



Gas-phase reduction of cyclic and acyclic α,β -unsaturated ketones by hydrogen transfer on MgO. Effect of the ketone structure

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ARTICLE INFO

Article history:

Received 30 November 2010
Received in revised form 4 February 2011
Accepted 14 February 2011
Available online 31 March 2011

Keywords:

α,β -Unsaturated ketone
Reduction
MgO
Hydrogen transfer
Meerwein–Ponndorf–Verley mechanism

ABSTRACT

The gas-phase hydrogen transfer reduction (HTR) of cyclic and acyclic α,β -unsaturated ketones to the corresponding unsaturated alcohols (UOL) using 2-propanol as hydrogen donor was studied on MgO as an alternative to the less selective conventional hydrogenation using high pressure H_2 . The HTR of 2-cyclohexenone and mesityl oxide were used as model reactions. The MgO activity and selectivity toward the unsaturated alcohol depended on the ketone chemical structure. Cyclic 2-cyclohexenone was in fact less reactive but more selective to UOL formation than acyclic mesityl oxide, yielding about 85% UOL (91% selectivity) at 573 K. The rigid structure of 2-cyclohexenone enforces a *s-trans* conformation that favors selective reduction of the C=O bond and thereby enhances the UOL formation. In contrast, the less rigid structure of the acyclic ketone affords the simultaneous reduction of both unsaturated bonds, C=C and C=O, forming also the saturated alcohol; as a consequence, maximum UOL yields of about 45% (47% selectivity) were obtained at 573 K from HTR of mesityl oxide.

The unsaturated ketone conversion pathways toward UOL and other compounds also depended on the ketone structure. UOL formed on MgO as a primary product from both reactants 2-cyclohexenone and mesityl oxide, via a cyclic six-membered intermediate according to the Meerwein–Ponndorf–Verley mechanism. However the saturated alcohol was produced by consecutive UOL reduction in 2-cyclohexenone reactions but directly from mesityl oxide reduction. Reduction of the C=C bond toward the saturated ketone was negligible regardless of the reactant structure whereas competing reactions such as the C=C bond shift were more likely to contribute during reduction of the acyclic reactant.

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1. Introduction

Primary and secondary unsaturated alcohols (UOL) are important organic intermediates for pharmaceutical, fragrance and food flavoring industries. Among UOL, those derived from unsaturated ketones (UK), i.e., secondary alcohols, are in particular valuable products used in polymer industry.

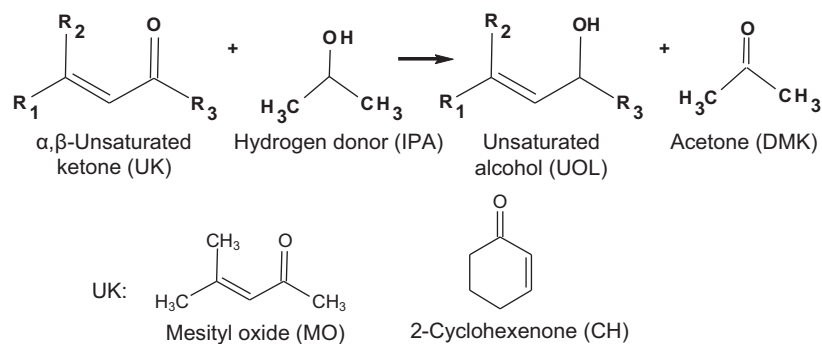
Selective synthesis of secondary UOL by conventional hydrogenation of UK using high-pressure H_2 in multiphase batch reactors and noble metal catalysts is hardly achieved because reduction of the C=C bond is thermodynamically and kinetically favored over that of the C=O group [1,2]. The substituent at the carbonyl hinders coordination of the C=O bond on the surface thereby decreasing the chemoselectivity for the C=O bond saturation [3,4]. In addition, the consecutive UOL isomerization to the corresponding saturated ketone (SK) is

usually an unavoidable side reaction on metallic catalysts [5].

Therefore, hydrogen transfer reduction (HTR), Scheme 1, arises as an alternative tool for the catalytic synthesis of UOL by asymmetric reduction of UK. In the HTR reaction the reactant is contacted with a solid acid–base catalyst and a hydrogen source (usually a secondary alcohol) without supply of molecular hydrogen. However, in order to selectively obtain UOL by HTR of UK many aspects have to be taken in consideration such as ketone structure (alkyl, aryl, cyclic), gas- or liquid-phase reaction and the interaction of the C=C bond with the catalyst surface sites. All these factors determine the requirements of catalyst acid–base properties.

