Chapter 2

HETEROGENEOUS HYDROGENATION CATALYSTS BASED ON QUARTZ

Abstract

This chapter summarizes data about the application of chiral metal catalysts supported on optically active quartz crystals in hydrogenation and other reactions. Despite the low enantioselective efficiency of these catalysts, recent result show that almost 100% enantioselectivity results when they are involved in autocatalytic processes.

2.1. General

Adsorption of molecules on a catalytic surface is fundamental to any heterogeneous catalytic process. Therefore, it is necessary to distinguish between cases in which the catalyst itself is chiral, e.g. contains on its surface chiral complexes directing asymmetric reactions, and cases in which the catalyst surface is achiral but the catalyst is supported on a chiral carrier. In both cases the mechanism of action seems to be the same and reactions proceed through intermediate chiral complexes, including complexes on the surface of the catalyst, or through chiral fragments on the chiral carrier. It might be expected that both cases lead to asymmetric catalysis.

There were several attempts to prepare asymmetric catalysts without a chiral carrier. It was shown [1] that irradiation of thin films of AgCl by right or left circularly polarized light (R-CPL and L-CPL) resulted in their ability to rotate a plane of linear polarized light. It is, of course, not a true optical activation of the material, because the grains of remaining AgCl do not reveal any chiral structure. Indeed, under the action of polarized light the definite orientation of grains of AgCl occurs as a result of the so called Weigert effect. However, repetition of these experiments met many difficulties in reproducing the results [2,3]. But Ghosh [4] succeeded in the preparation of layers of 30 nm thick AgCl by irradiating a thin film of AgCl with R-CPL or L-CPL. These thin films of AgCl produced an observed optical rotation of -0.06°, or a specific rotation about -10000°. Prepared in such a way optically active films can be covered with Pt or Pd and after removing the AgCl (and Ag) by treatment with nitric acid the resulting thin films of Pt or Pd also exhibit optical activity with an observed rotation of -0.10°.

These films were suggested to be used as chiral catalysts for absolute asymmetric synthesis. But further communications in this field were absent; thus it is assumed that such experiments failed. Similar catalytic systems are of interest because in this manner it will be possible to turn common catalysts without chiral carrier into chiral catalysts like the "Bredig ferment" [5,6]. When the Et_2N group is introduced into the cellulose of cotton fibres, they are transformed into active catalyst which can reproduce the asymmetric activity of carboxylase, the enzyme for the asymmetric decomposition of enantiomers of camphorcarboxylic acid, and the activity of oxynitrilase for catalyzing the synthesis of (-)-mandelonitrile. A catalyst of this type was obtained in 1932 by Bredig and Gerstner [6]. These authors regarded this example as the first case of heterogeneous asymmetric catalysts. Indeed, the mechanism of the chiral action of a catalyst by this sort depends on asymmetric adsorption on the optically active cellulose carrier. Such asymmetric adsorption on natural materials is well documented by the numerous reports of stereoselective adsorption of enantiomers and of chromatographic techniques resolving racemates of amino acids on cellulose columns. Thus, Yuasa [7] succeeded in resolving without derivatization a number of racemic amino acids on native cellulose columns.

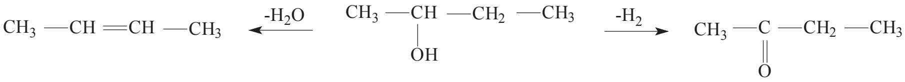
A similar mechanism of action was found in the case of a Pd catalyst supported on silk fibroin [8,9] in the asymmetric hydrogenation of C=N bonds in prochiral compounds. The mechanism of action consists of the formation of the chiral complexes on the silk fibres of the Pd-fibroin which act as chiral catalysts. This principle was later developed for a number chirally modified catalysts that are very effective in the asymmetric hydrogenation of *beta*-keto esters [9,10].

2.2 Asymmetric hydrogenation on metal-quartz catalysts

The asymmetric adsorption of some organic and complex compounds on quartz crystals was described in Chapter 1.2. In 1932 Schwab and coworkers were first to show that chiral quartz crystals can be used as chiral supports for metal catalysts [11-14]. Seven years later Stankiewicz, in his dissertation [15], confirmed these results, and later Terentyev and Klabunovskii extended the scope of asymmetric reactions using "Metal-Quartz Catalysts" [16-24].

Schwab and Rudolph [11] prepared chiral catalysts by supporting the metals on the surfaces of ferreted fine powdered optically active quartz crystals, which proved to be active during asymmetric dehydrogenation and dehydration of racemic butan-2-ol. The dehydration-dehydrogenation reactions of butan-2-ol (Scheme 2.1.) were carried out in the vapor phase at

400-500^{0}C and atmospheric pressure with catalysts composed of Cu, Ni, or Pt deposited in thin layers on *d*- or *l*-quartz.



Scheme 2.1. Dehydration and dehydrogenation of butan-2-ol.

The reactions resulted in very small preferential decompositions of one of the enantiomers of racemic butan-2-ol. The remaining unreacted butan-2-ols exhibited small optical rotations. Catalysts were prepared by immersion of fine powdered crystals of Dophinee quartz into solution of salts of metals in concentrations needed for formation of monoatomic layers of metals on the surfaces of the quartz crystals. These impregnated crystals were ignited, the salts decomposed, and the resulting catalysts reduced in flowing hydrogen. The catalysts were placed in a circulating catalytic reactor system in which racemic butan-2-ol vapors were entrained in nitrogen or air and passed over the catalyst bed. The resulting liquid reaction products were investigated polarimetrically. Optical rotations were extremely small and did not exceed 0.2-0.3^o. Polarimetric measurements of liquid products are considered valid if rotations exceed ± 0.03^o. Likely, as a result of the asymmetric action of these chiral catalysts, the decomposition of the enantiomers of racemic butan-2-ol proceeded with different rates and resulted in unreacted butan-2-ol with an optical rotation of approximately 0.10^o. For a Ni-quartz catalyst a maximal optical rotation of +0.13^o was observed for the product. If that product was passed again through a new bed of the same catalyst, the optical rotation could be increased up to +0.20^o, as shown on Figure 2.1.

Catalysts based on *l*-quartz predomonantly decomposed the (+)-enantiomer of butan-2-ol, so the product mixture had a (-)-optical rotation. Considering the mechanism of action of that chiral catalyst the authors [12] concluded that a maximal effect may be attained at small coverings of metal (close to a monoatomic layer) on the chiral surface of the optically active quartz. Increasing the content of metal increased the rate of reaction but decreased the asymmetric effect and as well as the resulting optical rotation of the product (Figure 2.2.).

At high reaction temperatures (400-500^{o}C) the rate of racemization of the optically active butan-2-ol becomes fast enough that the optical rotation of the product goes through a maximum as a function of reaction time. Results received with a 0.10% Ni-*d*-quartz catalyst at 550-560^{o}C are shown below in Table 2.1.

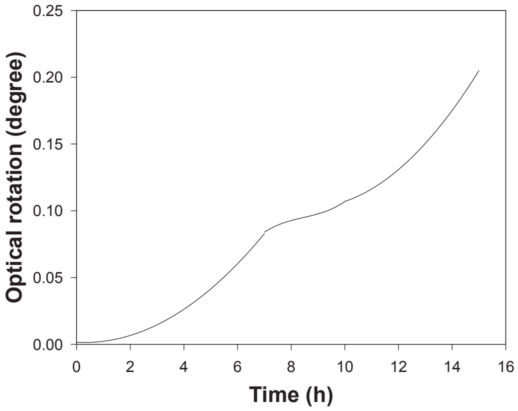


Figure 2.1. The increase in optical rotation during the decomposition of racemic butan-2-ol over Cu-*d*-quartz catalyst at 400°C, after addition of a fresh portion of the catalyst at 8h (Schwab et al. [11,12]).

