HOMOGENEOUS CATALYSIS OF O–SILYLATION REACTIONS USING TRIS (ACETYLACETONATO) COBALT (III)

BY HIKMAT S.HILAL

Chemistry Department, An-Najah National University, Nablus.

ملخــــــص

استعمل المركب ثلاثي (استيل اسيتونانو) كوبالت(III) ($Co(acac)_3$) كعامل مساعد في تفاعل السايلان R_3SiH ($R = Et, EtO$)، مع الكحولات $R'OH$ ($R'= Et, i-Pr, t-Bu, C_6H_5$) . لم يلاحظ اى تفاعل كيميائي حين اجراء التجارب على درجة الحرارة العادية ، ولكن التفاعل كان واضحا حين اجراء التجارب على درجة حرارة اعلى . ويتأثر معدل التفاعل بتغيير تراكيز السايلان والكحول . كذلك فان استعمال انواع مختلفة من الكحولات والسايلانات يوئثر بدرجة كبيرة على معدل التفاعل . كما يوئثر اختلاف تركيز المركب ($Co(acac)_3$) على معدل التفاعل ايضا .

ABSTRACT

Tris (acetylacetonato) cobalt (III), $(Co(acac)_3)$, has been used to catalyse o-silylation reactions of R_3SiH ($R = Et, EtO$) with $R'OH$ (R=Et, i-Pr, t-Bu and C_6H_5). No reaction has been observed at room temperature, but the reaction is apparently enhanced when carried out at a higher temperature. The rate of the reaction varies with varying the concentration of the saline or the alcohol. Using different types of alcohols and silanes greatly affects the rate of the reaction. The rate of the reaction is affected by varying the concentration of the complex $(Co(acac)_3)$

INTRODUCTION

O-Silylation reactions (Eq.1) have been catalysed by a variety of transition-metal complexes, such as those of iron[10,11], ruthenium[3], rhodium [3,4,7], iridium[5], and to a lesser extent, cobalt [2,6,8,9],

$$R_3 SiH + R'OH \xrightarrow{\;cat.\;} R \quad SiOR' + H2 \text{------------}(1)$$
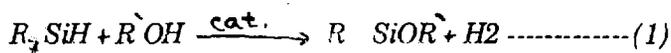
The complex $(Co(acac)_3)$ has been found to activate these reactions, and the aim of this work is to study the effectiveness of this complex as a catalyst for o-silylation reactions.

EXPERIMENTAL

$(Co(acac)_3)$ was prepared by standard methods[1]. The silanes were purchased from Aldrich Co. Ltd. in a pure form. The solvent and the alcohols were purified and dried prior to use by standard methods [13,14].

Catalysis Experiments: Reactions were conducted at constant pressure in a 50 ml round-bottomed flask, fitted with a subaseal, a condenser, a gas-burette, and a magnetic stirrer The condenser was used to prevent evaporation of the solvent and the reactants. The prevention of such evaporation was confirmed by carrying out blank experiments in the absence of catalyst, silane or alcohol. Throughout these experiment no change in the burette reading was observed, indicating that the change in the catalytic experiments is due to hydrogen gas produced not due to reactant vapors. The catalyst and the solvent (toluene, 8.5 ml) were placed in the flask which was dipped in oil bath, heated to 90° C. The silane was injected by a syringe and after 10 min of constant burette reading the alcohol was injected by a syringe.

RESULTS AND DISCUSSION

Addition of the alcohol to a thermostated catalytic mixture of $(Co(acac)_3)$ and the silane at 90 C in toluene resulted in the hydrogen gas evolution. The reaction was quantitative, and the rate of decay of the Si-H i.r. band at 2210 cm^{-1} coincided with the rate of evolution of hydrogen gas. At room temperature, the reaction is immeasurably slow, thus all catalytic reactions were caried out at 90 C.

Effect of varying catalyst concentration: The reaction of *EtOH* with $(EtO)_3$· *SiH* is sensitive to variations in $(Co(acac)_3)$ concentration (Fig 1). The highest rate was obtained when 0.1 mmole of catalyst was used. Plot of Ln(initial rate) vs. Ln(cobalt concentration) shows a linear relation, with an order of approximately one with respect to the catalyst, for concentrations of up to 0.1 mmole of cobalt. This is characteristic with many other catalytic systems [2,5,6,7] . Thus the optimum amount of the complex, 0.1 mmole, has been used throughout all runs unless otherwise stated.

