,2-dichlorobutane) in 70% yield. The reaction proceeded much faster than the hydrogenation of other dichlorobutenes and after 30 minutes the reaction mixture did not contain the starting compound.

On the other hand, the hydrogenation of *cis*-1,4-dichloro-2-butene proceeded unexpectedly slowly (Table 6). Even after 4 hours' hydrogenation the reaction was not complete and the yield of 1,4-dichlorobutane in the reaction product was very low. The formation of 1-chlorobutane by partial hydrogenolysis prevailed in this case. So far, this fact has not been explained. It might be caused by considerable reactivity of chlorine atoms, both of which are allyl-type, in the molecule of *cis*-1,4-dichloro-2-butene and by steric reasons as well.

By hydrogenation of 2,3,4-trichloro-1-butene all the theoretically possible products were obtained (see Table 7); 1,2,3-trichlorobutane in relatively high yield, 1,2- and 1,3-dichlorobutanes, both monochlorobutanes, and butane as the product of total hydrogenolysis. It is interesting that in the first phase of the above reaction *trans*-1,3-dichloro-2-butene, formed probably in the course of consecutive dehydrochlorination reaction, appears. This is then due to the presence of an unsaturated bond in the molecule, again hydrogenated in the course of prolonged reaction time.

Based on the described experiments it can be stated that rhodium black can be used as a catalyst for hydrogenation of chloroalkenes. This catalyst showed the greatest selectivity in spite of the fact that besides hydrogenation also reductive dehalogenation took place in all cases, so that the reaction products contained a varied mixture of compounds.

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