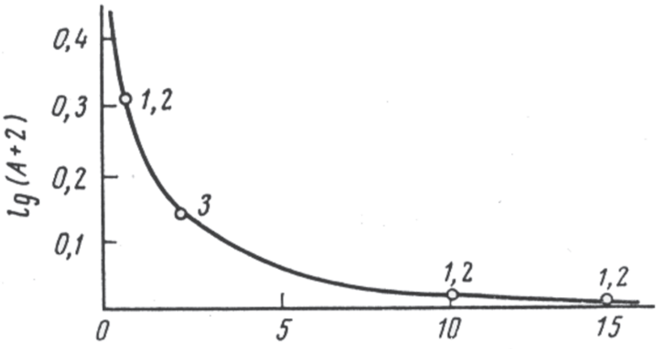


Figure 2.2. Dependence of optical rotation of butan-2-ol on reaction time and on extent of surface coverage by Pt on the *d*-quartz.
(1) 1 atomic layer of Pt, (2) 1.5 atomic layers of Pt, (3) 2 atomic layers of Pt (adapted from Schwab et al. [12] and Klabunovskii [32]).

Reaction time (h)	Conversion (%)	α (^{o})	*ee* (%)
5.2	3.6	+ 0.016	0.07
8.0	5.8	+ 0.073	0.32
Reaction mixture was passed through a new bed of the catalyst.			
5.2	3.0	+ 0.03	0.15
9.2	5.4	+ 0.12	0.53
13.7	7.8	+ 0.05	0.21
18.7	11.0	+ 0.01	0.03

Table 2.1. Asymmetric decomposition of butan-2-ol over a 0.10% Ni-*d*-quartz catalyst at 550-560^{0}C; length of tube, 20 cm (adapted modified data from Schwab et al. [12]).

In 1938 Stankiewicz [15] reproduced the asymmetric 2-butanol decomposition experiments of Schwab (1932) at a higher temperature and atmospheric pressure and extended studies to the asymmetric decomposition of racemic menthol and 3-methylheptan-3-ol. Over a Cu-*d*-quartz catalyst the latter substrate produced a maximal optical rotation of -0.26^0 and the decomposition of 2-butanol gave a reaction mixture with a rotation of $+0.25^0$.

For the preparation of catalysts the crystals of *d*-quartz from the Idar deposit were used (quartz crystals from the mineral-collection of Crantz (Bonn) did not give good results). Crystals were sawed into plates of 12-15mm thick perpendicular to the optical axes and plates were carefully studied in a polariscope for absence of the Brasilian twinning area. An analogous procedure for obtaining *l*-quartz was applied. Crystals were then crushed in a mortar to 2-4 mm particles and washed with king's-water. Specific areas were estimated at 8 cm^2/g. Catalysts were prepared by two methods:

1) by high vacuum cathodic scattering of Pt on quartz powder with periodic shaking to obtain uniform layers
2) by immersion of quartz powder into water solutions of salts of Cu and Ni.

After calcinations and reductions in flowing hydrogen at 450^0 the resulting catalysts were used in the vapor phase decomposition of alcohols. It was calculated that the Cu-catalysts received in such a way contained 19 atomic layers and the Ni catalyst 160-240 atomic layers.

Carrying out vapor phase experiments in N_2 or N_2/air and attaining a polarimetric accuracy of $\pm 0.01^0$, Stankiewicz[15] found that such catalysts were more effective than those containing monoatomic layers, which contradicted the data of Schwab (1934).

For the case of the asymmetric decomposition of racemic butan-2-ol, the asymmetric effect depends on the conditions of the reaction and results in either dehydration or dehydrogenation (Scheme 2.1.). The asymmetric dehydrogenation of butan-2-ol on Cu-*d*-quartz in N_2-air mixture as flowing transport gas results in levorotatory products (Table 2.2.).

Temperature of reaction (^{o}C)	α_D (^{o})
280	- 0.08
320	- 0.15
330	- 0.16
340	- 0.21
390	- 0.08

Table 2.2. Temperature dependence of the optical rotation of the product mixture in the asymmetric dehydrogenation of butan-2-ol over a Cu-*d*-quartz catalyst in transport flow (nitrogen + air) (modified adapted data from Stankiewicz[15]).

In flowing dinitrogen, however, mainly the dehydration of butan-2-ol occurred and the remaining 2-butanol was dextrorotatory (Table 2.3.).

Table 2.3. shows that 500-505^{o}C is the optimal temperature range at which the (-)-enantiomer of butan-2-ol reacts somewhat faster than the (+)-enantiomer, and under this condition of dehydration the orientation of a molecule of butan-2-ol on the surface of the catalyst changes in accord with data of Schwab (1934).

In flowing CO_2 at 500^{o}C mainly dehydrogenation proceeds to the (-)-product with a rotation of -0.13^o. But these results disagree with the data of Schwab (1934), which can be explained by too fast of a rate (9 mmol/min).

Temperature of reaction (°C)	Conversion (%)	Rate (mmol/min)	α_D (°)
460	10.6	0.89	+ 0.07
470	17.6	1.18	+ 0.05
500	26.8	1.0	+ 0.10
505	22.6	0.50	+ 0.14
510	25.0	0.70	+ 0.06

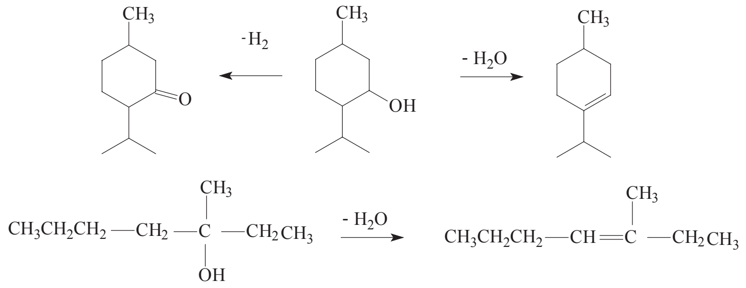
Table 2.3. Temperature dependence of asymmetric dehydration of butan-2-ol over Cu-*d*-quartz catalyst in dinitrogen transport gas (modified adapted data from Stankiewicz [15]).

On a Cu-*l*-quartz catalyst in flowing N_2 dehydration gives a product with rotation up to -0.25° (Table 2.4).

Temperature of reaction (°C)	Conversion (%)	Rate (mmol/min)	α_D (°)
500	5.4	1.6	- 0.07
515	5.4	0.8	- 0.09
525	5.4	0.8	- 0.11
530	3.9		- 0.25
545			- 0.04

Table 2.4. Temperature dependence of asymmetric dehydration of butan-2-ol over Cu-*l*-quartz catalyst in transport gas flowing N_2 (modified adapted data from Stankiewicz [15].)

Decomposition studies of racemic menthol and 3-methylheptan-3-ol gave similar results (Scheme 2.2.). Thus dehydration of racemic menthol over Cu-*l*-quartz in a flowing N_2-air mixture at 430-460°C results in a product with a rotation of -0.16^0, which indicated preferential decomposition of the (+)-enantiomer of menthol. The same picture was obtained, but to a somewhat greater extent, for the dehydrogenation of 3-methylheptan-3-ol on Cu-*l*-quartz in which the (+)-enantiomer reacted and the product exhibited a rotation of -0.12^0.



