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Effect of non-linear kinetics on the enantioselectivity in the H-transfer asymmetric homogeneous reduction of arylketones with a rhodium diamine catalyst

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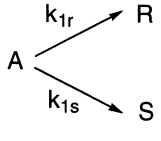
Abstract

Non-linear kinetics in asymmetric catalytic reactions may lead to non-linear enantioselectivity. In the H-transfer asymmetric reduction of arylketones with isopropanol/acetone catalyzed by a rhodium diamine complex, this has been quantified and used in order to achieve a significant increase in enantiomeric excess upon addition of reagents as simple as acetone. The question of the generalization of such a non-linear kinetic approach of enantioselective catalytic processes is also addressed.

1. Introduction

The understanding of how chiral information is transmitted along a catalytic asymmetric reaction is of importance for the development of enantioselective catalysis.[1] It seems rather obvious that the steric match and mismatch of the chiral catalyst site with the two faces of a prochiral substrate should be involved. However, while this concept has been useful in the design of new chiral ligands and catalysts it should be recognized that the interaction (adsorption or co-ordination) of the prochiral substrate with the catalytic site is just one of the potentially numerous steps involved in the mechanism of the chemical transformation. Considering the simplest asymmetric reaction (Eq. 1), the selectivity *R*/*S* will be given by integration of the ratio r_{1r}/r_{1s} of the rate of the parallel reactions 1r and 1s.



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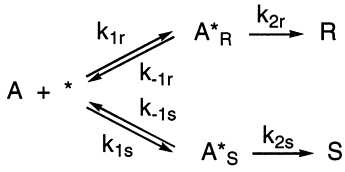
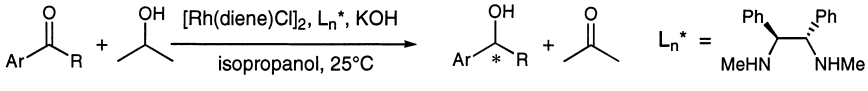
Only in the case where steps 1r and 1s are the actual elementary steps, is the selectivity *R*/*S* mathematically given by the ratio k_{1r}/k_{1s}. Indeed, in such a simple case, both rates of reactions are linear $r_r=k_{1r}[A]$ and $r_s=k_{1s}[A]$. In terms of energetics, the weight of the mirror image reactions 1r and 1s in the enantioselection process may conveniently be presented as the difference between the free enthalpies of activation: $\Delta\Delta G_{1rs}^{\ddagger}=\Delta G_{1r}^{\ddagger}-\Delta G_{1s}^{\ddagger}$. Very often, for the sake of the qualitative discussion of enantioselective catalysis, this oversimplified model is considered. However, it cannot account for the reported increase or decrease of *ee* with H_2 pressure,[2] with substrate conversion,[3–5] or upon addition of achiral additives.[6] In such cases, multi-elementary step mechanisms must be considered which involve non-linear r_r and r_s rate laws. Thus, the estimation and understanding of the kinetic influence on the enantioselection process is required. This has been well sketched by Noyori who described asymmetric catalysis as a four-dimensional chemistry.[1] Today, the only well documented example of such a detailed analysis is the asymmetric hydrogenation of methyl-(Z)-α-acetamidocinnamate (A) catalyzed by the $[Rh(dipamp)]^+$ complex (Scheme 1).[2]



Scheme 1.

The beauty of Halpern's work was to show that although all of the six steps are contributing to the enantioselectivity, the steps mostly contributing are 2r and 2s.[2a] More precisely, the origin of enantioselection is to be found not so much in the recognition of the faces of the pro-chiral substrate by the chiral catalytic site (steps 1r and 1s) but rather in the difference of reactivity between the two diastereoisomeric intermediates A^*_R and A^*_S with the achiral reagent hydrogen.[2a] That is conveniently expressed by the comparison of the free enthalpies of activation of the reaction steps as defined earlier. From Halpern's work, this becomes $\Delta\Delta G_{1rs}^{\ddagger}$ (1.1)$<\Delta\Delta G_{-1rs}^{\ddagger}$ (7.5)$<\Delta\Delta G_{2rs}^{\ddagger}$ (15.7) (kJ/mol at 25°C) (Scheme 1). These features clearly reveal that the effect of hydrogen pressure on the enantioselectivity should be much more important than that of the substrate concentration, which is found experimentally. Halpern's finding has been the basis for a great deal of reports.[3,7,8] Does it apply to other asymmetric reactions? As noted earlier, the origin of enantioselection is to be found in the reactivity of the diastereoisomeric catalytic intermediates A^*_R and A^*_S rather than in that of the enantiomerically pure catalytic intermediate *. Keeping with this idea, any asymmetric reaction where diastereoisomeric catalytic intermediates similar to A^*_R and A^*_S are believed to react with achiral reagents, such as molecular hydrogen in Halpern's study, should be a good candidate. In order to test this concept, we became interested in the catalytic H-transfer reduction of acetophenone (AP) into (*R*)- and (*S*)-phenylethanol [(*R*)-PE and (*S*)-PE] with the achiral reagents isopropanol (IP) and acetone (AC) as the hydrogen donor/acceptor couple (Eq. 2).[4]