Many examples have been reported in the literature regarding the reduction of the C=O bond of saturated ketones by HTR either in liquid [6–11] or gas phases [12–14] but selective reduction of saturated ketones is easier to achieve in comparison to unsaturated ketones because the additional difficulty related to the competitive reduction of the C=C bond is not present. Thus, when a catalyst and reaction conditions developed for HTR of a saturated ketone are used for selective reduction of the C=O bond of the corresponding

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Scheme 1. Unsaturated alcohol (UOL) synthesis by hydrogen transfer reduction (HTR) of unsaturated ketones using 2-propanol as hydrogen donor.

α,β -unsaturated ketone, the resulting activity and selectivity are usually much lower [7,12,15]. For example, Ruiz et al. [15] studied the liquid-phase HTR of cyclohexanone and 2-cyclohexenone on basic Mg–Al mixed oxides and found that reduction of the C=O bond of the saturated ketone was one order of magnitude faster than that of the α,β -unsaturated one. Similar qualitative results were obtained by Jyothi et al. [12] for the gas phase reaction. Ruiz et al. [15] also reported that this effect is less noticeable when dealing with acyclic ketones as in the case of pentanones. On the other hand, Lewis acid sites such as those of tin- or zirconium-beta zeolite that convert cyclohexanone to alcohol in high yields are much less efficient for the reduction of the C=O bond of 2-cyclohexenone [7,16].

In addition to the presence of the competitive C=C in unsaturated ketones, the structure of the ketone also affects the kinetics of the HTR of the C=O bond. Glinski [13] studied the gas phase reduction of alkyl ketones and found that an increase of the bulkiness of both substituents to the C=O bond decreases the reactivity. On the other hand, Ruiz et al. [17] showed that the introduction of electron-withdrawing groups to the aromatic ring enhances the liquid-phase C=O reduction rate of acetophenone, whereas electron-releasing groups lower the rate, therefore indicating that the reactivity depends on the electron densities on the carbonyl carbon.

Development of gas-phase continuous flow processes for HTR of unsaturated ketones, as an alternative to the liquid-phase batch process would present several technological advantages. However, the gas-phase process entails selectivity problems resulting from the different reaction pathways possible at high reaction temperatures. In this regard, we previously investigated the gas-phase HTR of a α,β -unsaturated ketone, mesityl oxide (4-methyl-3-penten-2-one) with 2-propanol toward the unsaturated alcohol (4-methyl-3-penten-2-ol) on MgO and Mg-based mixed oxides [18]. We found that on Mg–Al mixed oxides mainly the saturated ketone and the saturated alcohol were obtained. We also studied the reaction conditions for maximum allylic alcohol yield on MgO [19]. Furthermore, we discussed the effect of the catalyst acid–base properties on the preferential activation of the C=C or C=O bonds on single oxides, identified reaction intermediates and analyzed stability of these species at different reaction conditions [20].

In this paper we continue our studies on the gas-phase HTR of unsaturated ketones and compare the catalytic performance of cyclic and acyclic ketones on MgO. We have interpreted the results in terms of the differences in chemical structure and surface adsorption modes. The reaction pathways for UOL synthesis by HTR of cyclic and acyclic unsaturated ketones are discussed as well as the pathways to other reduction or isomerization products. Changes in reactivity and stability of surface intermediates upon an increase of the reaction temperature are also investigated for the unsatu-

rated ketones. Reactivity of saturated and unsaturated ketones is also contrasted.

