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Vapour phase transfer hydrogenation of α,β-unsaturated carbonyl compounds. Thermodynamic and experimental studies

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ABSTRACT

This paper presents the first systematic thermodynamic study of the vapour phase transfer hydrogenation of α,β-unsaturated carbonyl compounds at temperatures: 423.15–723.15 K. Calculations were made for four compounds, namely: acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone. The Gibbs free energies and equilibrium mole fractions (EMFs) were calculated for transfer hydrogenation with ethanol and 2-propanol as hydrogen donors. It was noted that for transfer hydrogenation and hydrogenation with hydrogen the formation of the unsaturated alcohol (UOL) is the least thermodynamically favoured reaction and that saturated alcohol (SOL) and saturated aldehyde or ketone (SAL or SON) are the main products.

A set of eight carbonyl compounds have been transfer hydrogenated with ethanol and 2-propanol in the presence of MgO as the catalyst. The main conclusions are that: (a) the reduction of a carbonyl group into a carbinol group occurs with a very high selectivity, (b) for almost all carbonyl compounds, except acrolein, the reactivity of 2-propanol highly exceeded that shown by ethanol and (c) the high chemoselectivity of transfer hydrogenation of acrolein with alcohols resulted from the kinetic control caused by the presence of magnesium oxide.

1. Introduction

Chemoselective hydrogenation of α,β-unsaturated carbonyl compounds to the corresponding unsaturated alcohols (UOLs) is a topic of many recent studies, due to the fact that these alcohols are very important and versatile intermediates for pharmaceutical, polymer, fragrance and food industries. The reduction of these unsaturated carbonyl compounds by gaseous dihydrogen over transition or noble metal catalysts usually results in hydrogenation of the C═C bond. This happens, according to literature, because of two main reasons, first, thermodynamics favors the hydrogenation of the C═C bond over the C═O bond by c.a. 35 kJ mol^{-1} [1] and second, the C═C bond shows higher reactivity than the C═O bond [2]. Although in many articles from the field of heterogeneous catalysis both statements are frequently repeated [3–6] it seems that the former statement has its origin in only one article about selectivity of hydrogenation of crotonaldehyde [1]. In the article, the authors presented a figure which enables a rough estimation of the Gibbs free energy change of the mentioned reactions at a given temperature (298, 400, 600 and 700 K). However, no method of calculation was cited and no thermodynamic data were shown.

Recently, the latter case for the preference of hydrogenation of the C═C bond over the C═O bond was cited in literature and a value was given (127.0 kJ mol^{-1}) [7], however, no details were provided. In our opinion, the value must be erroneous in the light of the data presented above and by us in this work.

Catalytic transfer hydrogenation (CTH) is a reaction in which one organic compound, called the hydrogen donor (D), gives a pair of its hydrogen atoms to another compound (hydrogen acceptor—A) in the presence of a catalyst (Scheme 1). It is a convenient way to reduce many organic compounds for three reasons. First, gaseous hydrogen is not used as the reductant; second, the reaction is performed under normal pressure, which excludes using high pressure equipment; and third, high selectivities towards the desired products are very often observed. On the other hand, the high selectivity is connected with the restriction of the type of organic groups which can be reduced by this method. Among functional groups prone to the reduction by CTH, the reduction of the carbonyl group in various saturated aldehydes and ketones by alcohols used as hydrogen donors in the presence of heterogeneous catalysts is very well doc-

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Abbreviations: A, hydrogen acceptor; CTH, catalytic transfer hydrogenation; D, hydrogen donor; D/A, donor/acceptor molar ratio; EMF, equilibrium mole fraction; SAL, saturated aldehyde; SOL, saturated alcohol; SON, saturated ketone; UAL, unsaturated aldehyde; UOL, unsaturated alcohol; UON, unsaturated ketone.

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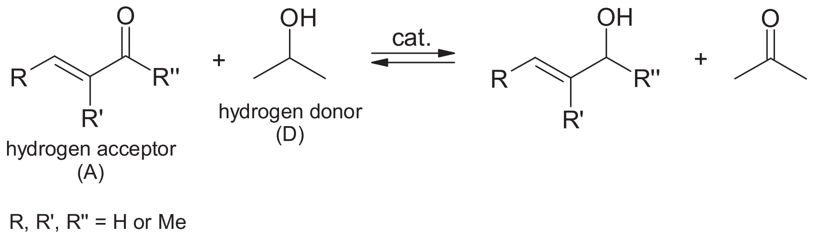


Scheme 1. Catalytic transfer hydrogenation (CTH). Hydrogen acceptor—e.g., carbonyl compound, hydrogen donor—e.g., aliphatic alcohol.

umented [8–13]. Therefore, it has been anticipated that the ease of the reduction of the carbonyl group in the CTH might be preserved also for α,β-unsaturated carbonyl compounds, which could result in a high chemoselectivity towards unsaturated alcohols. Indeed, CTH of α,β-unsaturated carbonyl compounds very often leads to the formation of unsaturated alcohols as the main products but the reaction chemoselectivity is not always as high as expected [14–16].

Among hydrogen donors the secondary alcohols are mainly used, with 2-propanol as the most frequent one, although primary alcohols: ethanol, 1-butanol or even methanol have also been studied [17]. The explanation of the popularity of 2-propanol is the result of its accessibility, a low price, low toxicity, as well as relatively high volatility, which is a great advantage during the separation of products. What is also important, the alcohol belongs to a group of secondary alcohols which seem to be better hydrogen donors than primary ones.

Although in literature there are publications in which the higher reactivity of ethanol than 2-propanol in the transfer hydrogenation of acrolein in the presence of MgO has been documented, the authors did not discuss this fact at all, probably due to a modest knowledge about the thermodynamic description of such reactions at that time [17,18]. In the light of the difficulties met during interpretation of the results of CTH tests with the participation of various α,β-unsaturated carbonyl compounds taken from literature and ours, we find our own very preliminary thermodynamic description of the transfer hydrogenation of acrolein with various alcohols which have been published recently [19] insufficient. First, in the mentioned description each reaction has been considered separately, which, of course, is only a very rough estimation, and does not enable the calculation of the thermodynamic compositions of the reactants under equilibrium. Second, for our calculations of the transfer hydrogenation we have chosen only one temperature (673 K), which is too high for most hydrogenations of multiple carbon–carbon or carbon–oxygen bonds. Third, we have made our calculations only for acrolein, so it is impossible to draw general conclusions about the reduction of a whole group of α,β-unsaturated carbonyl compounds. Unfortunately, there have been no previous reports of thermodynamics of transfer hydrogenation of α,β-unsaturated carbonyl compounds with alcohols as hydrogen donors, so the observed experimental phenomena could not be explained on the basis of thermodynamic considerations.

In short, it can be seen that the thermodynamic background for the hydrogenation/transfer hydrogenation of α,β-unsaturated carbonyl compounds cited in literature is scarce and uncertain. We believe that for designing heterogeneous catalytic systems which would chemoselectively hydrogenate the C═O bond in α,β-unsaturated carbonyl compounds, a deeper understanding of thermodynamics is needed. This is why the principal aim of the paper was to perform a comprehensive thermodynamics analysis of hydrogenation/transfer hydrogenation reactions, with gaseous dihydrogen or alcohols as reductants, of four chosen α,β-unsaturated carbonyl compounds. The obtained thermodynamic data would be very helpful to determine equilibrium yields of desired products under given reaction conditions, to understand some peculiarities occurring in a set of reaction pathways of CTH between α,β-unsaturated carbonyl compounds and ethanol or 2-propanol, and to find plausible generalizations. To authors' knowledge such a description has not been published yet. The present work fills this gap.

