Tin(IV) Ethoxide-catalysed Hydride Transfer from Alcohols to Carbonyl Compounds

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In aprotic, apolar solvents tin(IV) ethoxide has been proved to be an efficient catalyst for the selective hydride transfer from alcohols to carbonyl compounds. Primary, secondary, and benzyl alcohols have shown hydride-donating ability, and this ability decreases in the order benzyl $\gg$secondary $>$primary. The mechanism of hydride transfer from 1-phenylethanol to cyclohexanone has been investigated. Catalysis is inferred to proceed in the following order: (a) alcoholysis of Sn^{IV} ethoxide to form a mixed metal alkoxide, (b) co-ordination of the acceptor to the metal, (c) direct hydride transfer from the alkoxide moiety to the co-ordinated carbonyl compound and loss of the active catalyst. The kinetic isotope effect measurements and other data suggest that step (c) is the rate-determining step of the reaction.

THE metal alkoxide-catalysed redox processes between alcohols and carbonyl compounds [reaction (1)] were discovered over 50 years ago and have been successfully used in the reduction of a variety of aldehydes and ketones (Meerwein–Ponndorf–Verley reduction)[1] as well

$$R^1R^2CHOH + R^3R^4CO \rightleftharpoons R^1R^2CO + R^3R^4CHOH \qquad (1)$$

as in the oxidation of carbinols (Oppenauer oxidation).[2] In recent years, interest in this reaction has declined probably because of the rising success of catalytic transfer–hydrogenation procedures[3] and the application of complex hydrides.[4] Nevertheless, some mechanistic aspects have not been completely elucidated,[5] while very little work has been done in regard to the use of alkoxides other than aluminium derivatives.[6]

This study has been undertaken to examine in detail the hydride-transfer reaction from alcohols to aldehydes and ketones catalysed by tin(IV) ethoxide in aprotic, apolar solvents.

RESULTS

Outline of Catalysis.—The reaction was carried out by heating in a Pyrex glass tube a mixture of the carbonyl compound, the carbinol, and $Sn(OC_2H_5)_4$ (molar ratio, $1:2:2 \times 10^{-2}$) in refluxing dry toluene with stirring under nitrogen. The reaction took several hours (in general 20 h) and, after quenching in aqueous NH_4Cl, the products were analysed as described in the Experimental section and separated by standard techniques.

The hydride-donating ability of some alcohols to cyclohexanone was evaluated (Table 1). 1-Phenylethanol, benzyl alcohol, and 2-hydroxybenzyl alcohol show especially excellent hydride-donating ability which should be applied for synthetic purposes. Secondary alcohols have almost the same hydride-donating ability under the reaction conditions. Primary alcohols hardly reduce cyclohexanone in this system. Tertiary alcohols are inert and can be recovered unchanged. Both saturated and αβ-unsaturated carbonyl compounds are selectively reduced by heating with 1-phenylethanol and $Sn(OC_2H_5)_4$ (Table 2). In particular, good results are obtained in the reduction of cyclohexanone, α-bromoacetophenone, and 2-hydroxybenzaldehyde. On the other hand, the carbonyl group of aliphatic aldehydes is hardly affected. Crotonaldehyde and cinnamaldehyde, with two unsaturated bonds, C=C and C=O, are hydrogenated to the respective alcohols without reduction of the double bond.[7]

Measurement of Initial Rate.—Figure 1 shows an example of the conversion of cyclohexanone into cyclohexanol against reaction time with 1-phenylethanol as donor [equation (2)]. At the initial stage of the reaction the conversion is proportional to time.

$$[CH_2]_5{=}CO + C_6H_5CH(OH)CH_3 \xrightarrow[\text{toluene } 110^\circ]{Sn(OC_2H_5)_4} [CH_2]_5{=}CHOH + C_6H_5COCH_3 \qquad (2)$$

However, the linearity does not hold for $>30\%$ conversion, perhaps because the formed acetophenone competes with cyclohexanone for a co-ordination site of the catalyst. The initial rate of the reaction (R) is derived from the linear part. Apart from the reverse reaction, the process occurs without noticeable side reactions. Analyses of the products show that the reaction proceeds stoicheiometrically: thus the amount of the acetophenone is equal to that of cyclohexanol and the total amount of cyclohexanone and cyclohexanol to that of the original cyclohexanone.

