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Reduction of ketones and aldehydes to alcohols with magnesium–aluminium mixed oxide and 2-propanol

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Abstract

The Meerwein–Ponndorf–Verley (MPV) reaction allowed the successful reduction of various aldehydes and ketones by using an $MgAlO_x$ mixed oxide previously obtained from a layered double hydroxide as catalyst and 2-propanol as hydrogen donor. The reaction exhibited good yield and selectivity towards the corresponding alcohol in all cases. The results were quite consistent with a mechanism involving adsorption of the reactants on an acid–base pair in the catalyst.

Keywords: Meerwein–Ponndorf–Verley reaction; Mixed oxides; Hydrotalcite; Layered double hydroxide

1. Introduction

The reduction of carbonyl compounds provides a very useful method for handling functional groups in organic chemistry. Specially prominent in this respect is the Meerwein–Ponndorf–Verley (MPV) reaction, which involves the reduction of a carbonyl compound to the corresponding alcohol by using a stoichiometric amount of aluminium isopropoxide in 2-propanol [1–3]. A complementary oxidation process (viz. the Oppenauer oxidation reaction) was introduced via the MPV reaction in 1937 [4]. This reduction process provides an interesting pathway for reducing aldehydes and ketones to alcohols by virtue of its being highly selective towards C=O groups. In fact, other reducible groups such as C=C double bonds and C–halogen bonds are not attacked. However, the MPV reaction requires the use a large excess of isopropoxide in order to obtain an acceptable yield. Also, destroying the excess alkoxide at the end of the process can be rather difficult and removing the catalyst is a costly, time-consuming process that provides a non-reusable product in most cases.

A number of acid and basic heterogeneous catalysts have been developed in recent years that allow the MPV reaction to be conducted in the liquid phase and the need to remove the catalyst from the reaction mixture to be avoided. Specially favoured in this respect are the products resulting from the calcination of layered double hydroxides (LDHs). Our research group, and Professor Figueras of the CNRS of Lyon (France), have pioneered the use of these solids as catalysts in MPV processes, where they have so far provided good results with substrates of diverse nature including naturally occurring aldehydes [5,6], cyclohexanone and its derivatives [7,8], and aromatic aldehydes [9]. Other acid and basic solids used to facilitate this hydrogen-transfer process include zeolites [10–12] and metal oxides [9,13–15].

Layered double hydroxides, also known as “hydrotalcite-like compounds”, are brucite-like $[Mg(OH)_2]$ layered anionic clays where some Mg^{2+} cations are replaced by Al^{3+} or some other tervalent cation. By effect of the metal substitution, the layers acquire a charge deficiency that is countered by anions in the interlayer spacing. These compounds conform to the general formula $[Mg_{1-x}Al_x(OH)_2]^{x+}[A_{x/m}]^{m-}\cdot nH_2O$, where A is the interlayer anion. Calcination of these hydrotalcite-like compounds above 400 °C gives a mixture of magnesium and aluminium oxides with basic surface properties and a variety of uses in base-catalysed processes [16–19].

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This paper reports the results obtained in the reduction of various aldehydes and ketones with 2-propanol as hydrogen donor and a heterogeneous catalyst obtained from a magnesium–aluminium layered double hydroxide.

2. Experimental

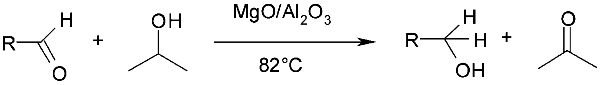
The basic catalyst used was obtained by following a previously reported procedure [20]. A volume of 250 mL of an aqueous solution containing 0.3 mol of $Mg(NO_3)_2{\cdot}6H_2O$ and 0.15 mol of $A1(NO_3)_3{\cdot}9H_2O$ (Mg/Al = 2) was slowly dropped over 500 mL of an Na_2CO_3 solution at pH 10 at 60 °C under vigorous stirring. The pH was kept constant by adding appropriate volumes of 1 M NaOH during precipitation. The suspension thus obtained was kept at 80 °C for 24 h, after which the solid was filtered and washed with de-ionized water. The resulting solid, named HT, was calcined at 500 °C for 8 h to obtain a magnesium–aluminium mixed oxide that was named HT-500 and used as the catalyst. All solids were calcined immediately prior to use as catalysts.