The second aim of this work was to look closer at the unpredictably (by thermodynamics) low reactivity of 2-propanol shown in the presence of magnesium oxide in the transfer hydrogenation of acrolein than that of ethanol. Another aspect of the studies was to compare the reactivities of both alcohols in transfer hydrogenations of many other carbonyl compounds in aim to find plausible regularities.

2. Experimental

2.1. Thermodynamic calculations

The thermodynamic calculations leading to the evaluation of the Gibbs function (ΔG), the equilibrium constant (K) and equilibrium mole fractions (EMFs) were based on data (enthalpies ΔH^0_{298}, entropies S^0_{298}, and molar heat capacities C_p) received from NIST database [20], from the group contribution methods [21–23] and from the experimental data found in literature [24]. The missing data were calculated using known methods [21,22]. The details of calculations together with basic thermodynamic data are given in the supplementary materials.

Our calculations were made for the temperature range of 423.15–723.15 K, for normal pressure, which corresponds to typical conditions at which all vapour phase transfer hydrogenation reactions were performed.

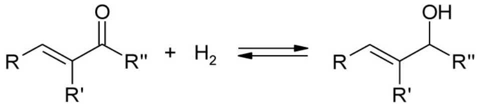
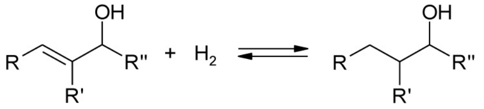
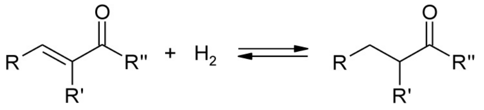
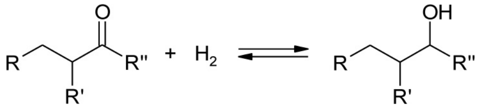
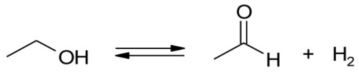
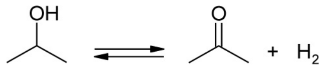
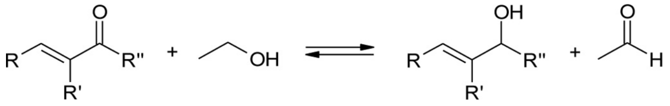
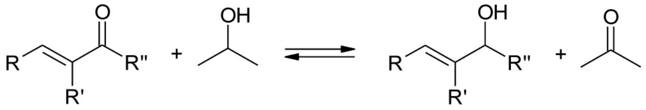
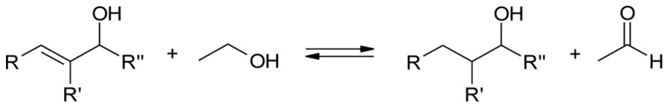
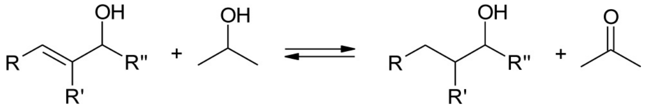
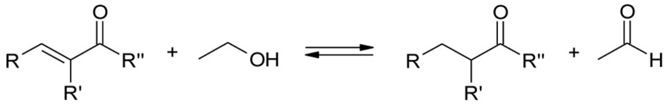
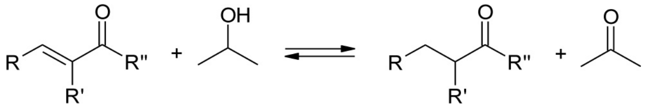
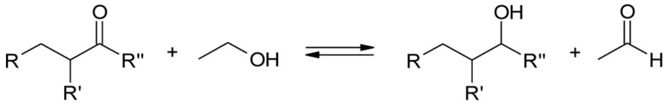
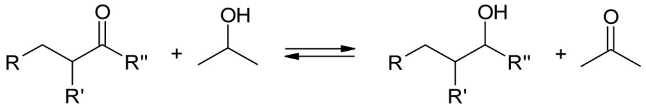
2.2. Catalyst preparation and characterization

Magnesium oxide was prepared by thermal decomposition of $Mg(OH)_2$ whose preparation is described elsewhere [19]. The sieved fraction of the hydroxide of 0.16–0.40 mm was calcined first at 873 K for 1 h in a stream of dry air, then for 5 h in a stream of dry deoxygenated nitrogen and stored under nitrogen. The specific area of MgO was 99.7 $m^2\,g^{-1}$, the pore volume 0.529 $cm^3\,g^{-1}$. The detailed characterization of thus prepared MgO is given in a previous paper for the same batch of catalyst [19].

2.3. Reagents

Acetophenone (99%), benzaldehyde (>99%), cyclohexanone (>99%), hexanal (97%), 5-hexen-2-one (allylacetone) (99%) and 3-methylbutan-2-one (methyl isopropyl ketone, 99%) were all Aldrich products. They were dried over anhydrous $MgSO_4$, distilled under normal/reduced pressure in the atmosphere of dry nitrogen and kept under nitrogen in Schlenk-type containers with the exception of both aldehydes for which the second distillation was made to remove contamination with carboxylic acids formed during contact with atmospheric oxygen and the products were distilled directly to

Table 1
List of possible reactions (R, R' and R" = H or Me).

Number	Reaction
1	
2	
3	
4	
5	
6	
7E	
7P	
8E	
8P	
9E	
9P	
10E	
10P	

Schlenk-type containers. Benzophenone (99%, Aldrich) was twice crystallized from ethanol. Acrolein (90%, Aldrich) was purified as described before [19] and stored under nitrogen in a Schlenk-type container at 243 K in a freezer. Ethanol (p.a., anhydrous 99.8%), 2-propanol (p.a.) both from POCh Gliwice, Poland, and 1-propanol (99%, Aldrich) were distilled over metallic sodium and kept dry in Schlenk-type containers under nitrogen.

2.4. *Catalytic activity measurements*

The measurements were carried out in a fixed-bed tubular quartz reactor equipped with a concentric tube where a thermocouple was placed, and heated by an electric furnace. A sample of the catalyst (250 ± 5 mg) was loaded into the reactor in a stream of dry nitrogen. The activity measurements were performed in the temperature range 423–573 K. A solution of a carbonyl compound in ethanol or 2-propanol at a given molar ratio was dosed using a microdosing pump with a Liquid Hourly Space Velocity (LHSV): 3 h^{-1} into a stream of nitrogen (50 cm^3 min^{-1}) which was passed through the catalyst bed. Before typical measurements of activity, the catalyst was maintained for 60 min at the first (lowest) reaction temperature, in the stream of reactants, and the products formed during that initial period were discarded.

2.5. *Analytical determinations*

The reaction products were analysed by GC using HRGC KONIK (Spain) equipped with a TRACER wax capillary (length 30 m, 0.25 mm i.d.) and an FID. A selected *n*-alkane, depending on the volatility of the reactants, from the C_8–C_{14} range was used as an internal standard. Compounds were identified by GC–MS (HP-6890N with a 5973N mass detector) and by comparison of the retention time with that of the internal standard.

3. Results and discussion

In the work of Campo et al. [6] concerning the catalytic hydrogenation of α,β-unsaturated carbonyl compounds it is mentioned that thermodynamics favours the hydrogenation of the C=C bond over the C=O bond by approximately 35 kJ mol^{-1} [1]. The same value has been cited in other works [3–5]. However, our calculations made at the early stage of this work for the hydrogenation of β-methylacrolein (crotonaldehyde), as it was published in the original work of Vannice and Sen [1], give values 42.5 and 42.3 kJ mol^{-1} for 423 and 723 K, respectively. Due to this discrepancy between the value found in literature and the values calculated by us and also the lack of data for hydrogenation of other compounds of this type, we decided to extend our studies to other α,β-unsaturated carbonyl compounds.