TABLE 1

Examples of tin(IV) ethoxide-catalysed reduction of cyclohexanone by various hydride donors under comparable conditions [b]

Experiment	Hydride donor	Yield of cyclohexanol (%) [a]	Dehydrogenation product
1	1-Phenylethanol	84	Acetophenone
2	Benzyl alcohol	76	Benzaldehyde
3	2-Hydroxybenzyl alcohol	78	2-Hydroxybenzaldehyde
4	Propan-2-ol	64	Acetone
5	Butan-2-ol	62	Butan-2-one
6	Propan-1-ol	12	Propanal
7	Butan-1-ol	14	Butanal
8	Ethanol	10	Acetaldehyde

[a] Reaction system was 0.5M-cyclohexanone, 1M-hydride donor, and 10^{-2}M-$Sn(OC_2H_5)_4$ in toluene at 110° for 20 h.
[b] By g.l.c. analysis.

Structure–Activity Correlation.—The initial rate of the reduction of cyclohexanone was measured in the presence of selected alcohols (Table 3). The data reveal, once more, that 1-phenylethanol and benzyl alcohol exhibit better hydride-donating ability than aliphatic alcohols. This fact may be rationalized by the stability of the formed ketone and/or by the promoting effect of benzene ring on the co-ordination of the donor to the catalyst. Furthermore, alcohols substituted by electron-releasing groups increase

TABLE 2

Examples of tin(IV) ethoxide-catalysed reduction of some carbonyl compounds by 1-phenylethanol under comparable conditions [a,b]

Experiment	Carbonyl compound	Yield of product (%) [c]
1	Cyclohexanone	Cyclohexanol, 84
2	α-Bromoacetophenone	1-Phenyl-2-bromoethanol, 64
3	2-Hydroxybenzaldehyde	2-Hydroxybenzyl alcohol, 70
4	Propanal	Propan-1-ol, 23
5	Acetaldehyde	Ethanol, 19
6	Heptanal	Heptan-1-ol, 20
7	But-2-enal	But-2-enol, 37
8	Cinnamaldehyde	Cinnamic alcohol, 42

[a] Reaction system was 0.5M-carbonyl compound, 1M-1-phenylethanol, and 10^{-2}M-$Sn(OC_2H_5)_4$ in toluene at 110° for 20 h. [b] Dehydrogenation product was acetophenone in all cases. [c] By g.l.c. analysis.

the activity and *vice versa*, suggesting that the abstraction of a hydrogen atom α to the hydroxy-group as hydride is involved in the rate-determining step (see below, kinetic isotope effect measurements).

The reaction rate is also affected by the structure of the acceptor (Table 4). The data indicate a decrease in rate with sterically hindered hydrogen acceptors, perhaps because of their difficulty in co-ordinating to the metal catalyst.[7] Instead, introduction of an electron-releasing or -withdrawing substituent in the 4-position in acetophenone has no significant effect on the reaction rate, suggesting that catalyst–acceptor co-ordination takes place prior to the rate-determining step.

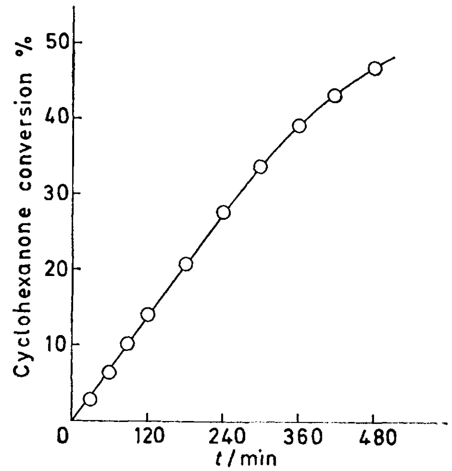


FIGURE 1 Plot of conversion *versus* reaction time for 0.5M-cyclohexanone, 1.0M-1-phenylethanol, and 10^{-2}M-$Sn(OC_2H_5)_4$ in toluene at 110°