(2)

We anticipated that because both two achiral reagents, isopropanol and acetone, are involved and that the enantioselectivity was reported to be a function of the substrate concentration, this reaction should display a complex, i.e. non-linear, kinetic behaviour.

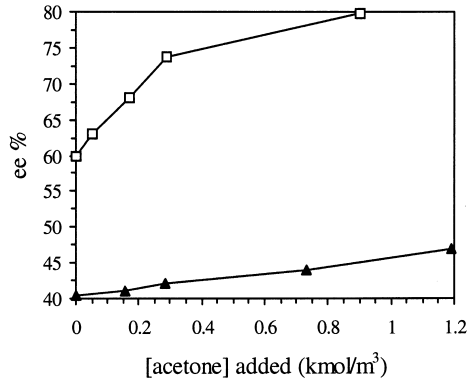


Fig. 1. Effect of added acetone on the enantiomeric excess in the reduction of acetophenone (□) and p-trifluoromethylacetophenone (▲)

Table 1
Influence of added ketone acceptors on the enantioselective transfer hydrogenation of acetophenone with isopropanol catalyzed by the chiral Rh/diamine complex

Acceptor added		ee	TOF	Conversion
Type	kmol/m^3	% (R)	h^{-1}	%
-	0	60	5.3	97
acetone	0.9	80	0.9	63
cyclohexanone	0.09	70	1.3	72
2-octanone	0.13	64	3.3	85
2,4-dimethyl-3-pentanone	0.09	58	3.2	96

Conditions: see experimental section.

2. Results

2.1. *Qualitative influence of ketones on the activity and* ee

In the presence of a catalyst prepared from [Rh(1,5-cyclooctadiene)Cl]$_2$, (1*S*,2*S*)-(−)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine as the chiral ligand and potassium hydroxide as a co-catalyst, the reduction of acetophenone derivatives proceed smoothly at room temperature.[4a] Fig. 1 provides data obtained with the same catalyst in the same reaction involving acetophenone and p-trifluoromethylacetophenone as substrates with increasing acetone concentrations. With acetophenone, the *ee* varies from 60% up to 80% in the presence of added acetone (Fig. 1 and Table 1). Note that the best result obtained with this catalyst in the reduction of acetophenone was 67%.[4a] A concomitant decrease in activity is noticed. Cyclohexanone also inhibits the reaction and affords a noticeable increase in enantioselectivity. The beneficial effect of other ketones such as 2-octanone and 2,4-dimethyl-3-pentanone on the *ee* decreases when increasing the steric hindrance.

Other ketone substrates have been tested under the same conditions. Some significant increases were obtained with trifluoroacetophenone and chiral (*R*)-3-methylcyclohexanone. For trifluoroacetophenone, the enantiomeric excess increased from 7 up to 12% with a 0.16 M acetone solution. Similarly, for (*R*)-

Table 2
Range of conditions used in the kinetic study

Condition	Concentration range
[acetophenone]	0.007-0.14
[acetone]	0.002-0.09
[water]	0.01-2.17
[2-phenylethanol]	0.033-0.036

Concentrations unit: kmol/m^3. Other conditions: see Experimental Section

3-methylcyclohexanone, *ee* values go from 5% without acetone to 16% when using a 0.83 M acetone solution. In both cases, a strong kinetic inhibition is observed while acetone is added.

