

Reduction of Alkyl Alkyl, Aryl Alkyl and Cyclic Ketones by Catalytic Hydrogen Transfer over Magnesium Oxide

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The reduction of a series of alkyl alkyl, aryl alkyl and cyclic ketones by catalytic hydrogen transfer (CTR) from isopropyl alcohol over magnesium oxide has been investigated. CTR over MgO was found to be an effective and selective route to the corresponding methanols. At temperatures above 523 K *para*-substituted phenylmethanols underwent consecutive dehydration leading to the formation of the corresponding styrene derivatives with satisfying yields. These processes were studied in a flow system working continuously. A long-time stability of the catalyst activity has been demonstrated.

Several practical applications of catalytic transfer reduction (CTR) in the synthesis of alcohols from the corresponding ketones have been reported recently. The majority of them were reviewed by Johnstone *et al.*¹ The most important studies concerned the uses of transition metals (mainly Ni, Pd, Ru, Os or Ir) as catalysts.²⁻⁴ Attempts have also been made to reduce ketones by CTR over oxide catalysts.⁵⁻⁸

This paper demonstrates the practical potential of hydrogen transfer over magnesium oxide for the reduction of various types of ketones using isopropyl alcohol as the hydrogen donor. The reaction proceeds according to a general equation:



This work is a continuation of our previous studies of the catalytic properties of MgO and their consequences for synthetic applications.⁹⁻¹¹ Our earlier results concerned the catalytic transfer reduction of aldehydes (saturated and unsaturated), epoxides and C=C bonds, as well as the dehydrogenation of long chain alcohols and alkyloaromatics realized as a reverse reaction over MgO.¹² Recently, we reported the selective reduction of the nitro group in aliphatic and aromatic nitro compounds by hydrogen transfer from various alcohols on MgO.¹³ Herein we report the results of the reduction of a series of alkyl alkyl, aryl alkyl and cyclic ketones with isopropyl alcohol over MgO performed in a continuous system in a flow reactor. The reaction studied seems to be very useful as a selective preparative method for the synthesis of the corresponding methanols. At higher temperatures corresponding styrenes can be obtained from acetophenone derivatives with high yields.

Results

Thermodynamics.—The thermodynamic potential change, ΔG , equilibrium constant, K_p , and equilibrium conversion, α , were calculated, for the hydrogen transfer reactions, using the Van Krevelen–Chermin procedure.¹⁴ These parameters were also calculated for the consecutive dehydration of the methanols formed and subsequent reduction of the alkenes. The method of Van Krevelen and Chermin correlates the structure group contributions with the change of thermodynamic potential of formation as a linear function of temperature, eqn. (1),

$$\Delta G_{f(\text{group})}^\circ = A + B \cdot 10^{-2} \cdot T \quad (1)$$

where A and B are constants characteristic for each group increment. The change of thermodynamic potential of compound formation may be expressed by eqn. (2),

Table 1 Thermodynamics of hydrogen transfer reactions: ketone + isopropyl alcohol; donor:acceptor molar ratio 3

Ketone	T/K	$\Delta G/kJ\ mol^{-1}$	K_p	α
Alkyl alkyl	423	0	1	0.75
	573	0	1	0.75
	723	0	1	0.75
Alkyl aryl	423	0	1	0.75
	573	0	1	0.75
	723	0	1	0.75
Cyclopentanone	423	-4.35	3.44	0.89
	573	-4.35	2.49	0.86
	723	-4.35	2.06	0.84
Cyclohexanone	423	-3.89	3.0	0.88
	573	-3.89	2.3	0.85
	723	-3.89	1.9	0.83

$$\Delta G_{f(\text{comp})}^\circ = \Sigma \text{contribution of composing groups} + \Sigma \text{correction for deviations} + RT \ln \sigma \quad (2)$$

where the last term is the symmetry correction. The structural groups and factors and the numerical values of the corresponding constants A and B are given.¹⁴

The thermodynamic data calculated for the studied hydrogen transfer reactions are collected in Table 1.

Regardless of the type of reactant reduced the equilibrium conversion α reaches the same high level: 0.75–0.89 in the temperature range studied.

In comparison with hydrogen transfer reduction, the consecutive dehydration process was strongly favoured thermodynamically (Table 2).

The successive reduction of dehydration products, alkenes proceeding *via* hydrogen transfer from isopropyl alcohol, was also completely shifted to the products (Table 3).