TABLE 3

Effect of hydride donors [a]

Experiment	Hydride donor	Initial rate ($mol\ l^{-1}\ min^{-1}$)
1	1-Phenylethanol	6.3×10^{-4}
2	Benzyl alcohol	5.7×10^{-4}
3	Propan-2-ol	4.9×10^{-4}
4	Propan-1-ol	9.8×10^{-5}
5	4-Chlorobenzyl alcohol	2.3×10^{-4}
6	4-Methoxybenzyl alcohol	1.1×10^{-3}

[a] Reaction system was 0.5M-cyclohexanone, 1M-hydride donor, and 10^{-2}M-$Sn(OC_2H_5)_4$ in toluene at 110°.

Reaction Solvents.—The initial rates for the reduction of cyclohexanone with 1-phenylethanol [reaction (2)] in various solvents were recorded. The results are listed in Table 5. Some polar solvents such as bromo- and chloro-benzene and ethers have a large ability to dissolve the catalyst, but the reduction does not proceed so fast. This may be understood by the fact that these solvents co-ordinate the metal of the catalyst sufficiently strongly to show a decelerating effect. In poorly polar aromatic compounds, such as toluene, the reduction proceeds well and Sn^{IV} ethoxide dissolves easily. In this study, toluene was used as solvent.

TABLE 4

Effect of hydride acceptors [a]

Experiment	Hydride acceptor	Initial rate ($mol\ l^{-1}\ min^{-1}$)
1	α-Bromoacetophenone	3.2×10^{-4}
2	2-t-Butylacetophenone	1.2×10^{-5}
3	4-Chloroacetophenone	4.0×10^{-4}
4	4-Methoxyacetophenone	3.0×10^{-4}
5	2-Ethylbutanal	4.3×10^{-5}
6	Hexan-2-one	3.0×10^{-4}

[a] Reaction system was 0.5M-hydride acceptor, 1M-1-phenylethanol, and 10^{-2}M-$Sn(OC_2H_5)_4$ in toluene at 110°.

TABLE 5

Effect of reaction solvents [a]

Experiment	Solvent	Initial rate ($mol\ l^{-1}\ min^{-1}$)
1	Toluene	6.3×10^{-4}
2	Xylene [b]	6.1×10^{-4}
3	Chlorobenzene	1.9×10^{-5}
4	Bromobenzene	1.6×10^{-5}
5	Bis-2-methoxyethyl ether	0.0

[a] Reaction system was 0.5M-cyclohexanone, 1M-1-phenylethanol, and 10^{-2}M-$Sn(OC_2H_5)_4$ in the solvent at 110°. [b] Mixture of isomers, b.p. 142—146°.

Dependence on Donor, Acceptor, and Catalyst Concentration.—For these studies, the reduction of cyclohexanone by 1-phenylethanol [reaction (2)] was chosen. Plots of initial rate against the concentration of 1-phenylethanol (donor) and of cyclohexanone (acceptor) are shown in Figure 2.

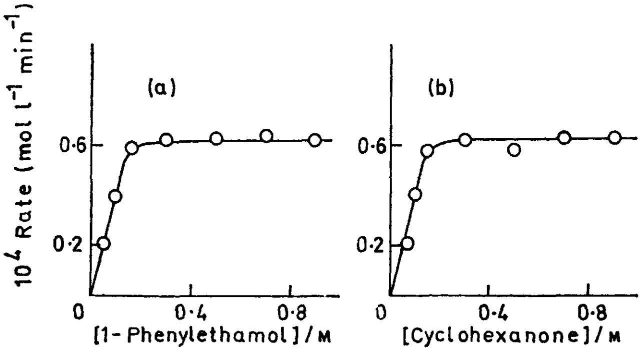


FIGURE 2 Dependence of initial rate on the concentration of (a) 1-phenylethanol and (b) cyclohexanone in toluene at 110°. Initial concentration of cyclohexanone and 1-phenylethanol 0.5M, 10^{-2}M-$Sn(OC_2H_5)_4$

Both functions are non-linear and the dependence of the initial rate on the concentration decreases gradually. The rates become independent of the concentration above 0.15M. The zero-order dependence above a concentration of 0.15M may be interpreted by the assumption that both donor and acceptor co-ordinate to the metal of the catalyst so completely to show a levelling effect.