2.2. Kinetic study: empirical rate laws

A quantitative kinetic study of the reaction was undertaken in order to assess the origin of the influence of acetone on the enantioselection process. The influence of the reaction parameters such as the concentration of acetophenone, (*R*)- and (*S*)-phenylethanol, acetone and water have been evaluated in an isothermal batch microreactor (Table 2).[9a]

The influence of acetone on the enantioselectivity has already been shown (Fig. 1). The rate of reaction strongly depends on the water, the acetone and the acetophenone concentrations (Fig. 2).

Thus, water and acetone inhibit the reaction whereas saturation kinetics at high acetophenone concentrations take place. However, no effect on the enantioselectivity was noticed with respect to these reaction parameters.

Addition of the product *rac*-1-phenylethanol does not affect the rate of reaction nor the enantioselectivity. In keeping with this point, the possibility of reduction of acetone with 1-phenylethanol, i.e. kinetic resolution, has been investigated. Under conditions similar to those used for the reduction of acetophenone (net isopropanol, [acetone]=0.1 kmol/m^3, 25°C, [1-phenylethanol]=0.035 kmol/m^3, [Rh]=0.0017 kmol/m^3) the kinetic resolution is very slow, a period of more than 7 days being required to reach an observable conversion of ca. 7% with very low *ee*s. On the basis of this experiment, the kinetic resolution of 1-phenylethanol which could have been a reasonable explanation for the observed increase in *ee*, was ruled out. All these results point to semi-empirical kinetic models for the rates of formation of (*R*)- and (*S*)-1-phenylethanol as depicted in Eqs. 3 and 4.

$$r_{R-PE} = \frac{k_r[Rh]_0[AP]}{1 + K^{AP}[AP] + K_r^{AC}[AC] + K[H_2O]} \quad (3)$$

$$r_{S-PE} = \frac{k_s[Rh]_0[AP]}{1 + K^{AP}[AP] + K_s^{AC}[AC] + K[H_2O]} \quad (4)$$

To sum up, the very interesting feature in these models lies in the different kinetic inhibition constants K_r^{AC} and K_s^{AC} which reflect the experimental observation that addition of acetone increases the *ee* with a concomitant decrease in activity.