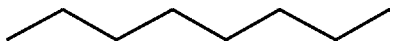
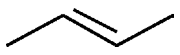
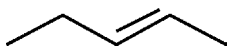
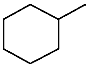
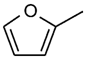
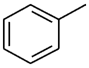
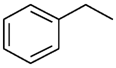
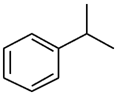
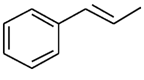
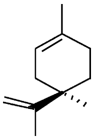
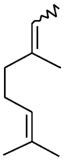
In previous work [20–23], solids of a similar nature were characterized in structural, textural and chemical terms, and found to possess basic surface properties.

The catalytic hydrogen-transfer reaction was conducted in a two-mouthed flask furnished with a magnetic stirrer and a condenser. An amount of 0.09 mol of the secondary alcohol was supplied with 0.003 mol of the carbonyl compound and the reaction mixture was refluxed with stirring at 1000 rpm. The reaction was started by feeding 1 g of freshly calcined catalyst to the mixture. Aliquots of the reaction mixture were withdrawn during the course of the reaction and analysed by gas chromatography (GC) and mass spectrometry (MS) on an HP 5890 GC instrument furnished with a 30 m × 0.32 mm Supelcowax 10 column and interfaced to an HP 5971 A MSD instrument.

All chemicals used were purchased from Panreac, Merck or Aldrich and used as received.

Table 1
Results obtained in the reduction of aldehydes with 2-propanol



Entry	R	Yield (%)	Reaction time (h)	$k \times 10^{-3}$ (min^{-1})[a]	Selectivity (%)[b]
1		96	4.0	9.36	100
2		95	4.0	9.18	99.0
3		96	4.0	9.11	99.1
4		98	4.0	9.26	98.0
5		97	4.0	9.06	97.8
6		96	5.0	8.07	98.4
7		97	3.2	10.51	100
8		96	3.5	13.74	100
9		92	4.5	9.58	100
10		97	7.0	7.60	100
11		95	4.0	12.30	96.5
12		97	23.5	3.49	98.2
13		98	24.0	4.19	92.1

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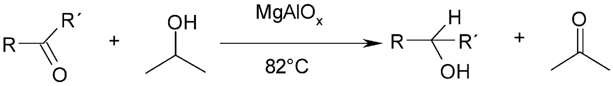
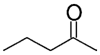
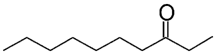
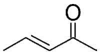
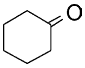
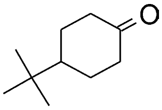
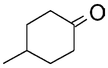
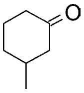
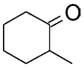
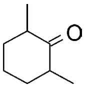
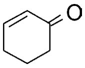
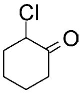
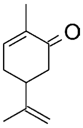
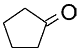
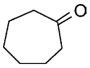
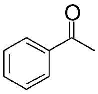
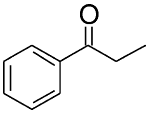
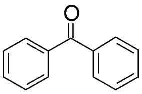
[a] Rate constant.

[b] Selectivity towards alcohol.