Scheme 2.2. Dehydration and dehydrogenation of menthol and dehydration of 3-methylheptan-3-ol.

Dehydration of racemic menthol on Ni-*l*-quartz at 560°C gave products containing 62.4% menthenes and a rotation of -0.15°. This catalyst was strongly carbonized during reaction and lost its activity, but after oxidation and reduction with hydrogen it gave a product with a rotation of -0.08°.

Increasing the amount of Ni on quartz somewhat diminished the rotation from -0.15 to -0.13°. On Pt-quartz catalysts 2-butanol produced a product with -0.14° at 353°C. Increasing the reaction temperature resulted in larger amounts of butenes and lower rotations.

In the dehydration of 3-methylheptan-3-ol at 170°C Pt-*l*-quartz proved to be the most effective catalyst with an observed rotation reaching -0.26°. Thus it was shown that Pt-quartz catalysts give particularly large effects, presumably owing to uniform deposits of Pt-particles on the surfaces of the quartz. Table 2.5. below summarizes the main results received by Stankiewicz [15].

In the fifties Terentyev and Klabunovskii [16-24] described details of the asymmetric decomposition of racemates and asymmetric synthesis using catalysts supported on optically active quartz crystals. Asymmetric resolution of racemic 2-butanol was extended by a number of new reactions of absolute asymmetric syntheses: hydrogenation of 2-phenylcinnamic acid and cyano-ethylation of cyclohexanone. Reactions were studied in vapor and liquid phases at ambient and elevated temperatures. Catalysts consisting of the metals Cu, Ni, Pt, Pd, andAg, with NaOH and aluminum alkoxides supported on Dophinee quartz or piezoquartz were used. Asymmetric decomposition of butan-2-ol was carried out in the liquid phase in flowing or circulating systems in the vapor phase at atmospheric pressure. Optical rotations of products were measured on a Schmidt & Haentsch polarimeter with an accuracy of 0.01°.

Alcohol	Catalyst	Optimal reaction temperature (°C)	Transport gas	α_D*	Correlation**
Butan-2-ol					
	Cu-*d*-quartz	340	$N_2 + O_2$	- 0.21	*d* and +
	Cu-*d*-quartz	505	N_2	+ 0.14	*d* and -
	Cu-*d*-quartz	500	CO_2	- 0.13	*d* and +
	Cu-*l*-quartz	530	N_2	- 0.25	*l* and +
	Pt-*l*-quartz	355	N_2	- 0.14	*l* and +
3-Methylheptan-3-ol					
	Cu-*d*-quartz	160-210	N_2	+ 0.10	*d* and -
	Cu-*l*-quartz	275	$N_2 + O_2$	- 0.12	*l* and +
	Pt-*l*-quartz	170	$N_2 + O_2$	- 0.26	*l* and +
Menthol					
	Cu-*l*-quartz	450	$N_2 + O_2$	- 0.16	*l* and +
	Ni-*l*-quartz	560	$N_2 + O_2$	- 0.15	*l* and +
	Pt-*l*-quartz	460	$N_2 + O_2$	- 0.15	*l* and +

Table 2.5. Asymmetric Dehydrogenation-Dehydration of Racemic Alcohols over Metal-Quartz Catalysts (summarized adapted data from Stankiewicz[15]).

* Optical rotation of the mixture after the reaction

** Correlation between the quartz used (*d* or *l*) and the sign of the optical rotation.

Crystals of natural quartz obtained from the Institute of Crystallography of the Academy of Sciences of the USSR in Moscow were sawed into plates 10-15 mm thick perpendicular to the crystals' optical axes and were selected by examination in a polariscope. The areas of Brasilian twinnings were removed and *d*- and *l*-Quartz crystals in piezoquartz plates were identified by methods of Lemmlein (1939) (see Chapter 1.3.1.). The selected *d*- and *l*-quartz crystals were carefully crushed in a mortar under water to avoid twinning and amorphisation occurring as in the cases of strong action on the crystals, e.g. crushing in ball-mill or vibro-mill (see Khodakov and Rebinder [25]). Then the powder was purified in hot king's water, washed, and sieved. The fraction of powder with a specific area of 180 cm^2/g was used for preparation of the catalysts. Metals were deposited on the quartz by two methods: by precipitation from salts, drying, ignition, reduction in flowing hydrogen; and by cathodic scattering in high vacuum with periodically shaking of the quartz sample to achieve uniform surface covering by the metal. In some cases, when reproducibility of selectivity was low owing to sintering or carbonization and segregation of the metal particles on the surface of the carrier, the catalysts were repeatedly crushed in a mortar and used again. By this operation the border zones between the metal and quartz were renewed and reproducibility was recovered. The extent of surface coverage of the catalysts composed of Cu on quartz could be divided into groups with broad distribution of metal layers: 0.4-73 atomic layers for the "Precipitation" catalysts and close to a monoatomic layer, 0.4-0.8 atomic layers for the “cathodic scattering" catalysts. Results received with these two groups of catalysts are shown on Table 2.6. [23].

It has been shown that enantioselectivity is increased at low conversions particularly with the catalysts using cathodic scattering of metals (0.4-0.8 atomic layers on the surface of quartz). The temperature dependence of asymmetric decomposition of butan-2-ol revealed two maxima of optical rotation of products: at temperatures between 320 - 400^o butan-2-ol mainly dehydrogenates and at higher temperatures, above 400^o, dehydration takes place. Therefore, in the reaction on Cu-*d*-quartz catalysts two maxima of optical rotation were found: at 340^{o}C $\alpha = 0.21^o$ and at 530^{o}C $\alpha = 0.25^o$ [15].

Cu content (%)	n	Temperature (^{o}C)	Conversion (%)	Rate (%/min x 10^2)	$[\alpha]_D$*	*ee** (%)
0.0075	0.78	320	1.2	3	+ 0.08	0.36
		370	1.9	3	+ 0.16	0.34
		423	7.6	12	+ 0.09	0.41
		459	14.5	30	+ 0.18	0.81
0.003	0.38					
		400	4.4	4	+ 0.14	0.63
		420	10.3	4	+ 0.10	0.45
		458	13.6	14	+ 0.16	0.72

Table 2.6. Asymmetric decomposition of racemic butan-2-ol on Cu-*d*-quartz catalysts with low metal contents.
n = Cu atomic layers on quartz; * = values of the unreacted butan-2-ol (adapted modified data from Terent'ev et al. [23]).

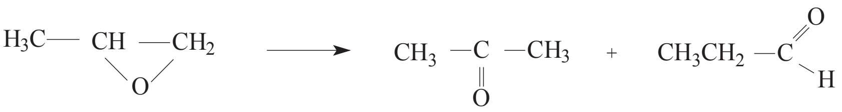
It was found that enantioselectivity of the catalyst diminished with reaction time due to poisoning of metal-quartz border zones on the surface. This caused the optical rotations of products to pass through maxima. The time of reaching maximal rotation depends on the extent of coverage of the surface of the quartz with metal. To obtain good results reaction time must be restricted to 30-50 min and the metal content must not exceed 0.001%. Increasing the Cu content on the surface of quartz accelerated the rate of the decomposition of butan-2-ol, but simultaneously increased the rate of its racemisation too. In summary, Table 2.7. gives results obtained from the asymmetric dehydrogenation-dehydration of racemic 2-butanol with various metal-quartz catalysts.