The dependence on catalyst concentration is shown in Figure 3. In typical experiments, in which cyclohexanone (0.5M) and 1-phenylethanol (1M) are treated with varying amounts of $Sn(OC_2H_5)_4$, a linear rate increase is observed for low catalyst concentration. Above 0.02M the rate increase diverges from linearity. At higher concentration (>0.035M) the rate approaches a constant value, probably due to solubility limits of the catalyst and/or to their tendency to form dimers and oligomers.[8]

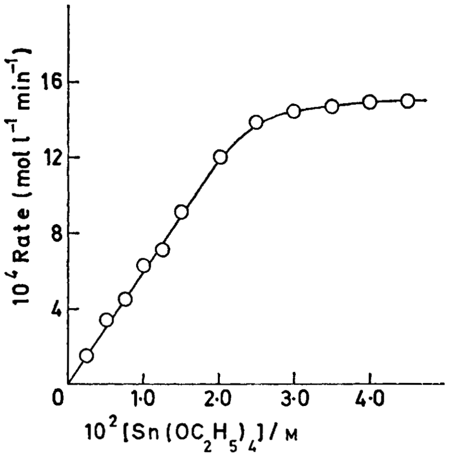


FIGURE 3 Dependence of initial rate on the concentration of the catalyst in toluene at 110°. Initial concentration of cyclohexanone 0.5M, 1.0M-1-phenylethanol

Dependence of Temperature.—Initial rates [reaction (2)] were measured at four temperatures ranging from 80 to 110°. Good linear plots of log k (see below) against $1/T$ were obtained for several cyclohexanone concentrations (0.1—0.5M), indicating that the kinetics of the system are not too complicated (Figure 4). From the Arrhenius plot a value for the activation energy (E_a) of 18.7 kcal mol^{-1} is obtained. $\Delta H^{\ddagger}$ is 17.9 kcal mol^{-1}. $\Delta S^{\ddagger}$, calculated with the observed rate constant (k), is -26.1 cal mol^{-1} K^{-1}. The large negative entropy of activation may be rationalized by a combination of factors like the large groups co-ordinated to the carbonyl function and the rigid six-membered ring, and the substantial increase in steric strain of the transition state of the catalysis.

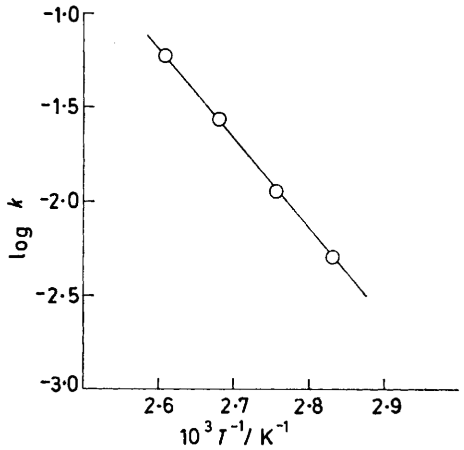


FIGURE 4 Arrhenius plot of reduction of cyclohexanone by 1-phenylethanol at 80—110°

Isotope Effect.—As previously shown, the initial rate of the reduction of cyclohexanone with 1-phenylethanol [reaction (2)] in the presence of tin(IV) ethoxide as catalyst, is 6.3×10^{-4} mol l^{-1} min^{-1}. The rate is 3.5×10^{-4} mol l^{-1} min^{-1} with 1-deuterio-1-phenylethanol. The kinetic isotope effect, $R_H/R_D = 1.8$, shows that α-hydrogen abstraction may be involved in the rate-determining step. Accurate ^1H n.m.r. and mass spectral analyses of the deuteriated cyclohexanol, formed in the reduction of cyclohexanone with $C_6H_5CD(OH)CH_3$, show that the benzylic hydrogen atom in 1-phenylethanol is transferred mainly to the α-carbon of the acceptor.