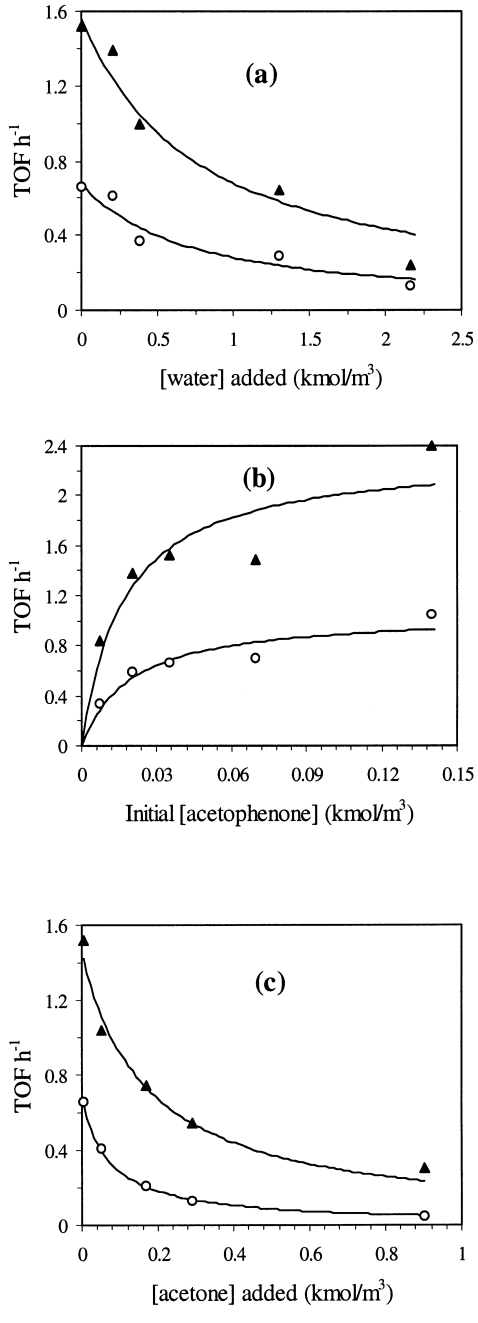


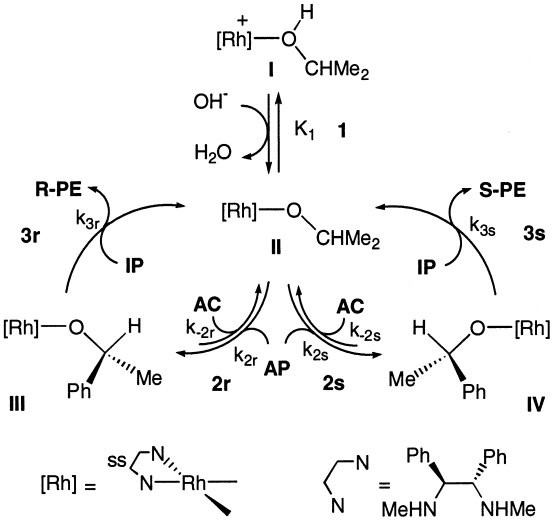
Fig. 2. Effect of (a) added water, (b) initial acetophenone concentration and (c) added acetone on the rate of production of (*R*)- (□) and (*S*)- (∘) 1-phenylethanol. TOF=mole of (*R*)- or (*S*)-phenylethanol produced/mole of Rh/hour at t→0. Dots are experimental data, continuous lines are computed from models of Eqs. 3 and 4

2.3. Kinetic study: mechanistic rate laws

Formal kinetic rate laws for the formation of (*R*)- and (*S*)-phenylethanol were derived from the mechanism of Scheme 2 using the Bodenstein approach for the catalytic intermediates (Eqs. 5 and 6) and with the assumption of equilibrium (1) to be very fast. The kinetic parameters have been estimated from the concentration vs time profiles for 16 experiments.[9b] Fig. 3 depicts the good fit between the models and the experiments. Note that only five of these experiments are shown for sake of clarity.

$$r_{R-PE} = \frac{k_{3r}k_{2r}[Rh]_0[AP]}{(k_{-2r}[AC]+k_{3r})\left(1+\frac{[H_2O]}{K_1[OH^-]}+\frac{k_{2r}[AP]}{k_{-2r}[AC]+k_{3r}}+\frac{k_{2s}[AP]}{k_{-2s}[AC]+k_{3s}}\right)} \quad (5)$$

$$r_{S-PE} = \frac{k_{3s}k_{2s}[Rh]_0[AP]}{(k_{-2s}[AC]+k_{3s})\left(1+\frac{[H_2O]}{K_1[OH^-]}+\frac{k_{2r}[AP]}{k_{-2r}[AC]+k_{3r}}+\frac{k_{2s}[AP]}{k_{-2s}[AC]+k_{3s}}\right)} \quad (6)$$



Scheme 2.

These mecanistic rate laws qualitatively account for the observed complex kinetic order in substrate concentration and the negative kinetic order with respect to both water and acetone. A statistical analysis of the set of kinetic constants of models of Eqs. 5 and 6 estimated with the dynamic parameter estimation software[9b] reveals that constants k_{3r} and k_{3s} are strongly correlated. This is a common problem when using global kinetics. Only a separate piece of information such as the evaluation of the concentrations of intermediates III and IV by in situ measurements may lead to an unambiguous determination of the full set of kinetic parameters. Unfortunately, in situ ^{1}H NMR, IR and UV spectroscopy was useless and any attempts to prepare III or IV failed.

To overcome this indetermination, several k_{3r}/k_{3s} ratios were tested in the range $3 \leq k_{3r}/k_{3s} \leq 500$ (Table 3). In terms of energy, such a range of k_r/k_s ratios corresponds to a $\Delta\Delta G_{rs}^{\ddagger}$ range of -2 to -15 kJ/mol (*R* configuration is preferred) as usually found for enantioselective processes.[10]