Type of quartz	Metal and mode of preaparation	Reaction temperature (^{o}C)	α_D of products
l-quartz			
	Cu*	360	- 0.12
	Ag**	350	- 0.08
	Ni*	65	- 0.12
	Pt** #	280	+ 0.08
d-quartz			
	Cu*	360	+ 0.16
	Cu**	460	+ 0.18
	Ag**	470	+ 0.10
	Pd***	360	+ 0.06
	Ni*	388	+ 0.11

Table 2.7. Optical rotation after asymmetric dehydration and dehydrogenation of racemic mixtures of 2-butanol over metal-quartz catalysts (length of tube: 20 cm).
* nitrate solution and reduction at 300^{o}C;
** cathodic scattering;
*** chloride solution;
\# reaction in flowing N_2+O_2 (modified adapted data from Terent'ev et al. [16]).

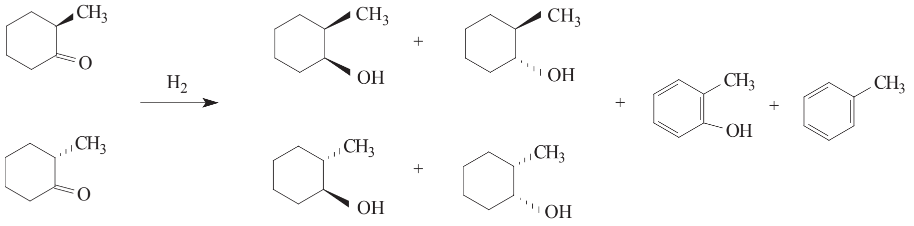
It was found that Cu-*d*-quartz catalysts are more effective than the others in the asymmetric decomposition of 2-butanol and that the sign of optical rotation of the product after the dehydrogenation reaction always corresponded to the sign of rotation of the quartz. Ag-quartz catalysts prepared by cathodic scattering contained 0.03-0.08% Ag and gave an α_D of +0.106^{o} on Ag-*d*-quartz and -0.07^{o} on Ag-*l*-quartz at the optimal temperature of 370^{o}C. Two maximal values of optical rotation were observed on Ni-quartz catalysts, too: -0.012^{o} on Ni-*l*-quartz and +0.16^{o} on Ni-*d*-quartz.

Cu-, Ag-, and Pt-quartz catalysts were used for the asymmetric isomerization of the racemic mixture of methyloxirane (Scheme 2.3.).



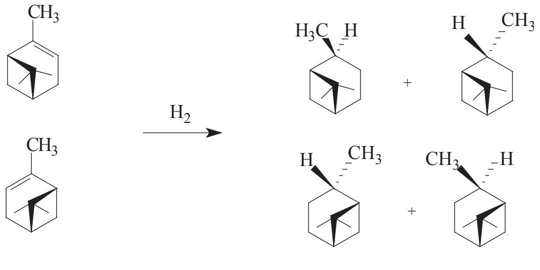
Scheme 2.3. Isomerization of methyloxirane.

Maximal rotations of the partially isomerized products at 180°C on Cu-*l*-quartz catalyst was -0.055° and on Ag-*l*-quartz catalyst was -0.052°. Another example of asymmetric decomposition is the asymmetric hydrogenation of racemic 2-methylcyclohexanone (Scheme 2.4.).



Scheme 2.4. Kinetic resolution and diastereomeric hydrogenation of 2-methylcyclohexanone (adapted from Terent'ev, Klabunovskii et al. [19]).

After reaction at 244°C the rotations of the reaction products were found to be -0.042° on Pt-*l*-quartz and +0.039° on Pd-*d*-quartz. Optical activity in the product could arise as a result of both kinetic resolution of the racemic starting material and creation of a new chiral center in the 2-methylcyclohexanol by enantioselective hydrogenation of the C=O group. The same transformation was realized in the liquid phase hydrogenation of racemic *alpha*-pinene in decalin solution (Scheme 2.5.).

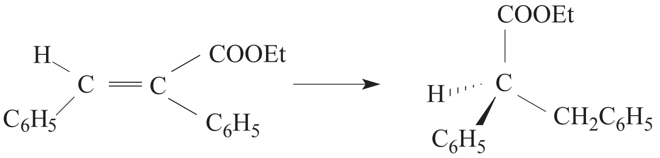


Scheme 2.5. Kinetic resolution and diastereomeric hydrogenation of *alpha*-pinene into pinane (adapted from Terent'ev, Klabunovskii et al. [19]).

Rotation was +0.046° on Ni-*l*-quartz and -0.046° on Ni-*d*-quartz. Besides the asymmetric resolution of racemates, metal-quartz catalysts were used to accomplish pure asymmetric syntheses. The first attempt was realized by Schwab (1934) in the hydrogenation of tiglic acid [(*E*)-2-methylbut-2-enoic acid] over Ni-quartz catalysts.

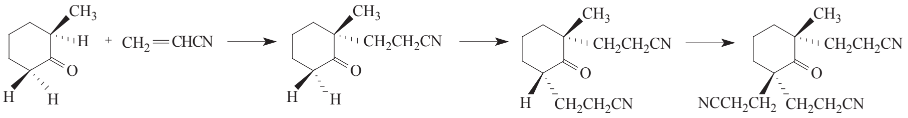
At low surface coverages of Ni on quartz no reaction occurred, probably as a result of poisoning of the small amount of metal. At high Ni coverages hydrogenation took place but at 200°C where no asymmetric effects would be expected.

Terent'yev and Klabunovskii [19,23] hydrogenated the ethyl-(2-phenylcinnamate) (Scheme 2.6.) in decalin solution at 135°C on a Ni-*d*-piezo-quartz catalyst and received a product with α_D = -0.09° ± 0.007°. On Ni-*l*-quartz the product had an optical rotation of +0.04°.



Scheme 2.6. Hydrogenation of ethyl 2-phenylcinnamic acid.

A more complicated case occurred in the addition of acrylonitrile to 2-methyl-cyclohexanone (Scheme 2.7.). This cyanoethylation reaction was studied at ambient conditions on a new chiral catalyst: NaOH on *d*- or *l*-quartz [19].



Scheme 2.7. Asymmetric cyanoethylation of 2-methylcyclohexanone.

The original ketone exists as a racemic mixture. During the reaction a new chiral center appears in the intermediate, but it disappears in the final product. In accordance with the reaction path in Scheme 2.7., the optical rotation proceeds through a maximum at α_{589} = 0.157° as Fig. 2.3. shows.

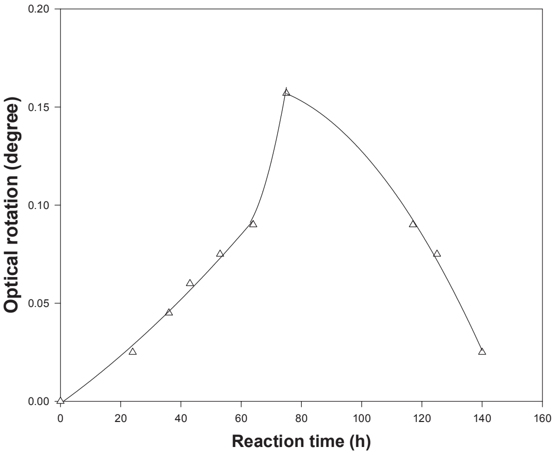
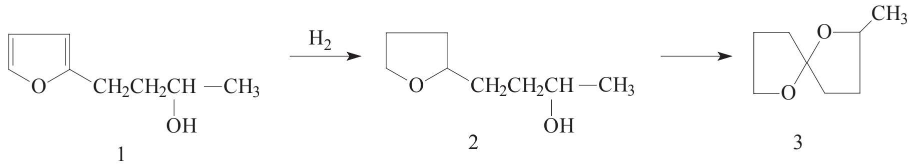


Figure 2.3. Dependence of optical rotation of product with reaction time during the asymmetric cyanoethylation of 2-methylcyclohexanone with acrylonitrile on a NaOH-quartz catalyst (adapted from Terent'ev, Klabunovskii et al. [20]).