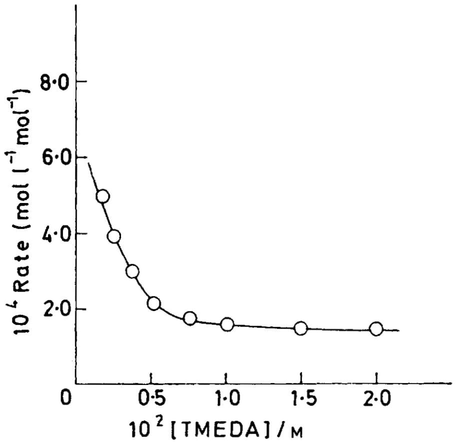


FIGURE 5 Effect of addition of TMEDA on the initial rate. 0.5M-Cyclohexanone, 1M-1-phenylethanol, and 10^{-2}M-$Sn(OC_2H_5)_4$ in toluene at 110°

Inhibitors.—Reaction (2) is strongly decelerated by basic and co-ordinating additives. A typical example of such an inhibition is shown in Figure 5. The rate can be lowered to 0.3 of its original value by addition of 0.5 equiv. of tetramethylethylenediamine (TMEDA), but further addition has no significant effect on the catalysis. The effect of several tertiary amines seems to be similar to that of TMEDA. Tributylamine, *e.g.*, causes the initial rate to drop from 6.3×10^{-4} (zero [amine]) to *ca.* 2.2×10^{-4} mol l^{-1} min^{-1} on addition of 0.5 equiv. Hexamethylphosphoramide (HMPA) acts as powerful inhibitor. Probably this compound easily co-ordinates with the catalyst to give a complex which is inactive in the hydride-transfer reaction.

TABLE 6

Catalytic activity of tin(IV) alkoxides [a]

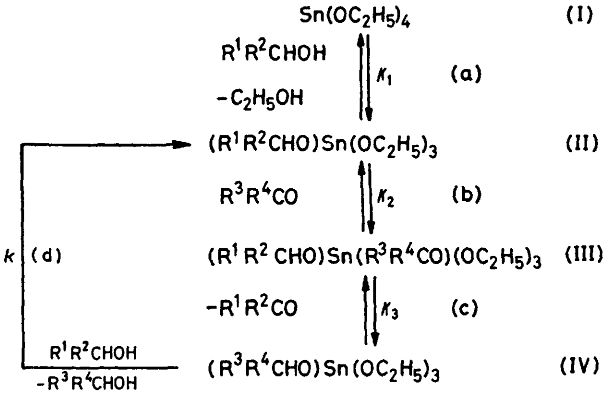
Experiment	Compound	Initial rate (mol l^{-1} min^{-1})
1	$Sn(OC_2H_5)_4$	6.3×10^{-4}
2	$Sn(OC_3H_7)_4$	6.2×10^{-4}
3	$(C_6H_5CH_3CHO)Sn(OC_2H_5)_3$	6.3×10^{-4}
4	$Sn(C_6H_5CH_2O)_4$	6.4×10^{-4}
5	$Sn(OCH_2CCl_3)_4$	6.1×10^{-4}

[a] Reaction system was 0.5M-cyclohexanone, 1M-1-phenylethanol, and 10^{-2}M-alkoxide in toluene at 110°.

Dependence on Catalyst Structure.—The influence of the structure of the catalyst upon reactivity was studied utilizing both symmetrical and mixed tin(IV) alkoxides in reaction (2). The initial rates for various alkoxides are listed in Table 6. Since the nature of the substituents in the catalyst shows no remarkable effect on reaction rate, one can say with confidence that the hydride is transferred from the alkoxide moiety directly to the co-ordinated carbonyl compound, thus excluding the formation of a metal hydride intermediate (see below, Scheme 3).