Summarizing the calculated thermodynamic criteria one could expect significant yields of the desired products of ketone reduction, however, the reduction selectivity should be strongly influenced by consecutive reactions, especially by the dehydration of methanols.

Reduction of Alkyl Alkyl Ketones.—A series of alkyl alkyl ketones of the general formula CH_3COR , where $R = Et, Pr, Pr^i, Bu, Bu^i, Bu^t$ and pentyl have been reduced with isopropyl alcohol to the corresponding methanols over magnesium oxide at temperatures 423–623 K (Table 4). The donor:acceptor molar ratio was 3. Up to 523 K the selectivity of desired methanols was higher than 95%. Their yields were close to 70%

Table 2 Thermodynamics of dehydration of methanols

Ketone	T/K	$\Delta G/\text{kJ mol}^{-1}$	K_p	α
Symmetrical alkyl alkyl methanols ^a	423	-35.38	2.3×10^4	1
	573	-57.67	1.8×10^5	1
	723	-79.97	6.0×10^5	1
Alkyl aryl and methyl alkyl methanols ^b	423	-24.10	946.3	1
	573	-45.82	1.5×10^4	1
	723	-67.53	7.6×10^4	1
Cyclopentanol	423	-59.70	2.4×10^7	1
	573	-81.10	2.5×10^7	1
	723	-102.50	2.5×10^7	1
Cyclohexanol	423	-66.80	1.8×10^8	1
	573	-90.49	1.8×10^8	1
	723	-114.18	1.8×10^8	1

^a Values calculated for dehydration of dipropylmethanol. ^b Values calculated for terminal alkenes.

Table 3 Thermodynamics of hydrogen transfer: alkene + isopropyl alcohol; donor:acceptor molar ratio 3

Alkene	T/K	$\Delta G/\text{kJ mol}^{-1}$	K_p	α
Alkyl aryl	423	-70.80	5.55×10^8	1
	573	-72.63	4.18×10^6	1
	723	-74.45	2.39×10^5	1

which practically corresponds to the calculated theoretical values. No steric effect due to the dimension of the alkyl substituent R on the reduction efficiency was observed. The lack of any steric hindrance is probably due to the small diameter of the second alkyl group (Me). In spite of its thermodynamic preference over the hydrogen exchange reaction, the dehydration of primarily produced alcohols lowered the reaction selectivity only at temperatures higher than 523 K. This kinetic effect resulted from the non-acidic character of the magnesium surface. As a result of dehydration of the corresponding methanols, alkenes were formed with the double bond in position 1 towards the methanol carbon atom.

The spectacular hindering effect influencing the reaction yield and even selectivity was noted during a comparative reduction of dipropyl ketones. The branching of the substituent diminished the methanol yield from 60% to 34% and the reaction selectivity from 95% to 85%.

Reduction of Aryl Alkyl Ketones.—Aryl alkyl ketones of the general formula ArCOCH_3 , where Ar = *p*-C₆H₄Me, *p*-C₆H₄-Prⁱ, *p*-C₆H₄OMe and *p*-C₆H₄Cl were reduced with isopropyl alcohol to the corresponding methanols over MgO at temperatures in the range 473–673 K (Table 5). The donor:acceptor molar ratio was 3. The lowest reaction temperature was limited by the reactant boiling point.

The maximum yield of the desired methanol depended strongly on the type of substituent at the phenyl ring and varied from 26.2% for 4-chloroacetophenone reduction to 63.3% for 4-isopropylacetophenone reduction. This second yield corresponded to ca. 90% of the calculated theoretical value. The type of substituent in the *para* position in the acetophenone molecule was also decisive for the reaction selectivity, especially at temperatures above 573 K, at which the consecutive dehydration of the methanols formed started to be a dominating reaction. The corresponding styrenes were formed from phenylmethanol derivatives. Maximum yields of alkenes reached values higher than 95% at 673 K in the case of the reduction of *p*-methyl, *p*-ethyl and *p*-isopropyl acetophenones. The product mixture of acetophenone, *p*-methoxy

Table 4 Yield and selectivity of alkyl alkyl and cyclic ketone reduction, donor:acceptor ratio 3, HLSV: 3 cm³ g⁻¹ h⁻¹