In 1953, Ponomarev and Zelenkova [26] applied the Ni-quartz catalysts for the asymmetric hydrogenation of furan derivatives (120 °C, 135-150 bar, liquid phase) in order to elucidate the mechanism of reaction. It was well known that in the hydrogenation of 4-(2-furyl)butan-2-ol, **1**, 4-(tetrahydrofuran-2-yl)butan-2-ol, **2,** and 2-methyl-1,6-dioxaspiro[4.4]nonane, **3,** were formed (Scheme 2.8.).



Scheme 2.8. Asymmetric hydrogenation of 4-(2-furyl)butan-2-ol.

In this reaction the spirane can be formed but its stereostructure was unknown. The spirane molecule can be chiral only in that case when the two five-membered rings are perpendicular to each other. Optical rotation of the spirane received in this reaction confirmed the structure of the supposed spirane [26]. Thus, over Ni-*l*-quartz catalyst, spirane **3** with α_{589} = -0.066°, while over Ni-*d*-quartz catalyst, spirane **3** with $\alpha_{589} = +0.06^{\circ}$ and **2** with $\alpha_{589} = +0.04^{\circ}$ were obtained. Results showed that the spirane can exist in two enantiomeric forms.

Owing to the small specific area of quartz powder as carriers, in metal-quartz catalysts and their low ability for adsorption, these catalysts in general proved to be of interest only in connection with the theory of the origin of chirality in Nature. Moreover as was noted above, the use of quartz as a carrier demands a very careful special selection procedure for preparation of optically pure samples. Therefore, it is not surprising that several attempts to realize asymmetric catalysis with the use of quartz crystals were not always successful. For example, Tsuchida et al. [27] in 1936 attempted to repeat the results of works of Schwab (1932) but failed. Likewise, Amariglio [28-31] in 1967 attempted to reinvestigate studies on adsorption and metal-catalysts based on quartz crystals but also failed. The hydrogenation of butan-2-one and the asymmetric dehydrogenation-dehydration of racemic butan-2-ol were studied on Ni- and Pt-quartz catalysts. Catalysts were prepared by immersion of quartz powder in solutions of Ni or Pt salts, followed by liofilic drying, calcination and reduction in flowing hydrogen. Decompositions of butan-2-ol was carried out in flowing systems at atmospheric pressure. Products were condensed and examined polarimetrically with an accuracy of 0.01°. From the decomposition of racemic butan-2-ol on 0.03-0.04% Ni-*l*-quartz and 0.16-0.30% Pt-*l*-quartz catalysts at 200-300°C optical rotations of products did not exceed 0.001°.

Hydrogenations of butan-2-one were carried out at 140-150°C. The optical rotation of the product was observed to be 0.10°, which fell over time to 0.02°. Other generally disappointing irregularities also occurred. Independent of the sign of the rotation of quartz, all products were levorotatory, and the optical activity disappeared in several hours. Quartz crystals without metal layers also catalyzed the dehydration of butan-2-ol at 350° and gave rotations of -0.075° and -0.085°, which after filtration of the products fell to -0.005°. Thus the products obtained with the Pt-*l*-quartz catalyst at 307°C had an initial rotation of -0.045° that fell to zero in 3 hrs.

Based on their negative results in attempts to repeat the works of Schwab (1934) and Klabunovskii (1950) and others authors Amariglio et al. [28-31] criticized these works and claimed that the results were artifacts. Also using gas chromatography with quartz powder packing they could not resolve racemic propylene oxide, butan-2-ol, 1-phenylethanol, and other compounds[31].

But careful examination of the published works [28-31] leads to the conclusion [32] that their criticism is flawed and their own experiments are insufficient as follows:

1) Quartz plates were purchased from Centre National d'Etude des Telecommunications and as indicated by Amariglio-Simon (1967) made of synthetic quartz rather then of natural quartz crystals. In their publications [34,35] they did not indicate the method of identification and selection of *d*- and *l*-quartz crystals.

2) Samples of quartz crystals were crushed into micron size particles using vibro-set with W-carbid. They did not indicate the condition of the pounding of the crystals although it is well known that crushing of the optically active quartz particularly with vibro-mil can cause twinnings formation, amorphisation of quartz, and its hydrophilisation [25].

3) Moreover, the amorphisation of quartz powder was confirmed by Amariglio-Simon (1967) because treatment with HF of the crushed quartz crystal powders with specific areas of 2 m^2/g diminished this value to 0.2 m^2/g.

4) The method of purification of the quartz powder after that treatment also was not indicated [28] and the catalysts of high catalytic activity contained rather thick layers of metal on the surface of the quartz (extent of coverage was 15-26%) [28-31], which exceeded significantly the characteristics of the previous catalysts used [11-24].

5) Polarimetric measurements were carried out on a polarimeter with very large half-shadow angle (5^o) that could not give sufficient accuracy in the estimation of the optical rotation of products.

6) Products of dehydrogenation-dehydration of butan-2-ol were examined in the polarimeter without distillation, after only filtration.

7) All products gave only levorotatory compounds independently of the optical sign of the quartz used. Thus Pt-*l*-quartz catalyst, based on quartz washed with HF, gave in dehydrogenation of butan-2-ol rotation of catalysate with optical rotations of -0.085^o and -0.09^o that went to zero in several hours after sedimentation of the suspension of quartz. In another experiment a rotation of $-0.058^o$was obtained, but that disappeared in 4-5 hrs. The same (-)-rotation in solution was received even from the suspension of crushed quartz or pyrex glass and silica.

All these facts placed into question the experiments and general criticism of Amariglio [28-31]. Moreover it should be noted that at 306^oC during conversion of α-quartz to β-quartz the twinning of quartz proceeds [33]; therefore catalysis by quartz crystals is not recommended at high temperatures.

Unfortunately, explanations [32] of the problems associated with the results of Amariglio et al.[28-31] have not been incorporated into considerations of quartz as a chiral adsorbent [34].

2.3 General comments on adsorption and catalysis using quartz crystals

Published results on asymmetric catalysis and asymmetric adsorption using quartz crystals have a number of problems, the main one being a very small effectiveness of the catalysts or adsorbents in producing high optical rotations in products: observed angles of rotation of products did not exceeded 0.2°. Optical rotations were measured by polarimeters at one wavelength, 589 nm. At that time, 40-60 years ago, other methods of examining enantiomers (enantiomeric chromatography, spectropolarimetry, radiochemical analysis), were not yet available. The structures of the catalysts (surface of metal in metal-quartz catalysts, the state and dispersion of the metal, and others) were not employed. In a number of experiments, catalysts contained increasing amounts of metal on the surface of quartz, up to 100-200 atomic layers, that likely excluded the action of the chiral quartz surface.