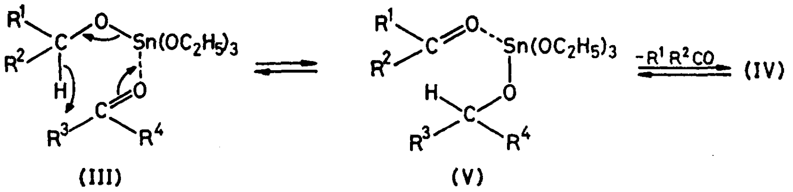
DISCUSSION

Kinetic studies of the metal alkoxide-catalysed reduction of carbonyl compounds have been reported.[5] Based on the studies and results described in the previous sections, we propose a catalytic cycle for the reaction mechanism of the reduction of carbonyl compounds by alcohol donors (Scheme 1). The first stage of this reaction [(a)] is presumed to be the formation of tin alkoxide (II) (probably as a mixed alkoxide) *via* alcoholysis of tin(IV) ethoxide (I) by the hydride donor.* An alkoxide such as (I) can form dimers and polymers in highly concentrated solutions,[8] but in high dilution the monomeric species predominates, hence the linear dependence of rate on the catalyst at least below 3.5×10^{-2}M. Kinetic measurements show that partial alcoholysis is a very fast process. We found also that the order of mixing of reactants has no effect on the reaction rate. Thus the rate of reaction when cyclohexanone, 1-phenylethanol, and the catalyst were simultaneously mixed was nearly equal to the rate of a reaction in which 1-phenylethanol and the catalyst were refluxed in toluene for 3 h before adding cyclohexanone. These data and the above mentioned independence of the rate on catalyst structure (Table 6) suggest that this stage is fast and occurs in a practically irreversible way.



Scheme 1

The second stage (b) is the interaction of the acceptor with (II) resulting in the formation of a pentacoordinated complex (III) and in the contemporaneous activation of the carbonyl compound. The equilibrium constant K_2 is expected to be only slightly influenced by electronic variation, but more severely by steric effects in the ketone (Table 4). Examination of the ^{1}H n.m.r. spectra of the solutions of α-bromoacetophenone and the mixed alkoxide $(C_6H_5CH_3CHO)Sn(OC_2H_5)_3$ indicates rapid and reversible co-ordination of the carbonyl compounds with the mixed alkoxide. The spectra (100 MHz in C_6D_6) show only a singlet for CH_2, its position depending on the ratio of alkoxide to ketone concentration and the temperature. Further unambiguous evidence derives from the examination of ^{13}C n.m.r. spectra of solutions of cyclohexanone and $(C_6H_5CH_3CHO)Sn(OC_2H_5)_3$ in deuteriated benzene at ambient temperature.[9] Natural abundance ^{13}C chemical shift of carbonyl carbon (δ_{obs} 211.1 p.p.m.) is found to increase when mixed alkoxide (II) is added. This value begins to level off at a $\Delta\delta$ value of *ca.* 9.5 p.p.m. at a 1 : 1 mol ratio of (II) to ketone.† At this ratio nearly all the cyclohexanone is complexed and, consequently, the value observed at a 1 mol ratio of tin alkoxide (δ_{obs} 220.6 p.p.m.) can be considered as characteristic of the complex itself. The direct hydride transfer from the alkoxide moiety in the complex (III) to the co-ordinated carbonyl compound represents the third stage of the process (c). The kinetic isotope effect indicates that this step is rate-determining in the overall reaction.‡ The ratio of reaction constants $R_H/R_D = 1.8$ at 100° (corrected to 25° = 2.57) is typical for a concerted hydride-transfer reaction.[11]



Scheme 2

The hydride transfer yields presumably a new complex (V) which releases the donor residue as the corresponding aldehyde or ketone and produces the mixed alkoxide (IV) (Scheme 2). An alternative route (Scheme 3) *via* a tin(IV) hydride complex intermediate as in step (III) → (VI) is expected to be affected by the nature of substituents on the tin(IV) catalyst. By contrast the experiments with variously substituted tin(IV) alkoxides (Table 6) are shown not to be affected.