Ketone	T/K	Yield (%)	Selectivity (%) ^a
Methyl ethyl	423	72.4	100.0
	473	71.9	100.0
	523	71.3	98.4
	573	61.0	94.6
	623	53.6	85.0
Methyl propyl	423	67.0	100.0
	473	68.6	100.0
	523	68.7	99.0
	573	65.0	95.5
	623	60.6	91.8
Methyl isopropyl	423	63.8	100.0
	473	68.6	100.0
	523	67.7	100.0
	573	66.8	100.0
	623	60.4	95.9
Methyl butyl	423	66.4	100.0
	473	68.2	100.0
	523	68.6	100.0
	573	68.7	100.0
	623	62.5	96.4
Methyl isobutyl	423	59.3	100.0
	473	60.0	98.5
	523	59.4	96.4
	573	58.0	96.1
	623	54.4	96.4
Methyl <i>tert</i> -butyl	423	50.0	96.6
	473	65.2	98.0
	523	69.1	100.0
	573	60.4	97.7
	623	50.6	90.0
Methyl amyl	423	66.3	98.0
	473	64.1	95.0
	523	62.8	94.2
	573	60.2	93.2
	623	52.4	94.3
Dipropyl	423	38.4	100.0
	473	56.5	95.9
	523	53.3	96.0
	573	53.0	90.0
	623	26.0	47.4
Diisopropyl	423	8.1	72.0
	473	25.0	86.7
	523	34.4	84.4
	573	36.0	78.5
	623	30.6	70.2
Cyclopentanone	423	86.6	100.0
	473	82.1	100.0
	523	78.0	100.0
	573	59.6	100.0
	623	55.4	98.9
Cyclohexanone	423	86.4	100.0
	473	85.7	100.0
	523	85.0	100.0
	573	84.6	100.0
	623	82.0	100.0

^a The only side-products were the corresponding alkenes; in the case of methyl ethyl, methyl propyl, methyl isopropyl, methyl butyl, methyl isobutyl and methyl amyl ketones the mixture of internal and terminal alkenes was formed of isomers in a ratio ca. 5.

and *p*-chloroacetophenone reduction at the highest temperatures contained remarkable amounts of saturated alkyloaromatics, the products of total reduction of reactant. It is worth noting that the methanols, as well as the *para*-substituted styrenes obtained in the present work, are of great importance for perfumery.

Reduction of Cyclic Ketones.—Cyclopentanone and cyclohexanone were successfully reduced with isopropyl alcohol over MgO to the corresponding alcohols (Table 4). The yields of

Table 5 Products of aryl alkyl ketone reduction, donor:acceptor ratio 3, HLSV: 2 cm³ g⁻¹ h⁻¹

R	T/K	% mol			
		RCH ₃ CHOH	RCH=CH ₂	RCH ₂ CH ₃	RCH ₃ C=O
H	523	52.4	0.4	—	46.8
	573	53.4	1.0	—	45.6
	623	47.6	3.6	1.1	47.7
	673	6.1	28.0	9.0	56.9
	723	0.4	31.8	14.3	53.5
Me	473	52.3	2.8	—	44.9
	523	53.0	1.9	—	45.0
	573	47.0	15.1	—	37.8
	623	4.9	85.5	—	9.6
	673	0.4	98.9	—	0.6
Et	473	49.6	1.2	—	49.1
	523	54.6	3.9	—	41.5
	573	14.6	67.9	—	17.5
	623	1.2	91.4	—	7.4
	673	0.6	97.1	—	2.3
Pr ⁱ	473	63.3	2.0	—	34.7
	523	61.6	1.2	—	37.2
	573	36.2	39.2	—	24.6
	623	6.9	92.0	—	4.1
	673	0.4	97.2	—	2.4
OMe	473	33.8	11.1	—	55.1
	523	22.1	6.8	—	71.1
	573	17.0	42.0	1.0	40.0
	623	0.7	88.4	4.8	6.1
	673	0.8	76.3	14.1	8.8
Cl	723	0.2	67.6	26.4	5.8
	523	16.7	—	—	83.3
	573	26.2	4.4	—	69.6
	623	19.9	35.4	—	44.7
	673	4.7	88.5	—	6.8
	723	0.5	93.5	6.0	—
	773	—	81.0	19.0	—

Table 6 Yields of methyl propyl ketone and cyclohexanone reduction at various HLSV and donor:acceptor ratio, 473 K