Nevertheless, despites these experimental problems, consistent regularities were observed; for example, in the decomposition of butan-2-ol the sign of optical rotation of the product, caused by unreacted butanol partially enriched with one enantiomer, corresponds to the sign of rotation of the quartz. That result means that the other enantiomer of butanol was preferentially decomposed on the catalyst. However, this correlation can change depending on the nature of the catalyzing metal and on the character of the reaction: dehydration or dehydrogenation. Thus, with Cu-*d*-quartz a (+)-rotation was observed, but with Pd-*d*-quartz a (-)-rotation resulted. Moreover, the direction of reaction, dehydrogenation or dehydration, can change the correlation. And in some experiments the rotations did not give the "mirror picture" of order values of rotations; for example, on Pt-*d*-quartz the rotation of the reaction mixture was +0.13° but on Pt-*l*-quartz it was only 0.032°, and on Ni-*d*-quartz α_D = 0.048° but on Ni-*l*-quartz only 0.02-0.03°. Such results may have been caused by a lack of good uniformity in the quartz samples as well as differences in specific areas of the carrier.

Another complicating factor is that the surface of quartz is the only asymmetric factor in the metal-quartz catalysis and its specific areas in most cases were very small (only 44 cm^2/g [11-14]). This coupled with the fact that the amount of metal deposited on quartz was rather high, so the extent of racemization of butanol during reaction would be high, which detracts from the effectiveness of the catalyst. Thus, quartz appeared not to be an effective chiral carrier for catalysis or adsorption in asymmetric experiments. Nevertheless, in general the data using quartz crystals are of interest and received positive evaluations in several publications [34,35].

2.4 On the mechanism of "Quartz-Catalysis"

For the mechanism of asymmetric catalysis on metal-quartz catalysts there is no unifying point of view. There are the concepts of "contact activation", "specific adsorption", and "formation of specific chemical bonds" [12-14]. It has been proposed that on the surface of the catalyst intermediate surface diastereomers are formed which are decomposed at different rates. The data on the action of quartz-catalysts have been rather thoroughly discussed [36-42]; in addition positive estimations of data were given by Bonner [34] and Harada [35].

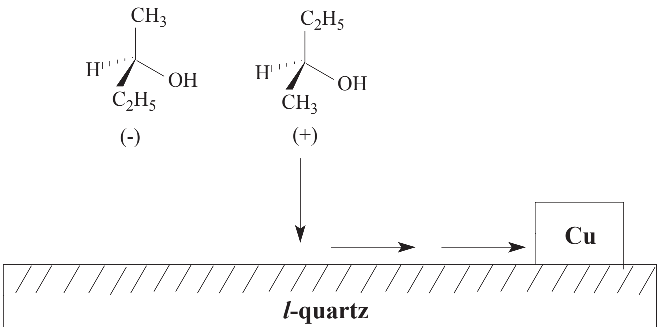
Schwab, Rost, and Rudolph [12] in 1934 proposed that the critical stage in asymmetric catalysis on metal-quartz catalysts is contact activation of the substrate adsorbed on metal-aggregates, which transfers asymmetry from the carrier-quartz to the reacting molecule of the substrate, rather than adsorption on the asymmetric adsorbent-quartz crystal. Schwab and Rost [13] in 1941 considered the catalyst to be an inorganic model of an enzyme in which the working group is represented by both the catalyzing metal and the asymmetrizing carrier-quartz. It was noted that "...only the borders between the metal and the free quartz surface are responsible for asymmetric action...".

Indeed, during the asymmetric decomposition of racemic butan-2-ol on Cu-*d*-quartz catalyst, the change of the sign of optical rotation of the product from (-) to (+) during dehydrogenation indicated no adsorption of the substrate on the asymmetric surface of quartz; however, “contact activation” of butan-2-ol takes place and asymmetry of the quartz spread from the border-zones of the Cu-quartz where the asymmetric reaction was carried out. This point of view also agreed with the fact that a significant asymmetric effect occurred in the cases of thin, close to monoatomic, layers of metals on quartz surfaces, which allowed for development of extensive networks of metal-quartz border-zones.

Such a point of view was first put forward by Bredig and Gerstner [6,36]. They studied the asymmetric induction action of a catalyst composed of an amine immobilized on fibers of native cellulose (Et_2NH-Cellulose) and found that this catalyst is active in the asymmetric formation of (-)-mandelonitrile from benzaldehyde and HCN. After saponification of the product, the (+)-mandelic acid was obtained with an ee of 22%. Considering the mechanism of this catalytic transformation, the authors [36] suggested that the optically active cellulose transfers its asymmetry to the substrate through the catalytically active amine. Kuhn [39,40,42] considering the action of "Bredig's catalysts" noted that these catalysts are very similar to enzymes. Adsorption spectra of these catalysts indicated that the amino group became part of the dissymmetric center as evidenced by the reaction results. Therefore, according to Kuhn’s experiments, it is impossible to distinguish the asymmetric and catalytic functions in such catalysts.

The mechanism of conversion of an achiral molecule into a chiral one was found by Kuhn in circular dichroism spectra. The type of natural quartz used, amethyst crystals, contained colloidal inclusions of Fe. The circular dichroism spectra revealed bonds involving Fe. It would be of importance from that point of view if the films of metals removed from surfaces of quartz crystal would show circular dichroism spectra, too.

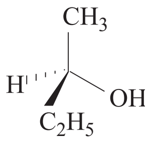
The experimental data indicates that metal-quartz catalysts are more selective if they contain a thin, near monoatomic layer of metal on their surfaces. In accordance with this requirement the complicated net of border zones between metal and quartz must be created. Only on these borders can effective asymmetric reactions take place. Guided by this point of view Klabunovskii and Patrikeev [22,32] considered the role of quartz as an asymmetric adsorbent that resolved the enantiomers and preferentially accumulated one of them on the border zones between metal and quartz where the reaction proceeds. In the case of the reaction of racemic butan-2-ol on Cu-*l*-quartz catalyst, (*S*)-(+)-butan-2-ol adsorbed and decomposed preferentially resulting in (-)-optical activity for the product mixture (Scheme 2.9.).



Scheme 2.9. Asymmetric adsorption and decomposition of the racemic mixture of (*R*)-(-)- and (*S*)-(+)-butan-2-ol over Cu-*l*-quartz catalyst (adapted from Klabunovskii et al. [22,32]).

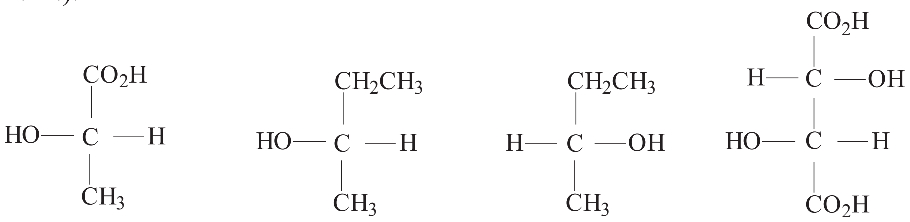
2.5. Evaluation of absolute configuration of molecules using data from "Quartz-catalysis"

Several authors have attempted to use data from quartz catalysis to determine the absolute configuration of molecules. Although the question of determination of absolute configuration of organic compounds or complexes can be considered as solved owing to the use of spectral structural analysis methods, interest continues in the search of other ways of determination of absolute configuration. This search is stimulated by the opportunities to examine changes of configurations of molecules during reactions and thus to determine the final spatial mechanism of the reactions [32]. As suggested earlier, a method was used for calculation of the configuration of the simplest organic compounds, but it proved to be insufficient. This was demonstrated by calculating the optical rotation of (*R*)-butan-2-ol (Scheme 2.10.) using the method given by Boys [37] and the theory of optical activity by Kirkwood [38]. This calculation gave erroneously a (+)-rotation for this compound.



Scheme 2.10. (*R*)-butan-2-ol.

In contrast, the calculation method given by Kuhn [39,40] resulted in the (+)-butan-2-ol being genetically connected with the (*S*)-(+)-lactic acid (Scheme 2.11.).