To rationalize our observations we assume that the

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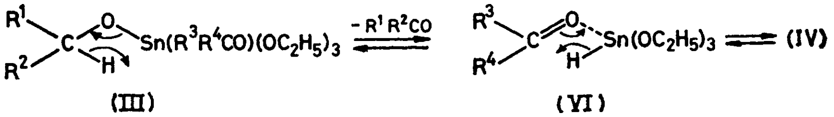
* Since all tin alkoxides react at the same rate (Table 6), a referee suggests the active catalytic species is always tetrakis-(1-phenylethoxy)tin. However, while in our reaction conditions 1-phenylethanol rapidly and quantitatively displaced 1 mol of ethanol at tin producing the mixed alkoxide (II), complete alcoholysis required longer reaction times and non-equilibrating conditions (*i.e.* azeotropic removal of the ethanol formed).

† A smaller shift (1.1 p.p.m.) was observed for the α-carbon.

‡ A simulation model for the Meerwein–Ponndorf reaction of acetophenone and *p*-nitroacetophenone indicates that the reaction is first-order and the rate-determining step is hydride ion transfer.[10a]

β-hydrogen atom in the alkoxide moiety is transferred directly to the carbonyl group in a concerted reaction as proved by deuterium labelling.

The last stage of reaction (d) is the release of hydrogenated acceptor re-forming the active catalyst (II). Since, under our experimental conditions, tin(IV) ethoxide can be assumed to be transformed almost completely in a practically irreversible way into the mixed alkoxide (II) which is present mostly in the monomeric form, we can apply the kinetic Scheme 4 for reaction (2).



SCHEME 3

The rate law would then be given by equation (3). When large excess of both acceptor and donor are used (above saturation concentration of 0.15M at which the

$$\text{rate} = -\frac{d[A]}{dt} = \frac{kK_1K_2K_3[C]_0[A][D]^2}{1 + K_1[D] + K_1K_2[A][D] + K_1K_2K_3[A][D]} \quad (3)$$

rate becomes invariable), the rate expression reduces to rate $= k[C]_0$ and the magnitude of k can be directly obtained from the initial rate of the reaction.

$$\begin{aligned} C + D &\overset{K_1}{\rightleftharpoons} CD \\ CD + A &\overset{K_2}{\rightleftharpoons} CDA \\ CDA &\overset{K_3}{\rightleftharpoons} CA' + D' \\ CA' + D &\xrightarrow{k} CD + A' \end{aligned}$$

SCHEME 4 C, Catalyst; D, donor; A, acceptor; A', hydrogenated acceptor; D', dehydrogenated donor

EXPERIMENTAL

N.m.r. spectra were obtained on deuteriobenzene solutions with Me_4Si as internal standard on a Varian XL 100 spectrometer. Mass spectra were recorded on a Varian MAT CH-5 mass spectrometer. G.l.c. analyses were effected on a Varian model 2700 instrument equipped with a flame ionization detector. Quantification for g.l.c. was accomplished using a Hewlett-Packard 3373B digital integrator. Atomic absorption analyses were performed on a Perkin-Elmer model 303 spectrophotometer. Air- and water-free conditions were maintained at all times.

Materials.—Aldehydes, ketones, and alcohols used in this study were purchased from commercial sources or prepared by standard methods. Tin(IV) alkoxides were prepared from tin(IV) chloride and the corresponding alcohol by methods reported in the literature.[8] Deuteriated 1-phenylethanol was prepared by reduction of acetophenone with $LiAlD_4$ in anhydrous diethyl ether. Alkoxides as well as other materials used in rate measurements were at least 98% pure, determined by atomic absorption spectrophotometry or by g.l.c. analyses.