Four α,β-unsaturated carbonyl compounds were selected for thermodynamic calculations: acrolein – the simplest unsaturated aldehyde, its α- and β-methyl derivatives, and methyl vinyl ketone – the simplest unsaturated ketone (Scheme 2).

The list of equations which describe the possible reactions which can occur when an α,β-unsaturated carbonyl compound reacts with gaseous dihydrogen or a hydrogen donor is given in Table 1. Calculations for three groups of reactions were performed:

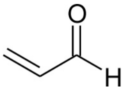
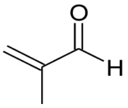
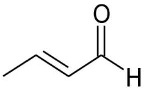
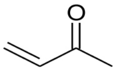
- hydrogenation of α,β-unsaturated carbonyl compounds (Eqs. 1–4);
- dehydrogenation of alcohols: ethanol and 2-propanol (Eqs. 5 and 6);
- transfer hydrogenation of α,β-unsaturated carbonyl compounds with ethanol (Eqs. 7E, 8E, 9E and 10E) and with 2-propanol (Eqs. 7P, 8P, 9P and 10P).

3.1. *Thermodynamic analysis of the vapour-phase hydrogenation reaction of acrolein, α-methyl- and β-methylacrolein, and methyl vinyl ketone with dihydrogen*

For hydrogenation of each α,β-unsaturated carbonyl compound three single reaction pathways were analysed, namely hydrogenation of:

- only the C=O bond (1);
- only the C=C bond (3);
- both C=C and C=O bonds (3 + 4).

Table 2
Calculated Gibbs free energies for hydrogenation of acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone with dihydrogen in gas phase under normal pressure at various temperatures.

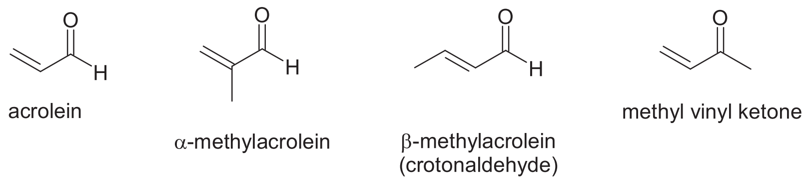
Compound	T [K]	$\Delta G_r(i)$ [kJ mol^{-1}]		
		(1)	(3)	(3 + 4)
	423.15	−5.76	−58.79	−79.74
	473.15	0.50	−52.23	−67.05
	523.15	6.87	−45.58	−54.20
	573.15	13.31	−38.86	−41.21
	623.15	19.83	−32.07	−28.12
	673.15	26.41	−25.23	−14.93
	723.15	33.04	−18.35	−1.67
	423.15	−7.83	−51.10	−73.26
	473.15	−1.47	−44.22	−60.24
	523.15	4.98	−37.30	−47.07
	573.15	11.50	−30.38	−33.77
	623.15	18.07	−23.48	−20.37
	673.15	24.70	−16.62	−6.89
	723.15	31.37	−9.82	6.65
	423.15	−5.27	−47.81	−67.76
	473.15	0.99	−41.46	−55.28
	523.15	7.36	−35.03	−42.65
	573.15	13.81	−28.54	−29.89
	623.15	20.33	−21.99	−17.03
	673.15	26.92	−15.39	−4.08
	723.15	33.56	−8.75	8.93
	423.15	-3.19	−75.28	−84.16
	473.15	2.57	−69.33	−72.30
	523.15	8.35	−63.30	−60.30
	573.15	14.13	−57.17	−48.18
	623.15	19.92	−50.97	−35.96
	673.15	25.71	−44.69	−23.65
	723.15	31.50	−38.33	−11.25

The values of the Gibbs free energy changes for all elementary reactions: the formation of unsaturated alcohol (UOL) (1), saturated aldehyde/ketone (SAL/SON) (3) and saturated alcohol (SOL) (3 + 4), carried out at seven different temperatures, from 423.15 to 723.15 K with a 50 deg step, are summarized in Table 2. It can be seen that for all three reactions, the Gibbs free energy values increase with temperature, which means that the reactions are becoming less and less thermodynamically favourable. Reaction (1) was found thermodynamically favourable at temperatures no higher than 473.15 K, except in the case of α-methylacrolein, for which a negative value of the Gibbs free energy change was also noted below 532.15 K. Reaction (3) is favoured in the whole range of temperatures. Reaction (3 + 4) is in general thermodynamically favourable. It is only not favoured in the case of α-methylacrolein and β-methylacrolein at 723.15 K.

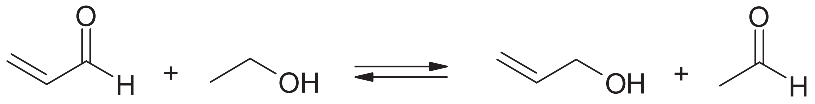
Based on the results presented in Table 2, the exact temperatures at which $\Delta G_r(1) > 0$, which means that the formation of unsaturated alcohols (UOLs) is not thermodynamically favoured, were obtained. They are: 469, 485, 465 and 451 K for acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone, respectively.

It has been stated in literature that thermodynamics favours the hydrogenation of the C=C bond over that of the C=O bond by c.a. 35 kJ mol^{-1} [1]. According to our calculations, at 423.15 and 723.15 K the appropriate values for acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone are equal 53.0 and 51.4, 43.3 and 41.2, 42.5 and 42.3, and 72.1 and 69.8 kJ mol^{-1}, respectively.

The results of the above mentioned calculations are in line with those we obtained using the method of group contributions developed by Van Krevelen and Chermin [25]. For acrolein it gave us the

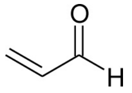
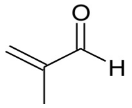
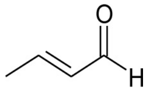
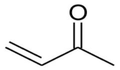


Scheme 2. α,β-Unsaturated carbonyl compounds–substrates in hydrogenation and transfer hydrogenation reactions.



Scheme 3. Catalytic transfer hydrogenation of acrolein with ethanol.

Table 3
Calculated EMFs for hydrogenation of acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone with dihydrogen, in gas phase under normal pressure at various temperatures. Molar ratio H_2/UAL(UON) = 6.

Compound	T [K]	EMFs			
		UAL/UON	UOL	SAL/SON	SOL
	423.15	$<10^{-4}$	$<10^{-4}$	0.0032	0.9968
	473.15	$<10^{-4}$	$<10^{-4}$	0.0280	0.9720
	523.15	$<10^{-4}$	$<10^{-4}$	0.1462	0.8538
	573.15	0.0002	$<10^{-4}$	0.4279	0.5719
	623.15	0.0018	$<10^{-4}$	0.7210	0.2772
	673.15	0.0116	0.0001	0.8733	0.1150
	723.15	0.0511	0.0002	0.9019	0.0468
	423.15	$<10^{-4}$	$<10^{-4}$	0.0023	0.9977
	473.15	$<10^{-4}$	$<10^{-4}$	0.0208	0.9792
	523.15	$<10^{-4}$	$<10^{-4}$	0.1164	0.8836
	573.15	0.0008	0.0001	0.3760	0.6231
	623.15	0.0089	0.0002	0.6821	0.3087
	673.15	0.0510	0.0005	0.8275	0.1209
	723.15	0.1803	0.0008	0.7770	0.0418
	423.15	$<10^{-4}$	$<10^{-4}$	0.0043	0.9957
	473.15	$<10^{-4}$	$<10^{-4}$	0.0358	0.9641
	523.15	0.0001	$<10^{-4}$	0.1771	0.8228
	573.15	0.0015	0.0001	0.4788	0.5197
	623.15	0.0130	0.0002	0.7491	0.2377
	673.15	0.0646	0.0004	0.8422	0.0928
	723.15	0.2095	0.0007	0.7566	0.0333
	423.15	$<10^{-4}$	$<10^{-4}$	0.0906	0.9094
	473.15	$<10^{-4}$	$<10^{-4}$	0.3665	0.6335
	523.15	$<10^{-4}$	$<10^{-4}$	0.7073	0.2927
	573.15	$<10^{-4}$	$<10^{-4}$	0.8883	0.1117
	623.15	0.0001	$<10^{-4}$	0.9561	0.0439
	673.15	0.0004	$<10^{-4}$	0.9806	0.0190
	723.15	0.0020	$<10^{-4}$	0.9889	0.0091