(*S*)-(+)-lactic acid (*S*)-(+)-butan-2-ol (*R*)-(-)-butan-2-ol (2*R*,3*R*)-tartaric acid

Scheme 2.11.

In a critical examination of methods for determining absolute configuration based on calculations Volkenshtein [41] came to conclusions based on the better grounded calculations of Kuhn [42] and the one-electron model of Condon, Altar, and Eyring [43], whose method of calculation allows one to derive configuration from a genetic spatial D-series of organic compounds originating from D-glyceraldehyde.

In 1884 Fischer noted that it is necessary to distinguish the spatial configuration of a molecule and its optical rotation. Thus, both (+)- and (-)-rotating amino acids and other compounds belong to the L-configurational series. As the original structure for the D-series Fischer suggested the structure of D-glucose. To this D-series belongs the (2*R*,3*R*)-(+)-tartaric acid, the absolute configuration of which was later determined by X-ray diffraction [44-46] and confirmed the earlier predictions of Fischer.

As (2*R*,3*R*)-(+)-tartaric acid can be genetically connected by chemical interactions with the D-series of organic compounds originating from D-glyceraldehyde, also (+)-tartaric acid can be considered a more reliable structure than D-glyceraldehyde. It turned out that the spatial formula adopted arbitrarily by Fischer proved to be the correct absolute configuration. On the other hand, Waser [47] ascribed the opposite configuration for (+)-tartaric acid, but that was not confirmed.

As found by Schwab et al. [11-14], metal-*d*-quartz catalysts preferentially adsorb and decompose (*R*)-(-)-butan-2-ol and the remaining unreacted butanol has the (+)-optical rotation. The structure of quartz consists of endless networks of SiO_2 units forming spatial right- or left-handed helices [38]. Using data on adsorption and catalysis on quartz crystals the absolute configuration of butan-2-ol can be determined:

i) if the correlation of the spatial helix structure of quartz to its sign of optical rotation is known

ii) if it is assumed that the left handed-helix structure of butan-2-ol makes better contact with the "right-helix" structure of quartz. The (+)-*beta*-quartz has the "right-helix" spatial structure [48].

Condon, Altar, and Eyring [43] came to the conclusion that the absolute configuration of (-)-butan-2-ol has a “right-helix" structure if the dehydration of butanol over Cu-quartz catalysts results mainly in (*E*)-but-2-ene and has a "left-helix" if dehydration results in but-1-ene. This conclusion followed from the data of Schwab (1934) and is based on the idea that the chiral structure of the surface of quartz complements the reacting molecule of butan-2-ol.

Results received in the studies of “quartz-catalysis” allow one to suggest that the mechanism of action of quartz catalysts is a result of asymmetric adsorption on the surface of optically active quartz. The effectiveness of asymmetric catalysis is determined by the ability of the catalytic system to form the labile diastereomeric complex intermediate, which will be determined by the extent of spatial correspondence of the configuration of the reacting molecule to the structure of the surface of the catalyst (or adsorbent); in this regard, the left-spiral structure of the surface of the catalyst (adsorbent) will correspond to the right-spiral model of the reacting (forming) molecule. But this conclusion is preliminary because the absolute configuration was unknown; the correspondence of sign of optical rotation of the quartz to the spatial arrangement of helix crystal lattice was unknown. The authors [43] attempted to use the results of calculations of Hilleraas [48] who assigned to (+)-rotating quartz the right-spiral structure. Besides the mechanism was unknown for the decomposition of butan-2-ol on the surface of metal-quartz. Schwab (1934) noted that in the dehydration of butan-2-ol over Cu-quartz catalyst the butene is formed but the stereochemistry of the products was unknown. Having in mind the preliminary character of their conclusions about the configuration of the butan-2-ol in Scheme 2.9., the (-)-rotation was attached in accord with the theory of Kuhn [39,40,42]. Such a conclusion was valid for a model of an intermediate state of butanol on the surface of the catalyst on which the reaction results in formation of but-1-ene. This can be realized only by orientation of butan-2-ol as a left-spiral model (the arrangement of groups at the chiral center corresponds to a left-spiral). However, in 1958 De Vries [49] by X-ray diffraction showed that (+)-rotating *alpha*-quartz has a left-spiral configuration rather than right-spiral and the (-)-rotating quartz belongs to the space group P3,2 and has a right-spiral lattice. These relationships are quite opposite to those accepted earlier [43] and based on calculations of Hilleraas [48]. Therefore the concepts of Condon, Altar, and Eyring [43] become very doubtful. However, from the model of a reacting molecule of butan-2-ol on the surface of a Cu-quartz catalyst it follows that if dehydration of butan-2-ol preferentially forms but-1-ene then a molecule of butan-2-ol must react in the left-spiral conformation, and if (*E*)-but-2-ene is formed, then it must react in the right-spiral conformation. The works of Schwab (1934), Terent'yev, and Klabunovskii (1953) did not give any data on structure of butenes formed in the reaction over Cu-catalyst at high temperature.

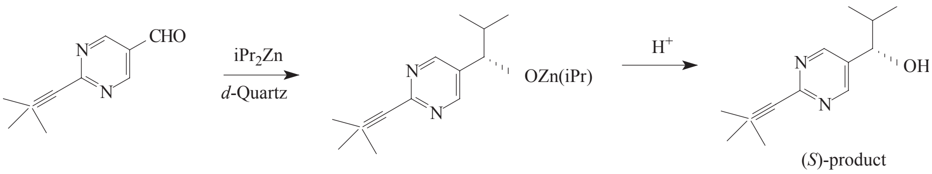
To attempt to solve this question Balandin, Klabunovskii et al. [50,51] have shown that the dehydration of butan-2-ol directly forms a considerable portion of (*E*)-but-2-ene on the catalyst surface rather than forming it as a result of the isomerisation of but-1-ene or (*Z*)-but-2-ene.

Labeling but-1-ene with ^{14}C and utilizing GLC-analysis allowed for the determination [51] that quite a definite part of (*E*)-but-2-ene is formed directly from the catalytic dehydration of butan-2-ol, rather than through but-1-ene. Thus, as in the case of the dehydration of butan-2-ol, (*E*)-but-2-ene was formed preferentially, so butan-2-ol in its surface reacting state adopts the right-spiral conformation (having (-)-rotation) and, therefore, is more easily adsorbed on the (+)-rotating quartz which has the left-spiral structure. Indeed, (+)-rotating quartz adsorbs (and then decomposes) preferentially the (-)-butan-2-ol. According to De Vries [49] (+)-quartz has left-spiral structure and hence (-)-butan-2-ol has (*R*)-configuration, in accordance with the calculations of Kuhn [39,40,42] and of Volkenshtein [41]. Thus, taking into consideration the results of the works of Klabunovskii and Balandin et al. [50,51], the uncertainty of determining the absolute configuration of butan-2-ol using the method of "Quartz-catalysis" was removed. These data confirm the selection of the absolute configuration of D- and L-glyceraldehydes and related compounds and demonstrate the important role of phenomena of complementary structures in forming the chiral spiral structure.

It is of interest that a positive optical rotation resulted from passing linear polarized microwave irradiation of wave lengths 3-20 nm through randomly oriented right-handed helices made from "chiral" models consisting either of right spirals of copper wire or of models made of similar chiral tetrahedral [52].