An Example of Reduction of a Carbonyl Compound.—A mixture of cyclohexanone (4.95 g, 50 mmol), 1-phenylethanol (12.2 g, 100 mmol), and $Sn(OC_2H_5)_4$ (0.3 g, 1 mmol) in anhydrous toluene (100 ml) was refluxed under nitrogen for 20 h. After cooling, the mixture was poured into an excess of a saturated aqueous solution of NH_4Cl and extracted stepwise with diethyl ether. The ether layers were washed with water and dried ($MgSO_4$). Analysis by g.l.c.–m.s. using a 5% Carbowax 20 M on Chromosorb W column indicated that 84% cyclohexanone was reduced to cyclohexanol. The yield of acetophenone was 85%. Separation of reaction products was performed by distillation under ambient pressure using a standard procedure. All other reactions were carried out in a similar way.

The kinetic measurements were carried out in Pyrex tubes (25 ml) equipped with gas inlets and outlets immersed in an oil-bath fitted with a thermostat (accuracy ±0.25°). Samples were withdrawn and immediately frozen every 30 min during the first 120 min of the reaction and in intervals of 1 h thenceforth. G.l.c. analyses were performed on a 5 ft × 1/8 in stainless steel column packed with 5% Carbowax 20 M on Chromosorb W at 100—190° in accordance with the sample injected. The reaction rate was obtained by the gradation of time against conversion plot and calculated from the average of at least three experiments.

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REFERENCES

[1] H. Meerwein and R. Schmidt, *Annalen*, 1925, **444**, 221; W. Ponndorf, *Z. Angew. Chem.*, 1926, **37**, 537; M. Verley, *Bull. Soc. chim. France*, 1925, **37**, 537; A. L. Wilds, *Org. Reactions*, 1944, **2**, 178.

[2] R. V. Oppenauer, *Rec. Trav. chim.*, 1937, **56**, 137; C. Djerassi, *Org. Reactions*, 1951, **6**, 207.

[3] I. S. Kolomnikov, V. P. Kukolev, and M. E. Vol'pin, *Russ. Chem. Rev.*, 1974, **43**, 399.

[4] P. Caubère, *Topics Current Chem.*, 1978, **73**, 106.

[5] W. N. Moulton, R. E. Van Atta, and R. R. Ruch, *J. Org. Chem.*, 1961, **26**, 290; V. J. Shiner, jun., and D. Whittaker, *J. Amer. Chem. Soc.*, 1963, **85**, 2337; B. J. Yager and C. K. Hancock, *J. Org. Chem.*, 1965, **30**, 1175; V. J. Shiner, jun., and D. Whittaker, *J. Amer. Chem. Soc.*, 1969, **91**, 394; V. Hach, *J. Org. Chem.*, 1973, **38**, 293.

[6] T. Tsuda, H. Habu, and T. Saegusa, *J.C.S. Chem. Comm.*, 1974, 621.

[7] J. P. H. Tyman, *J. Appl. Chem. Biotechnol.*, 1972, **22**, 465.

[8] J. C. Maire, *Ann. Chim. (France)*, 1961, **6**, 969; A. J. Bloodworth and A. G. Davies in 'Organotin Compounds,' ed. A. K. Sawyer, Dekker, New York, 1971, vol. I.

[9] J. Torri and M. Azzaro, *Bull. Soc. chim. France*, 1978, 283 and references therein.

[10] (*a*) M. Kiss-Asboth and T. Blickle, Proceedings 3rd Congress Applied Chemistry Unit Open Processes, 1977, p. 265; (*b*) M. Kiss-Asboth, L. Szotyory, and A. Ujhidy, *ibid.*, p. 393.

[11] Y. Sasson, P. Albin, and J. Blum, *Tetrahedron Letters*, 1974, 833; Y. Sasson and J. Blum, *J. Org. Chem.*, 1975, **40**, 1887; C. G. Swain, R. A. Wiles, and R. F. W. Bader, *J. Amer. Chem. Soc.*, 1968, **83**, 1945; see also 'Isotopes in Organic Chemistry,' eds. E. Buncel and C. C. Lee, Elsevier, Amsterdam, 1976, vol. 2, ch. 7.