EMF—equilibrium mole fraction; UAL—unsaturated aldehyde; UON—unsaturated ketone; UOL—unsaturated alcohol; SAL—saturated aldehyde; SON—saturated ketone; SOL—saturated alcohol.

following values: 57.2 and 57.9 kJ mol^{-1}, at 423.15 and 723.15 K, respectively.

Calculations of equilibrium compositions of the reactants under study in the temperature range of 423.15–723.15 K with a molar ratio of hydrogen to the α,β-unsaturated carbonyl compound equal to 6 have been performed (Table 3). The equilibrium mole fractions (EMFs) of the substrates in the postreaction mixture are close to zero at low temperatures and increase insignificantly with temperature. The EMFs for all UOLs are very low regardless of the temperature and do not exceed 0.0008, so these products are not favoured by thermodynamics. The EMFs for UAL-s (or UON-s) clearly indicate that for acrolein and methyl vinyl ketone the conversion is almost quantitative. In contrast, for the other compounds, namely α-methylacrolein and β-methylacrolein, the EMFs are larger and reach nearly 0.2 at the highest studied temperature.

Saturated alcohols (SOL-s) were dominating hydrogenation products in a lower range of temperatures, at 423.15 K their EMFs values exceeded 0.99 with the exception of methyl ethyl carbinol for which this value reached c.a. 0.91. An increase of the EMFs values for saturated aldehydes or ketones (SAL-s/SON-s) at the expense of SOL-s has been noted with temperature. They become the main products above 573 K or in the case of ethyl methyl ketone, already at 523 K.

Summing up these results, it can be seen that the main products of the reactions are SAL/SON and SOL. Based on the analysis of the obtained values for the four studied α,β-unsaturated carbonyl compounds we have shown that the structure of a given compound greatly influences the degree to which the hydrogenation of the C═C bond is preferred over that of the C═O bond. It has been concluded that temperature strongly influences the SAL/SOL ratio in the hydrogenation of studied α,β-unsaturated carbonyl compounds.

3.2. *Thermodynamic analysis of the vapour-phase dehydrogenation of ethanol and 2-propanol*

The dehydrogenation propensity of ethanol and 2-propanol is the key to understanding their thermodynamic capability for hydrogenation of organic acceptors (Table 4). It can be seen that the dehydrogenation of both alcohols is not favoured at low temperatures. The ΔG value decreases with temperature and, as calculated, becomes negative above 605.6 K for ethanol and 502.3 K for 2-propanol. By comparison of these two values it can be concluded that 2-propanol is more prone to dehydrogenation than ethanol, so the former should be a better hydrogen donor. Indeed, the review of publications concerning CTH has shown that 2-propanol is the most frequently used hydrogen donor. Its popularity as the donor, besides its low toxicity, and a low price, has a strong thermodynamic background (Table 4).

3.3. *Thermodynamic analysis of the vapour-phase transfer hydrogenation of acrolein, α- and β-methylacrolein, and methyl vinyl ketone with ethanol or 2-propanol as hydrogen donors*

In contrast to the hydrogenation with dihydrogen, in the thermodynamic analysis of the transfer hydrogenation reaction with alcohols the Gibbs free energy of formation of a chosen hydrogen donor, as well as its dehydrogenation product (an aldehyde or ketone) must be taken into account (Scheme 3).

The values of the Gibbs free energy change for all elementary reactions are collected in Tables 5 and 6.

The analysis of the results of the calculations of the Gibbs free energies of transfer hydrogenation with ethanol as the hydrogen donor (Table 5) indicates that:

Table 4
Calculated Gibbs free energies (Eqs. 5 and 6) and EMFs for dehydrogenation of ethanol and 2-propanol in gas phase under normal pressure at various temperatures.

Alcohol	T [K]	ΔG_r[kJ mol^{-1}]	EMFs		
			Alcohol	Acetaldehyde[a]	H_2
EtOH	423.15	22.32	0.9196	0.0402	0.0402
	473.15	16.28	0.7772	0.1114	0.1114
	523.15	10.18	0.5426	0.2287	0.2287
	573.15	4.02	0.2918	0.3541	0.3541
	623.15	-2.17	0.1258	0.4371	0.4371
	673.15	-8.40	0.0504	0.4748	0.4748
	723.15	-14.65	0.0210	0.4895	0.4895
2-PrOH	423.15	9.25	0.5880	0.2060	0.2060
	473.15	3.42	0.2958	0.3521	0.3521
	523.15	-2.44	0.1124	0.4438	0.4438
	573.15	-8.33	0.0402	0.4799	0.4799
	623.15	-14.23	0.0156	0.4922	0.4922
	673.15	-20.14	0.0068	0.4966	0.4966
	723.15	-26.05	0.0032	0.4984	0.4984

EMF—equilibrium mole fraction.

[a] Acetone for 2-PrOH.

Table 5
Calculated Gibbs free energies for transfer hydrogenation of acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone with ethanol in gas phase under normal pressure at various temperatures.

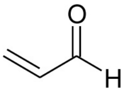
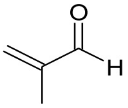
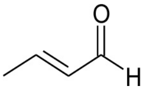
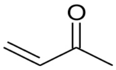
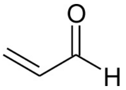
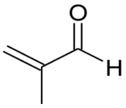
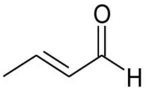
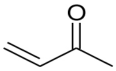
Compound	T [K]	ΔG_r(i) [kJ mol^{-1}]		
		(7E)	(9E)	(9E + 10E)
	423.15	16.56	−36.48	−35.11
	473.15	16.78	−35.95	−34.50
	523.15	17.04	−35.41	−33.85
	573.15	17.34	−34.84	−33.17
	623.15	17.66	−34.24	−32.46
	673.15	18.02	−33.63	−31.72
	723.15	18.40	−32.99	−30.96
	423.15	14.48	−28.79	−28.63
	473.15	14.81	−27.94	−27.68
	523.15	15.15	−27.13	−26.71
	573.15	15.52	−26.36	−25.72
	623.15	15.90	−25.65	−24.71
	673.15	16.30	−25.01	−23.68
	723.15	16.72	−24.47	−22.64
	423.15	17.05	−25.50	−23.13
	473.15	17.27	−25.19	−22.73
	523.15	17.53	−24.86	−22.30
	573.15	17.83	−24.51	−21.84
	623.15	18.16	−24.16	921.36
	673.15	18.53	−23.78	−20.87
	723.15	18.91	−23.40	−20.36
	423.15	19.13	−52.96	−39.53
	473.15	18.85	−53.05	−39.74
	523.15	18.52	−53.12	−39.94
	573.15	18.16	−53.15	−40. 13
	623.15	17.75	−53.14	−40.30
	673.15	17.32	−53.09	−40.44
	723.15	16.86	−52.98	−40.54

Table 6
Calculated Gibbs free energies for transfer hydrogenation of acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone with 2-propanol in gas phase under normal pressure at various temperatures.