In 1953 Frank [53] proposed an autocatalysis model in which the molecule of the product can catalyze its own formation. For a long time this theoretical model had no experimental confirmation until the works of Soai's group [54-59], who were able to realize this idea in an asymmetric alkylation reaction: addition of diisopropyl-zinc to 2-alkinylpyrimidine-5-carbaldehyde leading to the corresponding alkanol ((*R*)-1-(2-*tert*-butylethinyl-5-pyrimidyl)-2-methylpropan-1-ol) (Scheme 2.12.) with an enantiomeric excess of 51%; in contrast, in the presence of an asymmetric inductor, L-Valine, only of 1% enantiomeric purity was realized.

Recently it has been shown that optically active quartz crystals as asymmetric inductors become very effective in autocatalytic enantioselective reactions. Soai et al.[54-59] have shown that in asymmetric autocatalysis, the action of small amounts of chiral reaction products (involved in the reaction cycle) may enhance the enantioselective excess by a factor of 94 after introduction of an intermediate into the reaction. Optically active synthetic quartz crystals were used in this reaction with ratios of 1:1.9 quartz to aldehyde and 1:2.2 quartz to diisopropyl-zinc.



Scheme 2.12. Quartz promoted asymmetric synthesis with iPr_2Zn (Soai et al. [57]).

The most important results were the following. Using *d*-quartz as an asymmetric inductor gave the alkanol with an (*S*)-configuration and 93%

optical purity, while *l*-quartz produced the alkanol with a (*R*)-configuration and 97% enantiomeric purity [57].

For these experiments synthetic hemihedral *d*- and *l*-quartz crystals from Toyo Communication Equipment Co. were received. The crystals were identified only by shapes and then powdered by a ball-mill and by wet- and dry-type methods; therefore, the twinnigs was excluded for average particle sizes 2.9-7.6 μm. (according to a private communication of Prof. K. Soai to one of authors of this book, E.K.). The surface of quartz powder was cleaned by HCl, MeOH, acetone, water, HF and water, and dried in vacuo at 100°C. Reactions were carried out in toluene at 20°C. The ratio of quartz to 2-alkinylpyrimidine-5-carbaldehyde (A) and diisopropyl-zinc (B) was 120:9:20. The reaction mixture was stirred for 12h, the mixture of A and B was added, the mixture was stirred for 5h, the mixture of A + B was added again for amplification of asymmetric effect, and finally the mixture was stirred for 5h. The alkanol product was obtained with an *ee* of 96% with an *S*-configuration using *d*-quartz and with an *R*-configuratio and an *ee* of 97% using *l*-quartz.

The same very high optical yields of this alkanol, *ee* 97% *S* and 98 % *R*, were obtained in the presence of enantiomorphic crystals *d*- or *l*-sodium chlorates, $NaClO_3$, respectively (Sato et al. [58]). Similar high effects probably can be obtained in the presence of other natural crystals, like epsomite, potassium bichromate, and cinnabar in future investigations.

The mechanism of these processes can be explained in terms of amplification of very small chiral effects created by the formation of the intermediate, and its transformation into the alkanol (Scheme 2.11.) because the chiral crystal itself induces a very small enantiomeric enrichment in the formed pyrimidinic alkanol and the effect is a result of the involvement of a chiral crystal in the intermediate complex.

These results have a threefold significance: first, as a practical method of amplifying small chiral effects in organic reactions, second, as a possible way to discover and assign the chirality of substances, such as natural minerals, that can be used as chiral catalysts (or carriers), and third, as a way to search for the possibility of the origin of chirality on Earth, where enantiomorphic minerals like quartz can exist (see Klabunovskii [60,61]).

In the case of quartz as asymmetric inductor, Soai [57] noted: "...results provides chemical evidence that chiral quartz may be involved in the origin of the chirality of organic molecules through catalytic asymmetric synthesis...". Of course this statement is true in the relation of origin of chirality rather than homochirality. Earlier, Tranter [62] and McDermott [63] gave a calculation of parity violation of energy difference (PVED) for *l*-quartz stabilized by 10^{-17} kT per SiO_2 unit of quartz structure based on the allegation that a possible source of homochirality of organic materials is generated by excesses of *l*-quartz on the surface of Earth. But analyses of literature by Klabunovskii and

Thiemann [64] showed that this calculation of PVED for quartz crystal seems to lack a sound physical basis because in all examined quartz locations the amounts of *d*- and *l*-quartz crystals are equal. Hence the quartz crystals are erroneously considered as a possible source of one handedness in nature, although local formation of optically active molecules, for example, via autocatalytic processes, appears quite possible in revealing chirality rather than homochirality (Klabunovskii [60,61]).

In the works of Soai [55] a very important result was found: leucine, which was prepared by irradiation with circular polarized light of racemic leucine as a result of asymmetric decomposition of racemate (see Bonner [65]), could be used in the above mentioned addition reaction as achiral inductor of very low enantiomeric purity (2%) with autocatalytic amplification occurring. As a result, optically active alkanol in the reaction in Scheme 2.12. was obtained with 26% optical purity (see Avalos et al. [66], Szabo-Nagy and Keszthelyi [67], and Mislow [68]).

In similar ways circular polarized light irradiation of very low efficacy combined with enantiomorphic crystals and autocatalytic amplification reactions, could be the origin of homochirality of organic molecules (Bonner [65]).

For another way, based on PVED of enantiomers [67] Mislow [68] recently indicated: "...if an enantiomeric excess as tiny as 10^{-5}% is sufficient to initiate the amplification [55] then an *ee* value even as small as 10^{-9}% is surely capable in principle of initiating a similar cascade of processes leading to an optically active product. There is no reason to consider that for chiral initiators a critical *ee* value exists, somewhere between 10^{-9}% and 10^{-5}%, below which automultiplication of chirality can no longer take place..."

Indeed, even without any chiral inductor it was possible in the above mentioned autocatalytic reaction of chiral alkanol synthesis, Scheme 2.12., to obtain high optical yields (up to 91%) of both *R*- and *S*-products. These results can be compared with separation of racemates during crystallization [70].

This means that an absolute asymmetric synthesis from optically inactive prochiral molecules, free of chiral contaminations and run under chiral conditions can be realized, even without the action of circular polarized light or other chiral auxiliaries.

Indeed, Singleton and Vo [69] adopted the enantioselective reaction used in Soai's reaction [54], Scheme 2.12., to examine the replicative growth in enantomeric excess using 2-methylpyrimidine-5-carbaldehyde and diisopropyl-zinc without either an asymmetric inductor or a chiral intermediate as catalyst. In the first experiment an almost racemic product with an *ee* of 0.00003% and *R*-configuration was prepared. Then using 2.5-10% of each product solution containing the intermediate and without addition of any origin asymmetric inductor, 48 successive reactions were carried out preparaing the final product with an *ee* of 22% with the same *R*-configuration.

Of course, these reactions are not true examples of absolute asymmetric synthesis **[69]**, because the first excess of the *R*-enantiomer formed on the base of stochastic distribution served as the trigger for the next repeated reactions similar to the iniating crystal in "spontaneous" crystallization.

Soai et al **[59]** repeated these reactions without adding an asymmetric inductor carrying out 37 separate runs rather then successive reactions as in Singleton's experiments, and they obtained both *R*- and *S*-products, showing almost stochastic distribution: *S*-products were formed 19 times and *R*-products 18 times, with *ee* values of up to 91 %. The small deviation from stochastic distribution was "…due to unknown chiral factors…"**[59]**

It needs to be noted that this case is not a true asymmetric synthesis as Soai claimed, because during the 37 runs approximately an equal number of *R*- and *S*-alkanols were obtained with a stochastic distribution that was similar to racemic separations in "spontaneous" crystallization (Kondepudi et al. **[70]**).

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