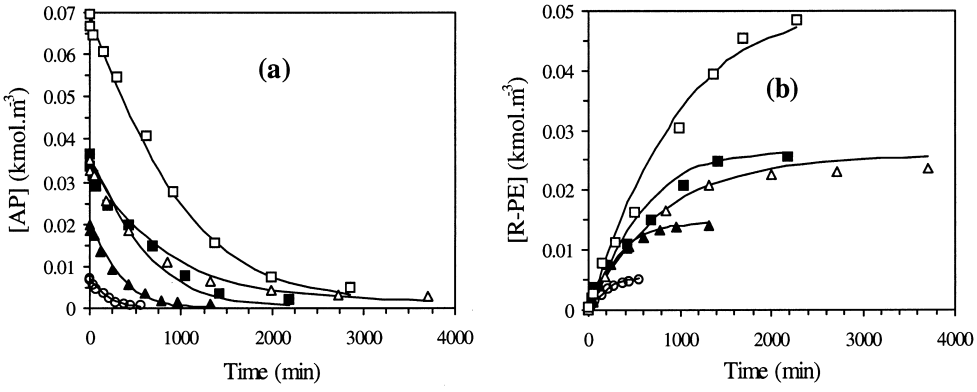


Fig. 3. Comparison between the experimental (dots) and model (lines) data for selected concentration vs time profiles of (a) acetophenone and (b) (*R*)-1-phenylethanol under selected conditions: (□) [AP] 0.07; (▲) [AP] 0.02; (○) [AP] 0.007; for (□,▲,○) no added acetone, no added water i.e. [AC]≤0.002 and [H_2O] 0.01; (■) [AP] 0.035; [H_2] 0.21; no added acetone (△) [AP] 0.034; [AC] 0.16; no added water. In examples, [rhodium] 0.0016. Concentrations in kmol/m^3

Table 3
Estimated kinetic parameters for models of Eqs. 5 and 6 at given values of k_{3r}/k_{3s}

Kinetic Parameter	k_{3r}/k_{3s} 3	5	10	50	100	500	Error %	Unit
k_{3r}	0.069	0.090	0.15	0.63	1.2	5.9	± 10	min^{-1}
k_{3s} *	0.023	0.019	0.015	0.013	0.012	0.012	± 10	min^{-1}
k_{2r}	3.6	3.7	3.6	3.6	3.6	3.6	± 16	$m^3.kmol^{-1}.min^{-1}$
k_{-2r}	0.87	1.2	2.1	9.0	17.5	79	± 24	$m^3.kmol^{-1}.min^{-1}$
k_{2s}	1.4	1.4	1.4	1.4	1.4	1.4	± 15	$m^3.kmol^{-1}.min^{-1}$
k_{-2s}	0.40	0.35	0.30	0.25	0.23	0.23	± 25	$m^3.kmol^{-1}.min^{-1}$
K_1	650	640	650	660	660	660	± 6	-
$\Delta\Delta G_{3rs}$	-2.7	-4.0	-5.7	-9.7	-11.4	-15.4		$kJ.mol^{-1}$
$\Delta\Delta G_{2rs}$	-2.3	-2.3	-2.3	-2.3	-2.3	-2.3		$kJ.mol^{-1}$
$\Delta\Delta G_{-2rs}$	-1.8	-3.1	-4.8	-8.8	-10.5	-14.5		$kJ.mol^{-1}$

* Computed from the ratio k_{3r}/k_{3s} and the estimated value for k_{3r}.

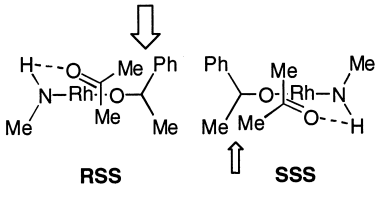
3. Discussion

The mechanism of Scheme 2 is a simplified version of the well accepted mechanism for the title reaction.[11] Such a simplified scheme may be criticized. Researchers in the field believe that a rhodium hydride intermediate is involved in the catalytic cycle.[4b 11,12] Recently, a Ru–hydride complex with nitrogen ligands was prepared, characterized by X-ray diffraction and used as a catalyst for the H-transfer reduction of ketones with alcohols.[13] However, the arguments for the simplified Scheme 2 are the following: (i) as few catalytic intermediates as possible are considered, i.e. the step involving the elusive rhodium–hydride intermediate is lumped; (ii) only those elementary steps that bear some macroscopic

information, e.g. co-ordination of the substrate, are considered; (iii) the rate determining step should proceed after the steps involving water, acetophenone and acetone since these reagents affect the rate of reaction; (iv) the backward reactions of 3r and 3s, i.e. the first step of the kinetic resolution, have been shown to be very slow compared to the forward reactions (see earlier).