Compound	T [K]	ΔG_r(i) [kJ mol^{-1}]		
		(7P)	(9P)	(9P + 10P)
	423.15	3.49	−49.55	−61.25
	473.15	3.92	−48.81	−60.21
	523.15	4.43	−48.02	−59.08
	573.15	4.99	−47.19	−57.86
	623.15	5.61	−46.30	−56.57
	673.15	6.27	−45.37	−55.20
	723.15	6.99	−44.40	−53.78
	423.15	1.41	−41.85	−54.77
	473.15	1.95	−40.80	−53.40
	523.15	2.54	−39.75	−51.95
	573.15	3.17	−38.71	−50.42
	623.15	3.85	−37.70	−48.82
	673.15	4.56	−36.75	−47.17
	723.15	5.31	−35.88	−45.46
	423.15	3.98	−38.57	−49.27
	473.15	4.41	−38.04	−48.45
	523.15	4.92	−37.48	−47.53
	573.15	5.48	−36.86	−46.54
	623.15	6.11	−36.21	−45.48
	673.15	6.78	−35.52	−44.35
	723.15	7.51	−34.80	−43.18
	423.15	6.06	−66.03	−65.67
	473.15	5.99	−65.91	−65.46
	523.15	5.90	−65.74	−65.18
	573.15	5.81	−65.50	−64.83
	623.15	5.70	−65.20	−64.41
	673.15	5.58	−64.83	−63.92
	723.15	5.45	−64.40	−63.36

- irrespective of the type of an α,β-unsaturated carbonyl compound the formation of UOL is not thermodynamically favoured in the whole range of temperatures (423.15–723.15 K);
- the formation of SAL/SON and SOL are practically equally thermodynamically favoured, with the exception of methyl vinyl ketone for which SON predominates over SOL;
- very weak dependence of all the Gibbs free energies of transfer hydrogenation with ethanol on temperature has been observed.

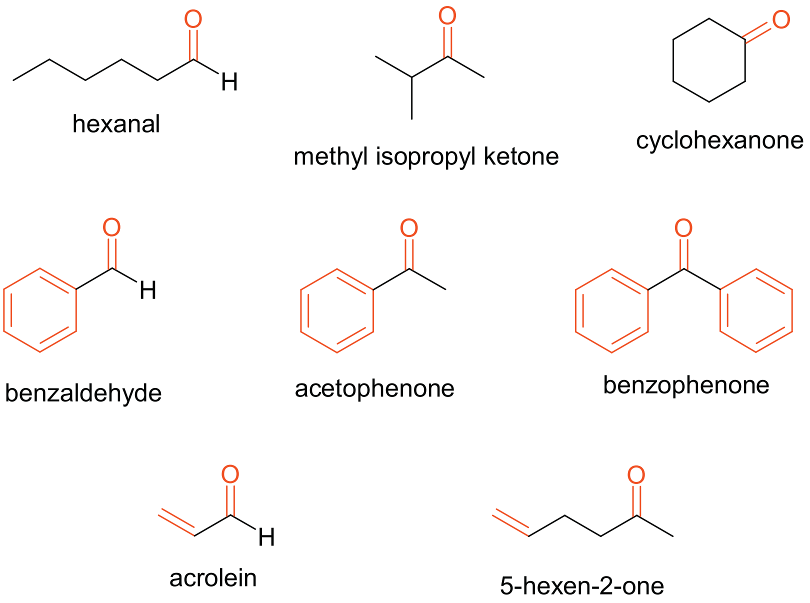
Based on the data presented in Table 6, the following conclusions have been put forward for 2-propanol as the hydrogen donor:

- irrespective of the type of an α,β-unsaturated carbonyl compound the formation of UOL is not thermodynamically favoured in the whole range of temperatures (423.15–723.15 K);
- for all α,β-unsaturated aldehydes SOL is the most thermodynamically favoured product, for methyl vinyl ketone SON and SOL are practically equal thermodynamically favoured;
- the values of the Gibbs free energies of transfer hydrogenation with 2-propanol are always lower in comparison to the appropriate values for ethanol. The gap equals 13.07 and 11.41 kJ mol^{-1} for 423.15 and 723.15 K, respectively.

Calculations of EMFs for transfer hydrogenation of studied α,β-unsaturated carbonyl compounds with ethanol (Table 7) or 2-propanol (Table 8) revealed that at the temperature range of 423.15–723.15 K a quantitative conversion of every carbonyl compound can be attained. This is accompanied by the presence of SAL/SON and SOL as the only products. For ethanol as the hydrogen donor SOL is the main product with the exception of methyl vinyl ketone, for which SON dominates. For 2-propanol SOL is in every case the main product, its EMF varies between 0.68 and 0.99. At low temperatures (423.15–473.15 K) for α,β-unsaturated aldehydes SOL is the only product; its EMF is in the range of 0.97–0.99.

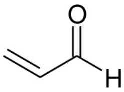
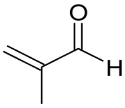
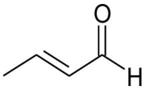
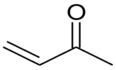
3.4. Reactivity of ethanol and 2-propanol as hydrogen donors in the vapour-phase CTH of various carbonyl compounds in the presence of MgO

The reactivity of ethanol and 2-propanol as hydrogen donors to eight carbonyl compounds (Scheme 4) has been studied in the presence of MgO as the catalyst. Three of these compounds, namely: hexanal, methyl isopropyl ketone and cyclohexanone, possess only a carbonyl group prone to hydrogenation. The next three, namely benzaldehyde, acetophenone and benzophenone, also have a phenyl substituent, which could be hydrogenated to a cyclohexyl group, although such a reaction does not occur under the stud-



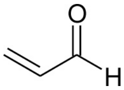
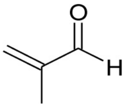
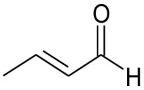
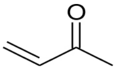
Scheme 4. Carbonyl compounds used as hydrogen acceptors.

Table 7
Calculated EMFs for transfer hydrogenation of acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone with ethanol in gas phase under normal pressure at various temperatures. Molar ratio EtOH/UAL(UON) = 6.

Compound	T [K]	EMFs			
		UAL/UON	UOL	SAL/SON	SOL
	423.15	$<10^{-4}$	$<10^{-4}$	0.3572	0.6428
	473.15	$<10^{-4}$	$<10^{-4}$	0.3538	0.6462
	523.15	$<10^{-4}$	$<10^{-4}$	0.3515	0.6484
	573.15	0.0001	$<10^{-4}$	0.3500	0.6499
	623.15	0.0002	$<10^{-4}$	0.3489	0.6509
	673.15	0.0003	$<10^{-4}$	0.3480	0.6517
	723.15	0.0005	0.0001	0.3472	0.6521
	423.15	$<10^{-4}$	$<10^{-4}$	0.2935	0.7065
	473.15	0.0001	$<10^{-4}$	0.2972	0.7027
	523.15	0.0002	$<10^{-4}$	0.3024	0.6973
	573.15	0.0005	$<10^{-4}$	0.3092	0.6902
	623.15	0.0009	0.0001	0.3176	0.6814
	673.15	0.0014	0.0002	0.3277	0.6706
	723.15	0.0022	0.0004	0.3396	0.6578
	423.15	0.0001	$<10^{-4}$	0.4132	0.5867
	473.15	0.0002	$<10^{-4}$	0.4036	0.5962
	523.15	0.0005	$<10^{-4}$	0.3962	0.6033
	573.15	0.0008	0.0001	0.3905	0.6087
	623.15	0.0013	0.0001	0.3857	0.6129
	673.15	0.0020	0.0002	0.3816	0.6162
	723.15	0.0028	0.0003	0.3780	0.6188
	423.15	$<10^{-4}$	$<10^{-4}$	0.9100	0.0900
	473.15	$<10^{-4}$	$<10^{-4}$	0.8723	0.1277
	523.15	$<10^{-4}$	$<10^{-4}$	0.8332	0.1668
	573.15	$<10^{-4}$	$<10^{-4}$	0.7944	0.2056
	623.15	$<10^{-4}$	$<10^{-4}$	0.7570	0.2430
	673.15	$<10^{-4}$	$<10^{-4}$	0.7217	0.2782
	723.15	$<10^{-4}$	$<10^{-4}$	0.6887	0.3112

EMF—equilibrium mole fraction; UAL—unsaturated aldehyde; UON—unsaturated ketone; UOL—unsaturated alcohol; SAL—saturated aldehyde; SON—saturated ketone; SOL—saturated alcohol.