Ketone	HLSV/ cm ³ g ⁻¹ h ⁻¹	donor:acceptor	Yield (%) ^a
Methyl propyl	1	0.5	44.0
		1.0	52.7
		1.5	54.6
		3.0	58.1
	2	0.5	40.4
		1.0	53.0
		1.5	49.4
		3.0	59.0
	3	0.5	36.9
		1.0	53.4
		1.5	55.3
		3.0	68.6
Cyclohexanone	1	0.5	44.3
		1.0	64.1
		1.5	70.8
		3.0	86.2
	2	0.5	43.0
		1.0	59.0
		1.5	71.6
		3.0	86.1
	3	0.5	27.6
		1.0	58.3
		1.5	62.5
		3.0	85.7

^a Selectivity was 100% for all tabulated experiments.

cyclopentanol and cyclohexanone reached *ca.* 86.5% which was very close to the calculated equilibrium values. The lack of a

Table 7 Product composition of *p*-methoxyacetophenone reduction at various HLSV, donor:acceptor ratio 3

HLSV/cm ³ g ⁻¹ h ⁻¹	T/K	% mol			
		C-OH ^a	C=C	C-C	C=O
1	523	31.9	34.3	0.3	33.5
	573	6.9	70.2	3.3	19.6
	623	0.3	77.6	16.9	5.2
	673	0.3	55.8	39.3	4.6
	723	0.2	34.8	58.6	6.4
2	473	33.8	11.1	—	55.1
	523	22.1	6.8	—	71.1
	573	17.0	42.0	1.0	40.0
	623	0.7	88.4	4.8	6.1
	673	0.8	76.3	14.1	8.8
4	723	0.2	67.6	26.4	5.8
	473	60.8	6.2	—	33.0
	523	54.5	7.4	—	38.1
	573	45.8	17.1	—	37.1
	623	21.8	50.6	—	27.7
4	673	4.3	77.4	—	18.3
	523	17.2	8.5	2.9	71.4
	573	8.4	8.6	0.6	82.4
	623	8.0	24.1	2.0	65.3
	673	3.4	38.1	4.9	53.6
4 ^b	723	0.8	57.1	14.2	27.9
	523	1.2	3.2	0.6	95.0
	573	5.6	3.5	0.2	90.7
	623	7.9	27.2	2.8	62.1
	673	3.0	56.0	6.8	34.2
	723	0.4	72.6	18.6	8.4

^a C-OH, *p*-methoxyphenylmethylmethanol; C=C, *p*-methoxystyrene; C-C, *p*-methoxyethylbenzene; C=O, *p*-methoxyacetophenone.

^b Donor:acceptor ratio 5.

consecutive dehydration of alcohols should be emphasized. This subsequent reaction was strongly favoured thermodynamically across the whole range of temperatures studied. Doubtless the absence of acidic sites strong enough to initiate dehydration on the basic magnesium surface was responsible for the observed kinetic effect.

Space Velocity of Reactants.—The influence of HLSV (hourly liquid space velocity) of the reactant mixture on the reaction yield and selectivity was studied for selected members of the group of ketones investigated, *i.e.* methyl isopropyl ketone, cyclohexanone (Table 6), and *p*-methoxyacetophenone (Table 7). The HLSV (cm³ of reactants per 1 g of catalyst × 1 h) is a real measure of the reactant:catalyst ratio and simultaneously of the contact time. During the methyl isopropyl ketone and cyclohexanone reduction no remarkable effect of the increase of HLSV on the reaction yield and selectivity was observed. Only at the lowest donor:acceptor molar ratio studied (0.5) was significant diminishing of methanol yield and reaction selectivity noted for the highest value of HLSV (3 cm³ g⁻¹ h⁻¹).

The catalytic transfer reduction of aryl alkyl ketone was much more sensitive to the reactant:catalyst ratio. At higher HLSV values *i.e.* shorter contact time, the undesired dehydration process was noticeably retarded. The results obtained at high HLSV values were especially promising for the large scale preparation of corresponding methanols or alkenes.