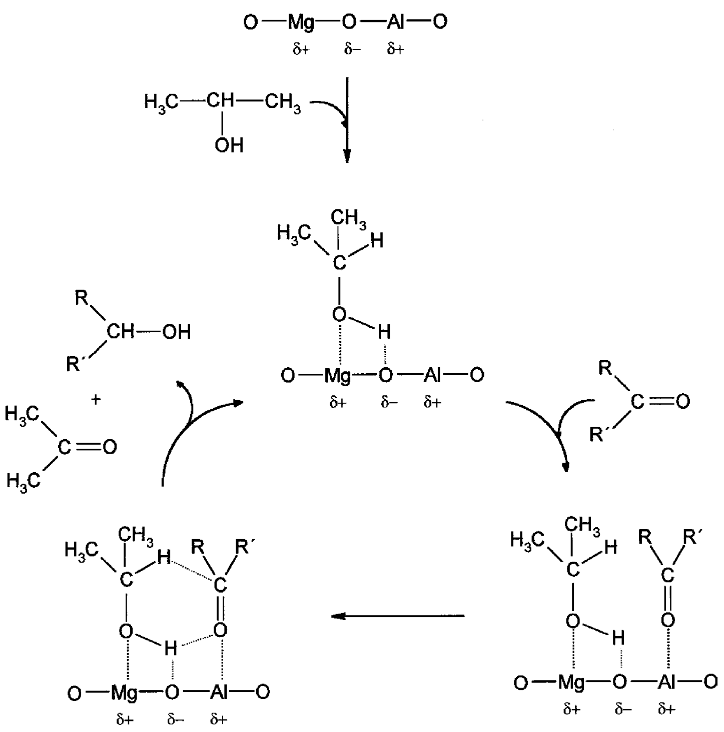
Table 2
Results obtained in the reduction of ketones with 2-propanol



Entry	Ketone	Yield (%)	Time reaction (h)	$k \times 10^{-3}$ (min^{-1})[a]	Selectivity (%)[b]
1		47	24	0.72	89
2		30	24	0.29	93
3		18	24	0.19	86
4		95	10	3.80	100
5		98	24	2.48	100
6		95	10	3.76	100
7		94	24	2.56	100
8		43	24	0.64	100
9		27	24	0.21	100
10		35	24	0.30	98
11		96	24	2.31	97
12		16	24	0.15	81
13		95	10	3.92	100
14		92	10	3.75	100
15		90	24	2.01	100
16		76	24	1.18	100
17		4	24	<0.01	100

[a] Rate constant.

[b] Selectivity towards alcohol.



Scheme 1. Mechanism proposed for the MPV reduction.

3. Results and discussion

3.1. Reduction of aldehydes and ketones

The reduction of aldehydes gave the corresponding primary alcohols. The selectivity of the process exceeded 90% in all cases. Also, all aldehydes exhibited a linear correlation between the natural logarithm of the concentration of the carbonyl group and the reaction time, which suggests that the reaction is first-order in the aldehyde concentration:

$$\ln\left(\frac{c_0}{c}\right) = \mathrm{k}t$$

where c_0 and c are the aldehyde concentrations at times zero and t, respectively, k the rate constant and t is the time. We used a plot of $\ln(c_0/c)$ versus t to determine the rate constant. As can be seen from Table 1, there were no substantial differences in reaction yield or rate constant among the aldehydes except for perilaldehyde and citral (entries 12 and 13 in the table). The decreased rate for these two compounds can be ascribed to their steric hindrance, which was also present, albeit to a lesser extent, in 2-phenylpropanal (entry 10).

The rate constants for the ketones, shown in Table 2, were determined similarly to those for the aldehydes. As noted in a previous paper [7], the presence of substituents at different positions on a cyclohexanone ring has a strong effect on the rate of the process; thus, the bulkier a substituent at position 4 is, the smaller is the rate constant (see entries 5 and 6 in Table 2). Also, the presence of a substituent at position 2 rather than 4 decreases the reaction rate (see entries 6–8 in the table). The effect is even more marked with two substituents at positions 2 and 6; in fact, the alcohol yield after 24 h of reaction under these conditions was only 27%.

The presence of a double bond conjugated with the carbonyl group also substantially reduced the reaction rate (see entry 10 in Table 2). This, together with steric hindrance, resulted in carvone (entry 12 in Table 2) exhibiting a very low yield and rate constant. On the other hand, the presence of a chlorine atom in α with respect to the carbon atom in the carbonyl group increased the reaction rate. Finally, the substituents of aromatic ketones had an effect similar to that of the substituents in cyclohexanone; thus, the MPV reduction of benzophenone proceeded to a virtually negligible extent.

3.2. Reaction mechanism

The rate constants obtained are consistent with a mechanism similar to that proposed by Ivanov et al. [24] (Scheme 1), based on which the hydrogen transfer is a concerted process involving the formation of a six-link intermediate between ethanol and the carbonyl compound. The rate-determining step of the process must be related to the interaction of the alcohol with acid–base sites, which causes its dissociation to the corresponding alkoxide. Carbonyl compounds have been found to interact with acid and basic sites in a solid to give condensation reaction, as have alcohols with metal acid sites to give olefins. In the proposed scheme, the surface-adsorbed alkoxide formed from the alcohol transfers a hydride ion that attacks the carbonyl group.