2. Materials and methods

2.1. Catalyst synthesis and characterization

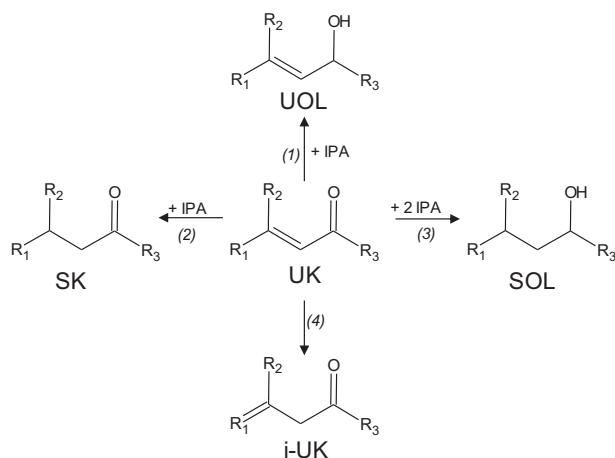
High surface area pure MgO was prepared by hydration with distilled water at room temperature of commercial MgO (Carlo Erba, 99%, 0.2% Na, 27 m²/g) and further decomposition in N₂ at typically 773 K. Details are given elsewhere [21]. BET surface area ($S = 136$ m²/g) was measured by N₂ physisorption at its boiling point using a Quantachrome Nova-1000 sorptometer. Pore size distribution was estimated by the Barrett–Joyner–Halenda (BJH) method within the pore diameter range of ≈ 10 –300 Å; total pore volume (v_g) was also measured during the analysis. Mean pore diameter (60 Å) was calculated with Wheeler's equation as $4v_g/S$. The periclase structure of MgO was confirmed by X-ray diffraction (XRD) using a Shimadzu XD-D1 instrument.

2.2. Catalytic testing

Catalytic tests were conducted at 473–573 K and atmospheric pressure in a fixed bed isothermal reactor with contact times (W/F_{UK}^0) in the range of 2–75 g h/mol. The MgO catalyst (4–100 mg) was sieved at 0.35–0.42 mm and then pretreated in N₂ at typically 773 K for 1 h before reaction in order to remove adsorbed H₂O and CO₂.

The unsaturated ketone (UK) either mesityl oxide (MO), Acros 99%, or 2-cyclohexenone (CH), Fluka 95%, and 2-propanol (IPA), Merck ACS 99.5% were introduced as a mixture with the proper molar composition via a syringe pump and vaporized into flowing N₂. Similar procedures were used when testing the saturated ketones (SK), either cyclohexanone (Fluka, >99.5%) or methyl isobutyl ketone (MIBK, Sintorgan, >98.5%). Typical reactant partial pressures in the feed were 6.80 and 1.36 kPa for IPA and the UK, respectively, but in several experiments the UK partial pressure was 0.33 kPa.

Reaction products were analyzed by on-line gas chromatography in a Varian Star 3400 CX chromatograph equipped with a flame ionization detector and a 0.2% Carbowax 1500/80–100 Carbowax C column. Regardless of the reactant UK, reaction products were identified as the unsaturated alcohol (UOL), the saturated ketone (SK) and the saturated alcohol (SOL), Scheme 2. Also, the double bond UK isomer was identified as i-UK. In particular, products from MO conversion were 4-methyl-3-penten-2-ol (UOL₁) and 4-methyl-4-penten-2-ol (UOL₂), iso-mesityl oxide (i-MO), methyl isobutyl ketone (SK) and methyl isobutyl carbinol (SOL). For the reduction of MO, UOL stands for total unsaturated alcohol isomers, i.e., UOL₁ + UOL₂. For the CH reaction, products were 2-cyclohexenol



Scheme 2. Products of the HTR of an α,β -unsaturated ketone (UK) with IPA [UOL: unsaturated alcohol; SK: saturated ketone; SOL: saturated alcohol; i-UK: double bond isomer].

(UOL), cyclohexanone (SK), cyclohexanol (SOL), 3-cyclohexenone (i-CH). Acetone (DMK) was produced by IPA oxidation in HTR reactions. Small amounts of propylene were formed by IPA dehydration. Due to catalyst deactivation, the catalytic results reported here were calculated by extrapolation of the reactant and product concentration curves to zero time on stream after collecting 10–15 data points at regular time intervals in the time of stream range of 0.1–7 h. Data points were fitted with exponential decay functions. Then, X and S represent conversion and selectivity at $t=0$, respectively. Thermal conversions were in all cases less than 1% at 523 K. Carbon mass balances were 90–95%.

3. Results and discussion

In addition to the reaction depicted in Scheme 1, several other C=C and/or C=O bond reductions as well as the double bond isomerization reaction can occur when UK is contacted with IPA on the catalyst surface, Scheme 2. In Scheme 2, step (1) is the reduction of the C=O bond leading to the UOL; step (2) is the reduction of the C=C bond leading to the SK; step (3) is the simultaneous reduction of the C=C and C=O bonds. All the reduction steps entail concomitant formation of one or two acetone molecules. Step (4) is an isomerization reaction in which the C=C bond of UK shifts forming the β,γ -unsaturated ketone (i-UK); this step does not involve the hydrogen donor. Double bond shift of α,β -unsaturated ketones is thermodynamically favored at high temperatures.