Effect of the type of the silane: The reaction of *EtOH* with the silane $(EtO)_3SiH$, is much faster than that with $Et_3 SiH$ (Fig. 2). Similar results have been reported with different catalysts [2,6] This is presumably due to

electronic effect associated with the *R*-groups on the silicon atom. The ethoxy groups in $(EtO)_3 SiH$ have high capacity to withdraw electrons from the silicon atom leaving it with higher partial positive charge than in case of $Et_3 SiH$. This is consistent with the proposed mechanism.
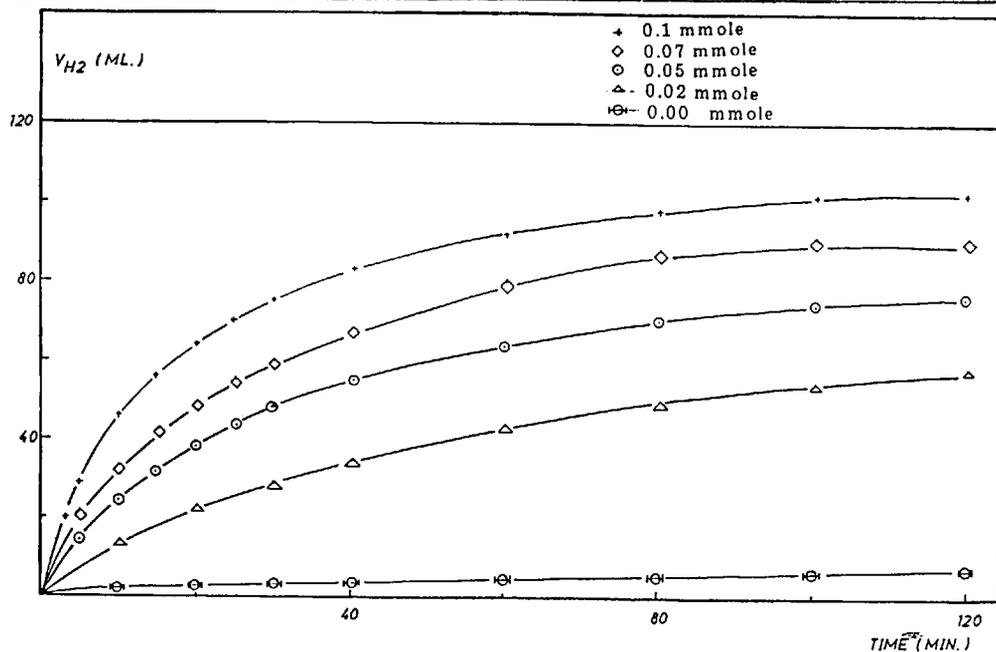
Fig.1 Effect of the concentration of *(Co(acac)$_3$)* on the rate of the reaction. Reactions were conducted using *EtOH* (6 mmole) and *(EtO)$_3$ SiH* (6 mmole) in toluene.
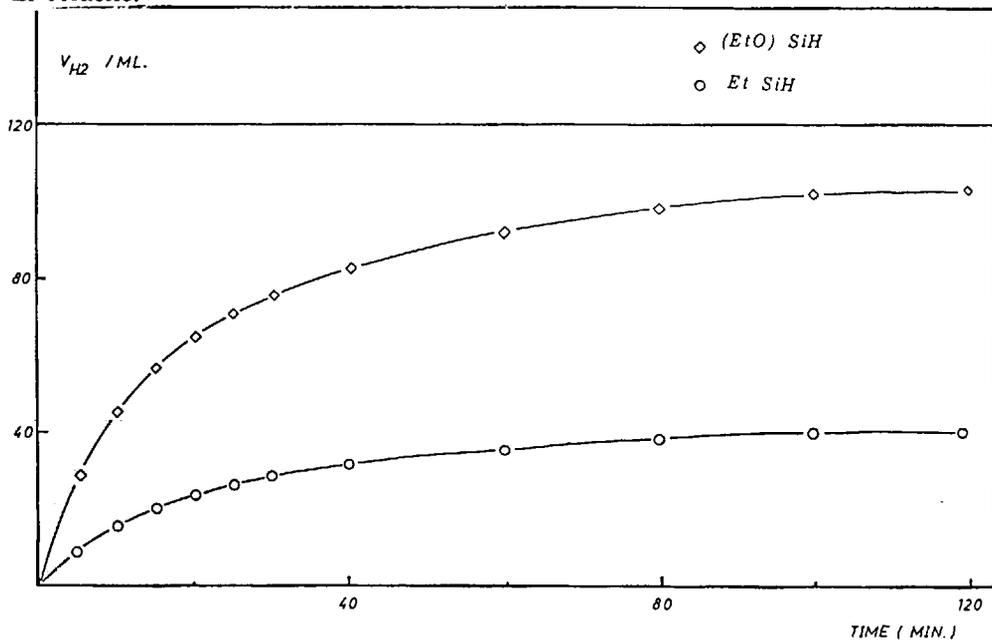
Fig. 2 Effect of varying the type of the silane. Reactions were conducted using mmolar ratios *Co: EtOH:R$_3$SiH* 0.1:6:6 in toluene respectively.

