EFFECT OF A Ru (II) CATALYST ON

THE RATE OF EQUILIBRATION OF CARBINOLS AND KETONES

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While the equilibration of carbinols and ketones   carbinol (1) + ketone (2) $\rightleftharpoons$ ketone (1) + carbinol (2)

can be achieved by the aid of some transition metals[1], alkoxydes[2] and inorganic bases[3], some *homogenous*

hydrogen-transfer catalysts [e.g., $RuCl_2(PPh_3)_3$ (1)] prove incapable to transfer-hydrogenate saturated ketones

in the presence of aldehydes. For this reason 1 can be used in the *selective* transfer-hydrogenation of

α, β-unsaturated to saturated ketones by primary alcohols. In the absence of an aldehyde (or its precursor —

a primary carbinol), however, $RuCl_2(PPh_3)_3$ does catalyze further transformation of the saturated ketone into

an equilibrium mixture of the carbonyl compound and the corresponding carbinol[4].

We report now the effect of the ruthenium complex 1 on the equilibration of ketones and carbinols as

an independent process. When e.g., a mixture of 1.22g (10^{-2} mole) 1-phenylethanol (2), 1.0g (10^{-2} mole)

cyclohexanol (3) and 9.6mg (10^{-5} mole) 1 is heated for 5h[5] at 180^0, the reaction mixture consists of 12%

2, 38% 3, 38% acetophenone (4) and 12% cyclohexanone (5). The same equilibrium mixture is obtained when

a mixture of 1.20g (10^{-2} mole) 4 and 1.02g (10^{-2} mole) 5 is heated with 9.6mg 1 for 5h[5] at 180^0.

The equilibrium constant (K = 10.0) is in agreement with the value calculated from the oxidation potentials

of the reacting ketones[6] [$E_0 = E_0' + 0.0445 \log K$; K = 9.6] .

Kinetic studies of the reaction of dibenzyl ketone and 1-phenylethanol

$$PhCH_2COCH_2Ph + PhCH(OH)CH_3 \rightleftharpoons PhCOCH_3 + PhCH_2CH(OH)CH_2Ph$$
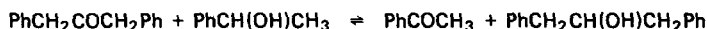
in the presence of 1 at 180^0 , show that at constant concentration of the carbinol, the rate of equilibration

changes from first order (at <0.1 M ketone) to a maximum and constant value above 0.3 M dibenzyl ketone.

Keeping the concentration of the ketone constant, the rate reaches its highest (constant) value only when the

carbinol exceeds 7M. These phenomena are observed with all the systems listed in Tables I and II.

TABLE I.   Initial Rates in Transfer-Hydrogenation of Some Ketones (0.5 M) in 1-Phenylethanol (Solvent) by

RuCl$_2$(PPh$_3$)$_3$ (10^{-3} M) at 180° [a]

Starting ketone	Initial rate (mmole/min)
Cycloheptanone	5.2
Benzophenone	4.4
Desoxybenzoin	5.1
Dibenzyl ketone	4.8
p—Chloroacetophenone	4.3
p—Methoxyacetophenone	5.0

[a]Ketones with very low oxidation potentials (e.g., α-tetralon— 80mv) hardly react with 1-phenylethanol

under these conditions and their rates could not be determined.

TABLE II.   Initial Rates in Transfer Hydrogenation of Dibenzyl Ketone (0.5 M) in Secondary Alcohols[a] by
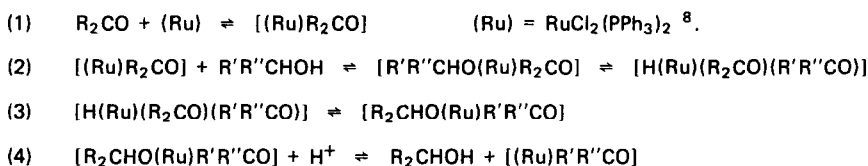
1 (10^{-3} M) at 180°

Starting Carbinol	Initial rate (mmole/min)
1-(p—Tolyl)ethanol	5.5
1-Phenylethanol	4.8
1-(p—Chlorophenyl)ethanol	3.6
2-Decanol	1.4
3,4-Dimethylcyclohexanol	1.3
Diisopropyl carbinol[b]	0.8

[a]Primary carbinols react at comparable rates (e.g., n-octanol 5.5 and benzyl alcohol 6.1 mmole/min)

but only for a short period. At aldehyde concentration of 5 x 10^{-2} M the rate has already dropped

by a factor of ~10.

[b]In a sealed tube.

The rate is practically independent of the nature of the ketone (Table I), but depends on steric and electronic factors of the carbinol applied (Table II). It follows , thus, the ease of formation of a metal hydride by abstraction of an α-hydrogen atom from the carbinol[7]. This conclusion can be drawn also from a) comparison of the kinetic isotope effect in the 1—catalyzed transfer hydrogenation of dibenzyl ketone with $PhCD(OD)CH_3$ (k_H/k_D = 1.68), $PhCD(OH)CH_3$ (k_H/k_D = 1.52) and $PhCH(OD)CH_3$ (k_H/k_D = 1.04), b) modification of the electronic nature of the ruthenium catalyst. The activities of $RuCl_2[P(4-X-C_6H_4)_3]_3$, for various substituents X, are in the order $Cl>F>H>CH_3>OCH_3$ (initial rates 6.4, 5.4, 4.8, 4.0, 3.6 mmole/min, respectively).

Based on these observations and studies to be published in a full paper, we assume the following steps to be the main feature of the reaction mechanism:

(1) $R_2CO + (Ru) \rightleftharpoons [(Ru)R_2CO]$ $(Ru) = RuCl_2(PPh_3)_2$ [8].

(2) $[(Ru)R_2CO] + R'R''CHOH \rightleftharpoons [R'R''CHO(Ru)R_2CO] \rightleftharpoons [H(Ru)(R_2CO)(R'R''CO)]$

(3) $[H(Ru)(R_2CO)(R'R''CO)] \rightleftharpoons [R_2CHO(Ru)R'R''CO]$

(4) $[R_2CHO(Ru)R'R''CO] + H^+ \rightleftharpoons R_2CHOH + [(Ru)R'R''CO]$

The initial formation of a ruthenium-ketone complex[9] is followed by fast addition of the carbinol to form a Ru-alkoxide[7]. In the rate determining step, migration of an α-hydrogen atom from the alkoxyl ligand to the Ru-bound ketone takes place. Protonation by the solvent[10] leads to the extrusion of a carbinol molecule from the complex, and then the bound ketone is either eliminated to give (Ru) or substituted by   new R_2CO.

As indicated, aldehydes inhibit the hydrogen transfer in our reaction, although they are rapidly reduced by themselves to primary carbinols. We believe this phenomenon is associated with the formation of a Ru-aldehyde complex $RuCl_2(PPh_3)_2(RCHO)$[11] that interferes with step (1).

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