In previous work [20] we discussed that under high temperature conditions such as those of the gas phase reaction, product formation via the reaction pathways of Scheme 2 depends on the catalyst acid–base properties. We showed that on electronegative catalysts the C=C bond reduction is favored over that of the C=O bond, forming predominantly SK. Contrarily, basic catalysts such

as high surface MgO, proved to be active and selective for the C=O bond reduction. We also showed that regardless of the acidic or basic catalyst character, the C=C bond shift conducting toward the β,γ -unsaturated ketone (i-UK) always takes place and that on Lewis acid catalysts i-UK is the primary product from which SK is obtained.

3.1. Ketone structure, reactivity and selectivity

The activity and selectivity of MgO for the HTR of different α,β -unsaturated ketones as well as saturated ketones was investigated under similar conditions. In particular, cyclic 2-cyclohexenone (CH) was compared with acyclic mesityl oxide (MO); CH is more difficult to deal with in the gas phase since its vapor pressure is 6 times lower than that of MO [22]. Table 1 summarizes some of the findings as well as the equilibrium conversions at 523 K and IPA/ketone = 20; entries 1 and 3 show that when both unsaturated ketones were reduced at similar contact times with an IPA/UK = 20 reactant ratio, conversion of the acyclic MO was much higher than that of the cyclic CH.

To get more insight into the effect of the ketone structure on the reactivity and product distribution, a more detailed and systematic investigation was carried out with the unsaturated ketones. The reactivity on MgO of both, the cyclic and acyclic α,β -unsaturated ketones, was compared by performing catalytic tests at different contact times (W/F_{UK}^0) and using a reactant mixture of IPA/UK = 5 molar ratio at 523 K, Fig. 1. Previously, the equilibrium conversions for the HTR of both ketones toward the respective UOL were calculated for these reaction conditions; values of 80% conversion for MO and 90% for CH were determined.

Fig. 1A shows that under identical reaction conditions MO conversion was much higher than that of CH in a wide contact time range. At $W/F_{UK}^0 \approx 20$ g h/mol, MO conversion was close to the thermodynamic equilibrium while CH conversion was less than half of the equilibrium conversion. MO conversions at higher contact times were slightly above the equilibrium conversions predicted for selective formation of UOL because of additional formation of other products. From the slopes of the curves of Fig. 1A, the initial reaction rate for both unsaturated ketones was calculated as

$$r_{UK}^0 = \lim_{X_{UK} \rightarrow 0} \left(\frac{dX_{UK}}{d(W/F_{UK}^0)} \right) \quad (1)$$

where X_{UK} is the UK conversion. The calculated values of r_{UK}^0 were 119 and 51 mmol/h g for MO and CH, respectively, thereby confirming the higher reactivity of the acyclic ketone.

Data in Table 1 allow also comparison of the reactivity and selectivity of unsaturated and saturated ketones on MgO under similar operative conditions. Entries 1 and 2 show that conversion of MO (the acyclic α,β -unsaturated ketone) was lower than that of MIBK (the corresponding saturated ketone). Entries 3 and 4 show similar catalytic activity difference for the cyclic ketones, CH and cyclohexanone, in agreement with previous reports either

Table 1
Catalytic performance and equilibrium conversions of cyclic and acyclic saturated or α,β -unsaturated ketones on MgO.

Entry	Ketone	Carbon atom number	Structure	Ketone equilibrium conversion ^b (%)	Ketone conversion (%)	Selectivity (%)			
						i-UK	SK	UOL	SOL
1	MO	6	Acyclic, α,β -unsaturated	94.0	76.2	31.3	3.1	33.2	32.4
2	MIBK	6	Acyclic, saturated	94.0	88.7	–	–	–	100.0
3	CH	6	Cyclic, α,β -unsaturated	97.4	49.0	12.3	4.7	79.8	3.4
4	Cyclohexanone	6	Cyclic, saturated	89.0	83.5	–	–	–	100.0
5	CH ^a	6	Cyclic, α,β -unsaturated	97.4	75.1	3.3	1.6	90.0	5.1

$T = 523$ K, IPA/ketone = 20 (molar), $W/F_{ketone}^0 = 15$ g h/mol.

^a $W/F_{CH}^0 = 73$ g h/mol.

^b For ketone C=O reduction.