4. Conclusions

Based on the results, the $MgAlO_x$ mixed oxide obtained from a layer double hydroxide is an excellent catalyst for the Meerwein–Ponndorf–Verley reduction of aldehydes and ketones with 2-propanol. Aldehydes are reduced with yields and selectivities in the region of 100% within a few hours, and so are ketones—albeit somewhat more slowly. Only some ketones that are severely sterically hindered or possess some conjugate alkene bond are less efficiently reduced. These results are quite consistent with the proposed reaction mechanism, based on which the hydrogen transfer from the alcohol to the carbonyl compound involves the transfer of a hydride ion between both substrates via a six-link cyclic intermediate adsorbed on an acid–base pair in the catalyst.

Acknowledgements

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References

[1] H. Meerwein, R. Schmidt, Justus Liebigs Ann. Chem. 444 (1925) 221.
[2] A. Verley, Bull. Soc. Chem. Fr. 37 (1925) 537.
[3] W. Ponndorf, Angew. Chem. 39 (1926) 138.
[4] R.V. Oppenauer, Recl. Trav. Chim. Pays-Bas 56 (1937) 137.
[5] P.S. Kumbhar, J. Sánchez-Valente, J. López, F. Figueras, J. Chem. Soc. Chem. Commun. (1998) 535.
[6] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Appl. Catal. A: Gen. 206 (2001) 95.
[7] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, J. Chem. Soc. Perkin Trans. 2 (2002) 1122.
[8] J. López, J. Sánchez-Valente, J.-M. Clacens, F. Figueras, J. Catal. 208 (2002) 30.
[9] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, J. Colloid Interfce Sci. 238 (2001) 385.
[10] O. Bortnovsky, Z. Sobalik, B. Wichterlova, Z. Bastl, J. Catal. 210 (2002) 171.
[11] J.C. van der Waal, K. Tan, H. Van Bekkum, Catal. Lett. 41 (1996) 63.
[12] E.J. Creyghton, S.D. Ganeshie, R.S. Downing, H. Van Bekkum, J. Mol. Catal. A: Chem. 115 (1997) 457.
[13] G. Szöllösi, M. Bartok, Appl. Catal. A: Gen. 169 (1998) 263.
[14] G. Szöllösi, M. Bartok, J. Mol. Catal. A: Chem. 148 (1999) 265.
[15] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, J. Mol. Catal. A: Chem. 171 (2001) 153.
[16] F. Basile, A. Vaccari, in: V. Rives (Ed.), Layered Double Hydroxides: Present and Future, Nova Science Publishers, Inc., 2001.
[17] A. Vaccari, Appl. Clay Sci. 14 (1999) 161.
[18] V. Rives, M.A. Ulibarri, Coord. Chem. Rev. 181 (1999) 61.
[19] F. Trifiro, A. Vaccari, Comprehensive supramolecular chemistry, in: J.L. Atwood, J.E.D. Davies, D.D. MacNicol, F. Vögtle, J.-M. Lehn, G. Albert, T. Bein (Eds.), Solid-State Supramolecular Chemistry: Two- and Three-Dimensional Inorganic Networks, vol. 7, Pergamon, Oxford, 1996, pp. 251–291.
[20] M.A. Aramendía, Y. Avilés, V. Borau, J.M. Luque, J.M. Marinas, J.R. Ruiz, F.J. Urbano, J. Mater. Chem. 9 (1999) 1603.
[21] M.A. Aramendía, Y. Avilés, J.A. Benítez, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Microporous Mesoporous Mater. 29 (1999) 319.
[22] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, Mater. Lett. 46 (2000) 309.
[23] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, J.R. Ruiz, F.J. Urbano, J. Solid State Chem. 168 (2002) 156.
[24] V.A. Ivanov, J. Beachelier, F. Audry, J.C. Lavelley, J. Mol. Catal. 91 (1994) 45.