In the results of Table 3, attention should be paid not so much to the values of the kinetic parameters but rather to the $\Delta\Delta G_{rs}^{\ddagger}$. In fact, these numbers somehow reflect the relative influence of the contribution of steps 2r, 2s, −2r, −2s, 3r and 3s to the enantioselection process. Except for when the k_{3r}/k_{3s} ratio is close to unity and similar to the case of methyl-(Z)-α-acetamidocinnamate hydrogenation, the co-ordination of the prochiral substrate onto the chiral catalyst, i.e. steps 2r and 2s, is not the enantioselective determining process. This is supported by the experimental results which do not show any noticeable effect of the acetophenone concentration on the enantiomeric excess within the range of concentrations used in this study. In contrast, a dramatic effect of the acetone concentration on the *ee* is observed in agreement with the rather high difference of reactivity of the diastereomeric intermediates III and IV with acetone. Thus the concentrations of these two diastereoisomeric catalytic intermediates are, to a large extent, controlled by the concentration of the achiral compound acetone. Obviously, the concentration of the other achiral reagent isopropanol which is lumped in the $k_{3r,s}$ constants, also plays an important role comparable to that of molecular hydrogen in hydrogenation reactions. Unfortunately, in practice, changing the isopropanol concentration would also result in the addition of a co-solvent which would lead to misleading conclusions.

The basis for the explanation that the transition states *RSS* or *SSS* for the backward reactions 2r and 2s are different is pictured in Scheme 3.



Scheme 3.

Several orientations of the incoming acetone molecule onto intermediates III and IV can be tested but the recent argument by Noyori about the possible interaction of the NH proton with the oxygen atom of carbonyl substrates was chosen.[14] As depicted, the one diastereoisomer *RSS* (intermediate III), would present a phenyl–methyl interaction, whereas the other *SSS* (IV) would not. Note that the nitrogen atom now plays the role of the stereogenic centre, its configuration being fixed by co-ordination to the rhodium, precluding any inversion.[15]

4. Conclusion

This work provides further evidence that the enantioselection process is connected to the difference of reactivity between the diastereoisomeric catalytic sites. Such a process is nowadays part of our approach to enantioselection.[1] However, this work shows that enantioselection may be caused, to a large extent, by reversible reaction steps in the mechanism. More generally in homogeneous catalysis, catalytic intermediates often undergo substitution reactions involving, e.g., solvent or ligand molecules. Thus, it is likely that the conclusions of the present work concerning the influence of non-linear kinetics on the enantioselectivity will apply to very diverse enantioselective catalytic reactions.[3–6] Finally, kinetic

investigations of the so called 'non-linear effects in asymmetric catalysis' may also lead to a better quantification of this important phenomenon.[16]

5. Experimental

5.1. Chemicals and analysis

The catalyst precursor $[Rh(cod)Cl]_2$ (98%, Strem) was used as received. Isopropanol was distilled over magnesium under nitrogen. The ketones (Aldrich) were degassed and purged under argon prior to use but not further purified. The diamine (1*S*,2*S*)-(−)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine (Acros) was used as received.

The composition of the reaction mixture and the enantiomeric excesses were determined by gas chromatography on an HP-5790A instrument (Cydex-B SGE capillary column, ca. 25 m d=320 μm, 2 bar He ml/min, FID detector, split injection mode, 1 μl sample intake, internal standard: dodecane, temperature program: 35°C for 4 min, 35°C to 110°C at 35°C/min; 110°C to 120°C at 1°C/min; 120°C to 230°C at 35°C/min, 230°C for 5 min). The column was checked periodically for its efficiency because metallic rhodium deposits were observed at the head of the column.

5.2. Catalytic tests

All the experiments involving the Rh complex were performed under argon or nitrogen at 25°C. The catalyst was prepared ex situ from $[Rh(1,5\text{-}COD)Cl]_2$, a 0.1 M solution of KOH and (1*S*,2*S*)-(−)-*N*,*N*′-dimethyl-1,2-diphenyl-1,2-ethanediamine in isopropanol. The mixture was stirred at room temperature for about 1 h and stored at −30°C at which temperature the catalyst was stable for up to six months as proved by reproducible catalytic tests. In a typical catalytic test, a gas chromatograph vial was charged with an aliquot of the catalyst (1 ml) prepared as described earlier, and a solution of the substrate, hexadecane as the internal standard and, eventually, the product or acetone, in isopropanol (0.5 ml). The final concentrations and molar ratio of the reagents are: [substrate]=0.035 kmol/m^3; substrate/Rh=20; diamine/Rh=2; KOH/Rh=6. The mixture was well shaken by hand and placed in the thermo-regulated automatic sampler of the gas chromatograph. Programming the automatic sampler allowed the automated monitoring of the reaction by gas chromatographic analysis using low sampling volumes (<10 μl).

Acknowledgements

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