Stability of Catalyst.—The stability of MgO activity during long-time experiments was investigated. As a model reaction, *p*-methoxyacetophenone reduction (Table 8) was selected, which under standard conditions gave a relatively rich spectrum of products (simultaneously methanol, alkene and alkane). At 473 K the yields of products and the reaction selectivity remained practically unchanged *vs.* time on stream. At 673 K an insignificant drop in the reactant conversion was observed at

Table 8 Product composition of *p*-methoxyacetophenone reduction vs. time on stream, donor:acceptor ratio 3, HLSV: $2 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$

<i>t</i> /min	<i>T</i> /K	% mol			
		C-OH ^a	C=C	C-C	C=O
0	473	33.8	11.1	—	55.1
30		32.1	12.4	—	54.9
60		33.6	10.4	—	55.0
120		34.4	10.5	—	55.1
180		35.2	9.9	—	54.9
450		34.9	10.3	—	54.8
600		35.1	9.8	—	55.1
0	723	0.9	84.6	12.2	2.3
30		0.3	87.2	11.2	1.3
60		0.4	87.1	10.1	2.4
120		0.5	86.1	9.3	4.1
180		0.2	83.5	9.4	6.9
450		0.2	74.3	18.4	7.1

^a C-OH, *p*-methoxyphenyl methyl methanol, C=C, *p*-methoxystyrene, C-C, *p*-methoxyethylbenzene, C=O, *p*-methoxyacetophenone

first, however, from 180 min of time on stream onwards the stabilization of the yield of the main product, *p*-methoxystyrene, at 75% was noted.

Large Scale Experiments.—The results described in the two foregoing paragraphs gave support for increasing the scale of the process. The reactions of methyl pentyl ketone and cyclohexanone were performed on a large laboratory scale (reactor with 200 g catalyst bed). The composition of products of a process realized at HLSV, equal to $3 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$, essentially did not differ from that corresponding to the test scale reaction. At 423 K reduction products contained 62% of methylpentyl-methanol and 3% of corresponding heptane, and respectively, 81% of cyclohexanol.

Reaction Mechanism.—It is generally thought that hydrogen exchange over oxides occurs according to the mechanism of the Meerwein-Ponndorf-Verley type.^{1,5,6,15} The results of our previous IR studies of the surface species derived from alcohols adsorbed on MgO during CTR revealed the appearance of partially dehydrogenated alcohol states.¹² This observation is, of course, not contradictory to the Meerwein-Ponndorf-Verley approach. However, it should be emphasized that the same intermediates from alcohols have been formed during all studied hydrogen transfer processes over MgO, including the reduction of phenylalkenes and nitro compounds. The last two processes occurring relatively easily on MgO cannot be considered as close to the Meerwein-Ponndorf-Verley reaction. Our previous efforts confirmed also the participation of basic and/or one-electron donor sites on the MgO surface in the CTR process.^{12,13} On the other hand, we did not ascertain the necessity of a co-action of acidic sites, being a *sine qua non* condition for construction of an intermediate similar to that postulated for Meerwein-Ponndorf-Verley reduction. Thus, in our opinion, there is still no sufficient proof for the proposal of a CTR mechanism on MgO, and probably in general on oxides. Recently, we began studies concerning the identification of the surface step of catalytic hydrogen transfer on oxides using the selective poisoning method.^{10,16}

Conclusions.—The catalytic transfer reduction is an effective and selective method for the preparation of methanols from the corresponding ketones. At temperatures above 523 K it is useful for the synthesis of arylalkenes, formed by the consecutive dehydration of alcohols. This would be profitable especially for the synthesis of styrene derivatives which are difficult to prepare using other methods.

The product yields are close to the calculated theoretical values; however, at lower temperatures a strong kinetic effect inhibiting the dehydration process is dominant. The steric hindrance appears only in the case of the reduction of ketones with two substituents of large dimensions.

Magnesia retains stable activity even after 10 h on stream. A large scale process can be successfully performed.

Experimental

All the reported products are known and were identified by GLC, IR, mass spectra and refractive index measurement. Reactions were carried out in a typical flow reactor with a fixed catalyst bed (10 g for the standard test, 200 g for large scale experiments). Reactant solutions (isopropyl alcohol:ketone, ratio 3) were dosed using a microdosing pump with HLSV from 1–5 cm³ of solution per 1 g of catalyst × hour. The preparation of a catalyst (MgO) was described elsewhere.⁹ Before the reaction the magnesia was calcined at 823 K in a stream of air during 5 h. The product separation from the large scale test was made using a 25-plates rectification column packed with Fenske helices and equipped with a total condensation head.

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