Table 8
Calculated EMFs for transfer hydrogenation of acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone with 2-propanol in gas phase under normal pressure at various temperatures. Molar ratio 2-PrOH/UAL(UON) = 6.

Compound	T [K]	EMFs			
		UAL/UON	UOL	SAL/SON	SOL
	423.15	$<10^{-4}$	$<10^{-4}$	0.0174	0.9826
	473.15	$<10^{-4}$	$<10^{-4}$	0.0263	0.9737
	523.15	$<10^{-4}$	$<10^{-4}$	0.0368	0.9632
	573.15	$<10^{-4}$	$<10^{-4}$	0.0488	0.9512
	623.15	$<10^{-4}$	$<10^{-4}$	0.0617	0.9383
	673.15	$<10^{-4}$	$<10^{-4}$	0.0754	0.9246
	723.15	$<10^{-4}$	$<10^{-4}$	0.0894	0.9105
	423.15	$<10^{-4}$	$<10^{-4}$	0.0125	0.9875
	473.15	$<10^{-4}$	$<10^{-4}$	0.0196	0.9804
	523.15	$<10^{-4}$	$<10^{-4}$	0.0287	0.9713
	573.15	$<10^{-4}$	$<10^{-4}$	0.0399	0.9601
	623.15	$<10^{-4}$	$<10^{-4}$	0.0532	0.9468
	673.15	$<10^{-4}$	$<10^{-4}$	0.0688	0.9312
	723.15	0.0001	0.0001	0.0868	0.9130
	423.15	$<10^{-4}$	$<10^{-4}$	0.0229	0.9771
	473.15	$<10^{-4}$	$<10^{-4}$	0.0335	0.9665
	523.15	$<10^{-4}$	$<10^{-4}$	0.0457	0.9543
	573.15	$<10^{-4}$	$<10^{-4}$	0.0591	0.9409
	623.15	$<10^{-4}$	$<10^{-4}$	0.0733	0.9266
	673.15	0.0001	$<10^{-4}$	0.0880	0.9118
	723.15	0.0001	0.0001	0.1030	0.8968
	423.15	$<10^{-4}$	$<10^{-4}$	0.3041	0.6959
	473.15	$<10^{-4}$	$<10^{-4}$	0.3063	0.6937
	523.15	$<10^{-4}$	$<10^{-4}$	0.3086	0.6914
	573.15	$<10^{-4}$	$<10^{-4}$	0.3108	0.6892
	623.15	$<10^{-4}$	$<10^{-4}$	0.3128	0.6872
	673.15	$<10^{-4}$	$<10^{-4}$	0.3147	0.6853
	723.15	$<10^{-4}$	$<10^{-4}$	0.3164	0.6836

EMF—equilibrium mole fraction; UAL—unsaturated aldehyde; UON—unsaturated ketone; UOL—unsaturated alcohol; SAL—saturated aldehyde; SON—saturated ketone; SOL—saturated alcohol.

ied conditions. The last two, acrolein and 5-hexen-2-one, are α,β- and γ,δ-unsaturated carbonyl compounds, respectively. It has been found that the transfer hydrogenation of a carbonyl group in studied compounds proceeds very selectively with the formation of alcohols (Figs. 1–5).

It has been found that the transfer hydrogenation of a carbonyl group in studied compounds proceeds very selectively with the formation of alcohols. An exception has only been observed for hexanal, for which aldol condensation occurs as a side reaction, diminishing the yield of 1-hexanol. In contrast, a very high chemoselectivity towards unsaturated alcohols has been noted for acrolein and 5-hexenone, despite the fact that in their case the reduction of the carbonyl group is not favoured thermodynamically unlike the hydrogenation of the C=C bond.

It has been shown that in the presence of MgO as the catalyst 2-propanol is more reactive than ethanol in the transfer hydrogena-

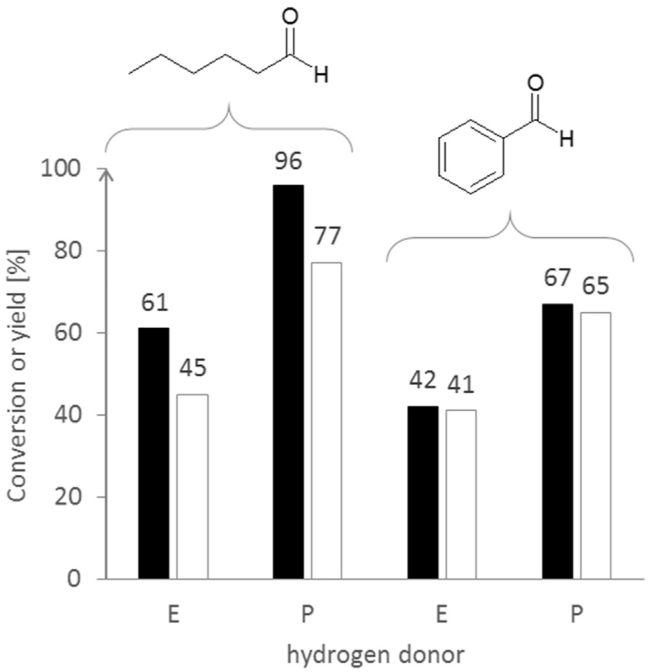


Fig. 1. Catalytic transfer hydrogenation of hexanal and benzaldehyde with ethanol (E) or 2-propanol (P); $T = 473$ K, D/A = 3, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, white—yield of carbinol.

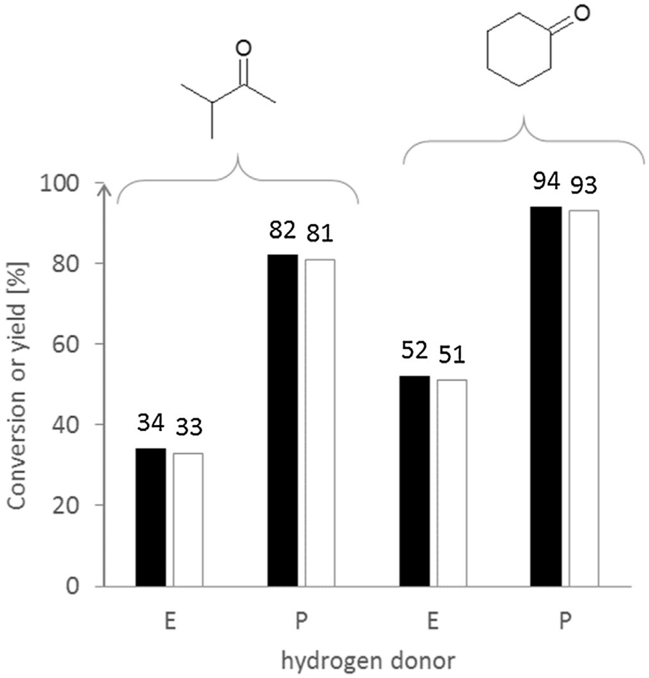


Fig. 2. Catalytic transfer hydrogenation of methyl isopropyl ketone and cyclohexanone with ethanol (E) or 2-propanol (P); $T = 473$ K, D/A = 3 for methyl isopropyl ketone, D/A = 4 for cyclohexanone, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, white—yield of carbinol.