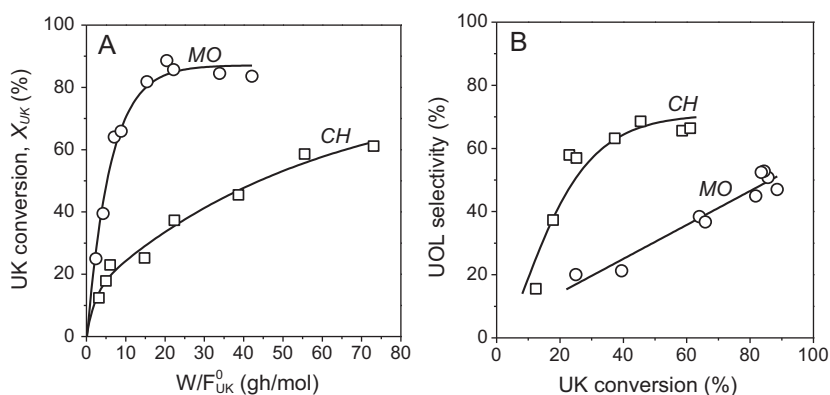


Fig. 1. Effect of contact time (W/F_{UK}^0) on activity and selectivity. (A) α,β -Unsaturated ketone conversion (X_{UK}). (B) UOL selectivity as a function of X_{UK} [UK: mesityl oxide (MO) and 2-cyclohexenone (CH); $T=523$ K; IPA/UK = 5; MgO].

in liquid or in gas phase [12,15]. Furthermore, we determined the initial ketone conversion rates for an IPA/ketone molar ratio of 5 and found that r_{MIBK}^0 (323 mmol/h g) was about 3-fold higher than r_{MO}^0 (119 mmol/h g) whereas for cyclic ketones the initial conversion rate of cyclohexanone (395 mmol/h g) was about 8-fold higher than r_{CH}^0 (51 mmol/h g). All these results show that on MgO the reactivity of saturated ketones, in which the competitive reduction of the C=C bond is not present, is higher than that of the corresponding unsaturated ones. Regarding catalyst selectivity, entries 2 and 4 in Table 1 show that saturated ketones formed exclusively saturated alcohols (SOL). In contrast, reduction of unsaturated ketones formed UOL and SOL and minor amounts of the saturated ketone (SK).

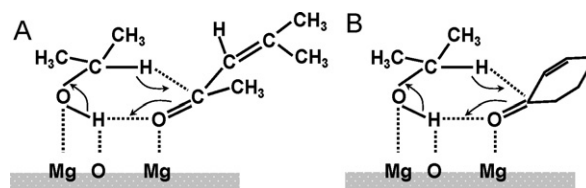
The unsaturated ketone structure affects not only the reactivity but also the product distribution so that the lower reactivity of CH compared with MO is compensated for by a higher UOL selectivity. Entries 1 and 5 of Table 1 show that when MO and CH were reduced at similar conversion levels using a feed with an IPA/UK = 20, UOL selectivity attained with CH almost tripled that of MO reaching 90%, an unusually high value for a gas phase reaction whereas the acyclic MO affords formation of almost equal amounts of the C=C bond isomer (i-MO) and reducing products (UOL and SOL).

Additional experiments carried out with both UK at 523 K and IPA/UK = 5 (molar ratio) are shown in Fig. 1B, where the evolution of UOL selectivity as a function of X_{UK} for CH and MO is presented. In both cases the selectivity to UOL increased with X_{UK} but for reduction of CH the UOL selectivity values tended to level off at high conversions. The best UOL selectivities obtained under the reaction conditions of Fig. 1B were 53% and 68% for MO and CH, respectively.

In summary, results of Fig. 1 and Table 1 show that on MgO cyclic CH is less reactive but more selective to UOL formation than acyclic MO.

3.2. Ketone structure, surface species and reaction pathways

HTR of unsaturated ketones are believed to occur according to the Meerwein–Ponndorf–Verley (MPV) mechanism. In homogeneous catalysis, the MPV mechanism is promoted by a metal alkoxide with participation of a Lewis acid center and involves formation of a cyclic six-membered intermediate in which both reactants are coordinated to the metal of the alkoxide [23]. A similar intermediate for the heterogeneously catalyzed process either in liquid or in gas phase has been postulated [4,24,25]. Therefore, in order for the heterogeneously catalyzed HTR to occur on MgO, UK coordination must take place via an “on top” adsorption of the C=O bond on a weak Lewis acid Mg^{2+} cation, with simultaneous non-dissociative IPA adsorption on a vicinal $Mg^{2+}-O^{2-}$ pair, giving rise to a cyclic 6-atom surface intermediate [20].

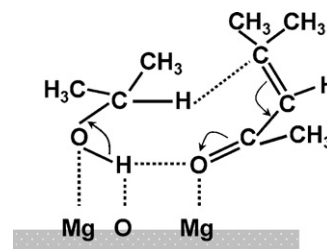


Scheme 3. Surface reaction intermediate for UOL formation by MPV mechanism on MgO. (A) mesityl oxide (MO); (B) 2-cyclohexenone (CH).

The different catalytic behavior of the cyclic and acyclic unsaturated ketones can be interpreted in terms of the surface coordination of both unsaturated ketone molecules and IPA, Scheme 3. Scheme 3A shows MO and Scheme 3B, CH; both molecules are depicted as surface s-trans conformers enabling 1,2-reduction. The enhanced UOL selectivity of the HTR of 2-cyclohexenone might reflect the geometric constraints of this molecule with an enforced s-trans conformation that favors reduction of the C=O bond [26]. Contrarily, the acyclic mesityl oxide molecule has a less rigid structure that might allow a surface s-cis conformation leading to competitive reduction of the C=C bond via a 1,4-reduction and the consequent SK formation, Scheme 4. The 1,4-nucleophilic addition would eventually shift the reaction pathway toward SOL formation as a final product formed by consecutive SK reduction.

The ketone conversion pathways on MgO can be elucidated from the results of Fig. 2 showing the product distribution of the HTR of both unsaturated ketones in terms of yields as a function of contact time. Primary products formed directly from the unsaturated ketones present yield curves with non zero initial slope; zero initial slope yields correspond to secondary products formed by consecutive reactions.

Reaction pathways for CH (Fig. 2A) and MO (Fig. 2B) conversion are similar but not identical. Both reactants produced UOL as a primary product which is consistent with the surface species involved



Scheme 4. 1,4-Reduction of an acyclic α,β -unsaturated ketone (C=C bond reduction) on MgO.

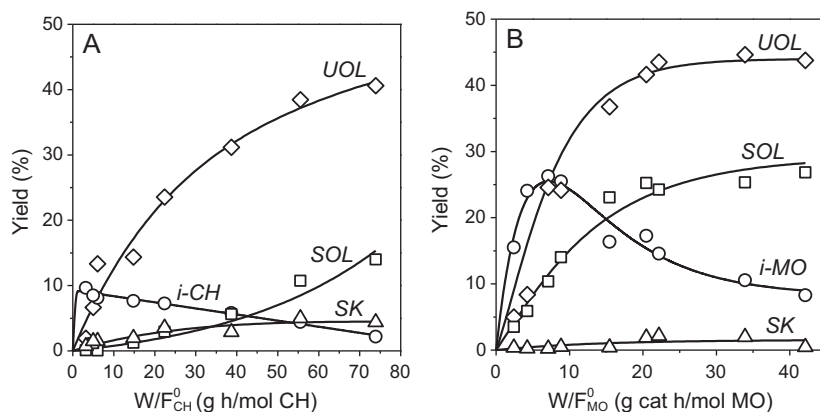


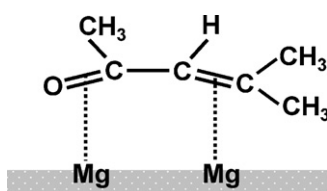
Fig. 2. Product yields of the HTR of α,β -unsaturated ketones on MgO. (A) 2-Cyclohexenone (CH); (B) mesityl oxide (MO) [$T=523\text{ K}$; $\text{IPA}/\text{UK}=5$].

in the formation of UOL, as postulated in Scheme 3. UOL was the main product formed from CH and MO, reaching in both cases about 45% at high W/F_{UK}^0 values.

At very short contact times the C=C bond isomerization reaction predominates giving the β,γ -unsaturated isomer (formation of either *i*-MO or *i*-CH directly from MO or CH, respectively). However, *i*-MO and *i*-CH yields reached maximum values as they were rapidly converted in other compounds such as UOL at higher contact times. Reduction of the C=O bond of the β,γ -unsaturated isomer is likely to occur through a surface intermediate similar to the one postulated in Scheme 3 for the α,β -unsaturated ketones.