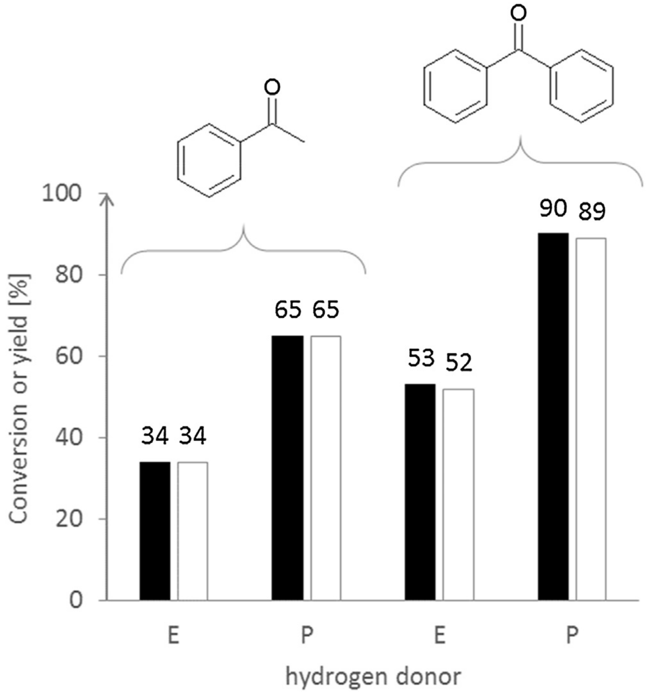


Fig. 3. Catalytic transfer hydrogenation of acetophenone and benzophenone with ethanol (E) or 2-propanol (P); $T = 573$ K, D/A = 3 for acetophenone, D/A = 8 for benzophenone, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, white—yield of carbinol.

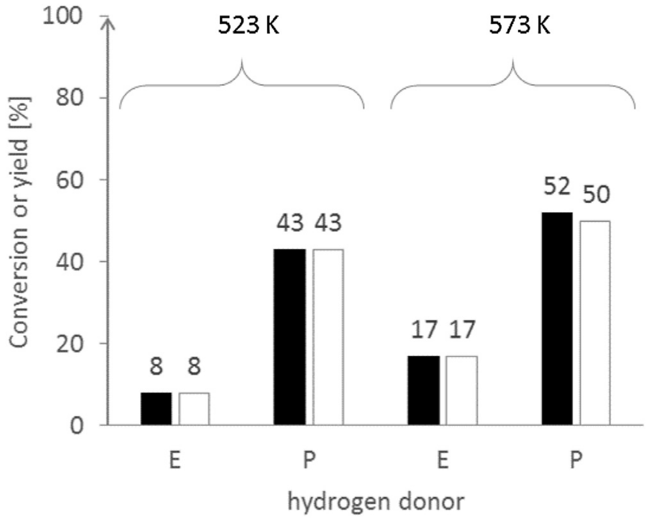


Fig. 4. Catalytic transfer hydrogenation of 5-hexen-2-one with ethanol (E) or 2-propanol (P); D/A = 3, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, white—yield of 5-hexen-2-ol.

tion of various types of carbonyl compounds including aliphatic and aromatic aldehydes, aliphatic ketones, cyclic ketones, aralkyl and aryl ketones as well as 5-hexen-2-one. This corresponds well with the results of our calculations, which show that 2-propanol is thermodynamically a better hydrogen donor than ethanol. However, 2-propanol shows a markedly low reactivity during transfer hydrogenation of acrolein. It has been observed that at 473 and 523 K the yields of allyl alcohol with 2-propanol as the hydrogen donor are only a half of those attained for ethanol. The reason for this unpredictable behaviour is yet unknown. The question arises whether or not 2-propanol shows low reactivity in the transfer hydrogenation of all α,β-unsaturated carbonyl compounds in the presence of MgO.

3.5. Vapour-phase transfer hydrogenation of acrolein with ethanol in the presence of MgO. The origin of reaction chemoselectivity

For this part of work ethanol has been chosen as the hydrogen donor due to its higher reactivity than 2-propanol, to study the origin of reaction chemoselectivity in vapour-phase transfer

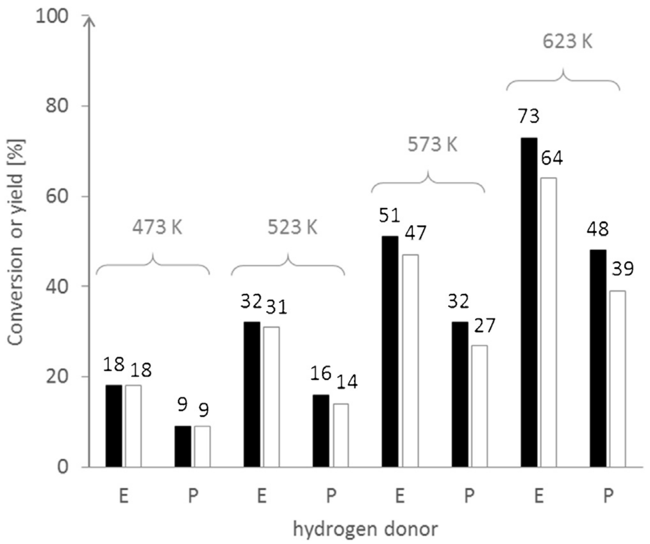


Fig. 5. Catalytic transfer hydrogenation of acrolein with ethanol (E) or 2-propanol (P); D/A = 6, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, white—yield of allyl alcohol.

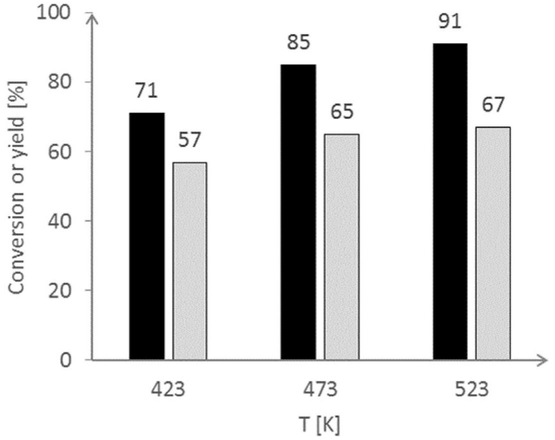


Fig. 6. Catalytic transfer hydrogenation of propionaldehyde (SAL) with ethanol; D/A = 6, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, grey—yield of 1-propanol (SOL).

hydrogenation of acrolein with alcohols in the presence of MgO. We have examined the transformations of the products of acrolein transfer hydrogenation, namely allyl alcohol (UOL) and propionaldehyde (SAL) in the presence of ethanol as the hydrogen donor (Figs. 6 and 7).

The comparison of conversion in catalytic tests performed with propionaldehyde (Fig. 6) and allyl alcohol (Fig. 7) as the hydrogen acceptors from ethanol reveal that in the presence of MgO, only the former is reduced to 1-propanol with high yields.