On the other hand, Fig. 2 also shows that SK yields were always lower than 5%. This result indicates that reduction of the C=C bond of both unsaturated ketones leading to SK is not favored at any W/F_{UK}^0 value regardless of the nature of the reactant. In addition, SK is a primary product that slightly changes with contact time thereby revealing its scarce contribution to formation of other products such as SOL at higher contact times. Therefore, a reaction pathway in which SOL is formed mainly by consecutive reduction of SK, as in the 1,4-reduction (Scheme 4), is not supported by the results of Fig. 2, neither for CH nor for the less rigid MO (no maximum in the SK yield vs W/F_{UK}^0 curves). However, a small contribution of SK to SOL formation at higher temperatures is likely to occur, as we will discuss later. For similar reasons, formation of SK by rapid isomerization of UOL as usually proceeds on metallic and organometallic catalysts in the liquid phase has to be ruled out [5,26,27].

The main difference between MO and CH reductions was the reaction pathway for SOL formation. Since the more rigid structure of CH does not afford 1,4-reduction toward SK, SOL that was clearly a secondary product of CH reduction (Fig. 1A), must be obtained from consecutive reduction of UOL and not from SK. In contrast, MO reduction gave SOL as a primary product (open squares in Fig. 2B), i.e., by simultaneous reduction of the C=C and C=O bonds. Therefore, the surface intermediate shown in Scheme 4 cannot account for direct formation of SOL from MO. The direct interaction of MO with the Mg^{2+} sites of MgO catalyst as depicted in Scheme 5 seems to more likely represent the simultaneous reduction of both



Scheme 5. Mesityl oxide di- π adsorption mode on MgO leading to the saturated alcohol (SOL).

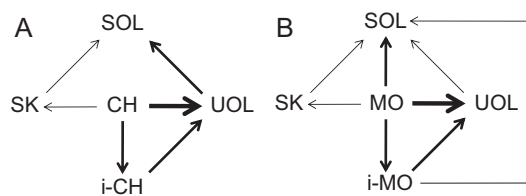
unsaturated bonds of MO [20]. SOL is a primary product of MO conversion, but the plateau reached by the UOL yield curve (open diamonds in Fig. 2B) at contact times higher than 20 g h/mol probably indicates some contribution of UOL reduction to SOL formation at high conversion levels.

Finally, from the results of Fig. 2 we have postulated in Scheme 6 the reaction pathways for MO and CH conversion on MgO, where the arrow width indicates the relative relevance of each reaction.

Additional catalytic runs were carried out at increasing reaction temperatures in order to get more insight into the reaction pathways and stability of the surface adsorption species of CH and MO conversion. Fig. 3 shows the conversion and yield evolutions as a function of reaction temperature for CH (Fig. 3A) and MO (Fig. 3B) reactions. Experimental conditions were chosen so that the conversion levels for both unsaturated ketones were similar. As expected, the conversion of both UK increased with the reaction temperature reaching values close to the thermodynamic equilibrium at 573 K. However, temperature had a different effect on the HTR of CH and MO due to the distinctive reaction pathways for each UK sketched in Scheme 6 and to the different surface intermediates involved.

UOL yield was favored at higher temperatures for both unsaturated ketones, CH and MO. In particular, an unprecedented UOL yield of 85% was determined during CH reactions at 573 K. As sketched in Scheme 6, UOL is formed from both reactants by direct UK reduction and by consecutive reduction of the primary *i*-UK. However, Fig. 3 shows that *i*-MO increased while *i*-CH decreased with the reaction temperature. The negative slope of the *i*-CH curve in Fig. 3A might be an indication of its consecutive transformation to UOL in a consecutive step with higher activation energy. In contrast, the *i*-MO yield rise with reaction temperature is probably the result of two-fold, the higher thermal stability of the simpler surface species involved in the double bond isomerization reaction with no participation of the hydrogen donor, and the concomitant diminution of competitive MO conversion to SOL, as discussed below.

The effect of temperature on SOL yield depends on whether SOL is formed directly from the α,β -unsaturated ketone (Fig. 3B) or



Scheme 6. Reaction pathways on MgO for the HTR of (A) 2-cyclohexenone (CH); (B) mesityl oxide (MO).

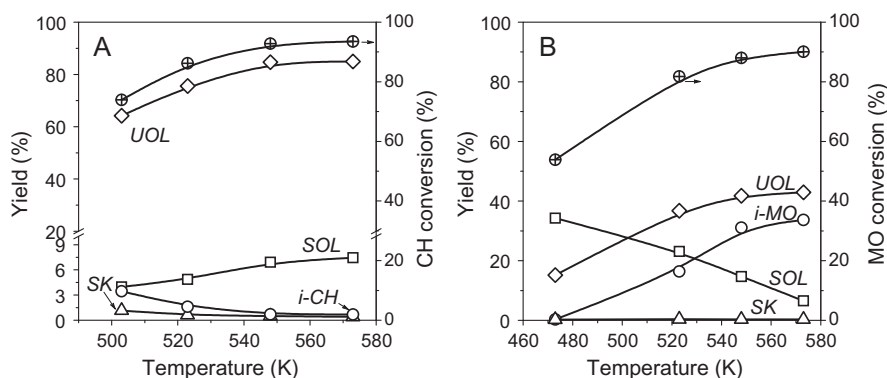


Fig. 3. Effect of reaction temperature on the HTR of α,β -unsaturated ketones on MgO. (A) 2-Cyclohexenone (CH) [IPA/CH = 20, $W/F_{\text{CH}}^0 = 73$ g h/mol]; (B) mesityl oxide (MO) [IPA/MO = 5, $W/F_{\text{MO}}^0 = 15$ g h/mol].

by reduction of UOL (Fig. 3A). During MO conversion, the negative slope of the SOL curve in Fig. 3B does not reflect consecutive transformation in other compounds but that a reaction temperature increase is detrimental for the stability of the quasi-planar adsorption mode of the C=C and C=O bonds leading to SOL (Scheme 5). In the case of CH reactions, the slight positive slope of the SOL yield curve in Fig. 3A is due to the enhanced UOL formation at higher temperatures since SOL is formed from UOL. In addition, the negative slope of the SK curve in Fig. 3A is the consequence of SK transformation in SOL.

The results of Fig. 3 indicate that an increase of the reaction temperature in the range of 473–573 K has a positive effect on the yield of both, the cyclic and acyclic UOL, reaching maximum values of 85% and 43%, respectively, at 573 K. Whereas the reduction of CH at 573 K gives only alcohols (UOL + SOL), MO reduction at that temperature suppresses SOL formation and yields UOL and *i*-MO (33%) as the main products. The 43% UOL yield obtained during MO reduction at 573 K could not be improved by increasing the contact time at that temperature due to proximity to equilibrium. For both UK, reduction of the C=C with SK formation was negligible in the temperature range under study.

In summary, the reaction temperature affects the HTR of cyclic and acyclic unsaturated ketones in a different way depending on the presence or not of consecutive reactions and on the decreased stability at high temperatures of competing surface intermediates.

4. Conclusions

The gas-phase selective reduction of the C=O bond of cyclic and acyclic α,β -unsaturated ketones (UK) such as 2-cyclohexenone and mesityl oxide, respectively, to yield the corresponding unsaturated alcohols (UOL) are efficiently achieved by a hydrogen transfer reduction process using 2-propanol as the hydrogen source and MgO as catalyst. Depending on the UK chemical structure, UOL yields of ≈ 40 –85% are obtained at mild temperatures (523–573 K), contact times between 15 and 75 g h/mol and 2-propanol/UK molar ratios of 5–20.

The UK molecular structure determines the preferential molecule surface coordination mode on the catalyst surface sites involved in reaction intermediates and thereby has an effect on the activity and selectivity toward formation of the unsaturated alcohol and other products. Thus, the rigid cyclic UK molecule (2-cyclohexenone) is less reactive than the acyclic one (mesityl oxide). However, the selectivity toward UOL is much higher for 2-cyclohexenone than for mesityl oxide, probably due to geometric constraints of the former that enforce a *s-trans* conformation that favors the selective reduction of the C=O bond.

The UK conversion pathways toward UOL and other compounds also depend on the UK structure. In fact, whereas UOL forms as a primary product from both, 2-cyclohexenone and mesityl oxide, the saturated alcohol is produced by consecutive UOL reduction in 2-cyclohexenone reactions but directly from mesityl oxide reduction. Surface activation of just the C=C bond of both UK molecules is negligible on MgO and consequently the corresponding saturated ketones are not likely to be formed by hydrogen transfer reduction. On the other hand, the competitive double bond isomerization reaction can be minimized at high contact times for both, the cyclic and acyclic unsaturated ketones.

Acknowledgments

Authors thank CONICET, Argentina (Grant PIP 5168/05), ANPCyT, Argentina (Grant PICT 01229/08) and the Universidad Nacional del Litoral (UNL), Santa Fe (CAID 34-187/06) for the financial support of this work.

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