It was found that magnesium oxide shows a residual activity in allyl alcohol transfer hydrogenation with ethanol, a 3% yield of the product has been only noted at the highest studied temperature (523 K). We have found that in the range of temperatures of 423–523 K, the catalyst is not active in the transfer hydrogenation of acrolein with ethanol into propionaldehyde.

Therefore, the lack of 1-propanol and the product of aldol condensation of propionaldehyde (viz. 2-methyl-2-pentenal), which always accompanies the transformations of the aldehyde in minute amounts (Scheme 5), indicate that the formation of propionaldehyde in transfer hydrogenation of acrolein with ethanol is strongly inhibited.

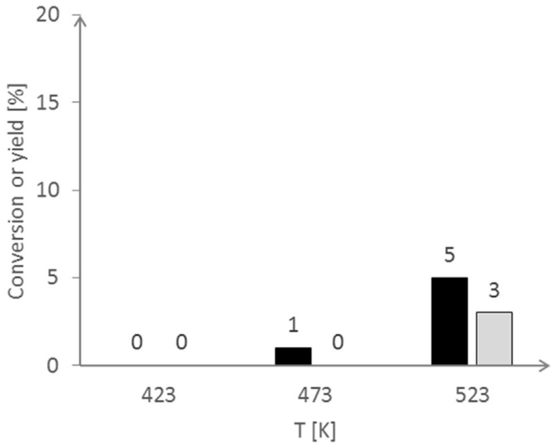
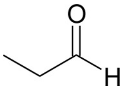
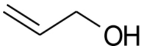
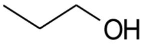


Fig. 7. Catalytic transfer hydrogenation of allyl alcohol (UOL) with ethanol; D/A = 6, LHSV = 3 h^{-1}, GHSV (N_2) = 4000 h^{-1}. Black—conversion, grey—yield of 1-propanol (SOL).

Table 9
Transformations of propionaldehyde, allyl alcohol and 1-propanol in the presence of MgO as the catalyst. LHSV = 3 h^{-1}; GHSV (N_2) = 4000 h^{-1}.

Compound	T [K]	Conv. [%]	Yield [%]		
			UOL	UAL	SAL
	423	13	–	10[a]	–
	473	4	–	3[a]	–
	523	3	–	1[a]	–
	423	0	–	–	–
	473	tr[b]	–	0	–
	523	2	–	0	–
	423	0	–	–	–
	473	tr[b]	–	–	tr[b]
	523	tr[c]	–	–	tr[c]

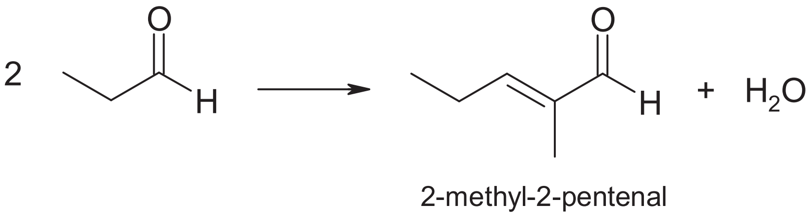
UOL—unsaturated alcohol, UAL—unsaturated aldehyde, SAL—saturated aldehyde.
[a] 2-methyl-2-pentenal.
[b] 0.1%.
[c] 0.3%.

Additionally, catalytic tests in the presence of MgO were performed with propionaldehyde, allyl alcohol and 1-propanol in the absence of ethanol. The results are collected in Table 9. The aim of these tests was to check if any reaction of the possible products derived from transfer hydrogenation of acrolein could react further in the presence of the catalyst, hence obscuring the results obtained earlier. We have found that in the range of temperatures of 423–523 K, magnesium oxide is not active in either the isomerization of allyl alcohol into propionaldehyde or in the dehydrogenation of 1-propanol into propionaldehyde. Under the same conditions propionaldehyde undergoes aldol condensation with the formation of 2-methyl-2-pentenal (Scheme 5). However, in this case, the conversion of propionaldehyde decreased strongly with temperature due to deactivation of the catalyst (Table 9; UAL yield).

The above mentioned facts lead to the conclusion that the very high chemoselectivity towards allyl alcohol in the transfer hydrogenation of acrolein is caused by a kinetic control induced by magnesium oxide as the catalyst. It seems obvious that the structure of the hydrogen acceptor plays a crucial role in the observed behaviour of the catalyst; otherwise, acrolein would be (transfer) hydrogenated preferentially into a SAL/SOL mixture.

4. Conclusions

The main achievement of this work is a comprehensive thermodynamic description of vapour phase transfer hydrogenation



Scheme 5. Aldol condensation of propionaldehyde.

of four representatives of α,β-unsaturated carbonyl compounds: acrolein, α-methylacrolein, β-methylacrolein and methyl vinyl ketone at 423.15–723.15 K with alcohols (EtOH or 2-PrOH) as hydrogen donors and comparison of the obtained data with those calculated for hydrogenation of the same set of compounds with dihydrogen. The calculations were performed in accordance to well-known methods and the Gibbs free energies and equilibrium mole fractions (EMFs) were obtained. The results obtained from both modes of hydrogenation reveal that the EMFs for the UOLs are very low (<0.0009) at all temperatures for all four studied compounds. When an α,β-unsaturated carbonyl compound is hydrogenated with dihydrogen at 423.15 K, the EMF for SAL/SON is in the range of 0.002–0.091 (the exact value depends on the structure). The values obtained for transfer hydrogenation differ from those from hydrogenation with dihydrogen in that even at the lowest temperature the SAL/SOL ratio is much greater, i.e. 0.36:0.64 for transfer hydrogenation of acrolein with ethanol and is strongly influenced by the structure of the hydrogen acceptor as well as hydrogen donor. Based on the analysis of the calculated values for these four α,β-unsaturated carbonyl compounds we have shown that the structure of a given compound greatly influences the extent to which the hydrogenation of the C═C bond is preferred over the hydrogenation of the C═O bond.

Our measurements of the reactivity of ethanol and 2-propanol in the transfer hydrogenation of chosen carbonyl compounds: hexanal, methyl isopropyl ketone, cyclohexanone, benzaldehyde, acetophenone, benzophenone, 5-hexen-2-one and acrolein in the presence of magnesium oxide as the catalyst revealed that:

- a very high selectivity of the reduction of a carbonyl group into carbinol group for all studied compounds except hexanal has been observed;
- for all carbonyl compounds except acrolein the reactivity of 2-propanol highly exceeded that shown by ethanol.

It has been proved that in the presence of magnesium oxide the reactivity of ethanol in the transfer hydrogenation of acrolein is higher than that with 2-propanol, despite the fact that from the thermodynamic standpoint, secondary alcohols are better hydrogen donors than primary ones. The chemoselectivity of vapour phase transfer hydrogenation of acrolein to allyl alcohol and its yield are the highest noted in literature. Although thermodynamics favours other products, the presence of magnesium oxide as the catalyst controls the reaction kinetically to give such a high chemoselectivity.

It has been shown that in the transfer hydrogenation of propionaldehyde and allyl alcohol with ethanol in the presence of magnesium oxide only the former is reduced to 1-propanol with high yields. The formation of propionaldehyde in the transfer hydrogenation of acrolein with ethanol is strongly inhibited, which is recognized by the lack of 1-propanol in the products. It has also been proved that the catalyst is not active in either the isomerization of allyl alcohol into propionaldehyde or in the dehydrogenation of 1-propanol into propionaldehyde. In the light of the thermodynamic calculations, it can be assumed that the observed high chemoselectivity of the transfer hydrogenation of acrolein with alcohols is caused by a kinetic control induced by magnesium oxide as the catalyst.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2015.11.046.

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