Effect of the type of the alcohol: The reaction of $(EtO)_3 SiH$ with R'OH varies in the order $R' = Et > i\text{-}Pr > t\text{-}Bu > C_6H_5$ (Fig. 3).

This is presumably a result of two factors. The first factor is the steric effect associated with the R-group, which is more pronounced in bigger R-group. The second factor is the electronic effect which is very obvious in the case of phenol due to the electron-withdrawing phenyl group. These two factors would possibly decrease the o-basicity of the alcohol and reduce its capacity to attack at the o-acidic coordinated silicon atom (see the mechanism section).
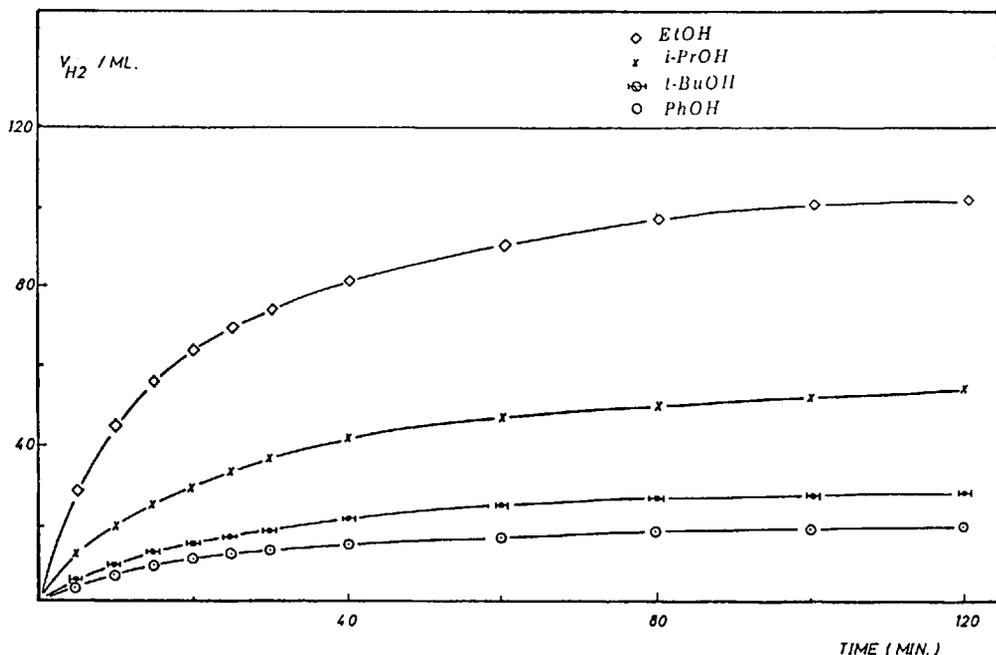
Fig. 3 Effect of varying the type of the alcohol. All reactions were conducted using mmolar ratio $Co: ROH: (EtO)_3 SiH$ 0.1:6:6 in toluene respectively.

Effect of varying the reactant concentrations: The reaction of *EtOH* and $(EtO)_3 SiH$ is dependent on the concentration of EtOH(Fig.4). Plot of Ln (initial rate) vs Ln (initial concentration of EtOH) shows that the reaction is first order with respect to the alcohol. The proposed mechanism is consistent with this fact. The reaction is also first order with respect to the silane (Fig.5).
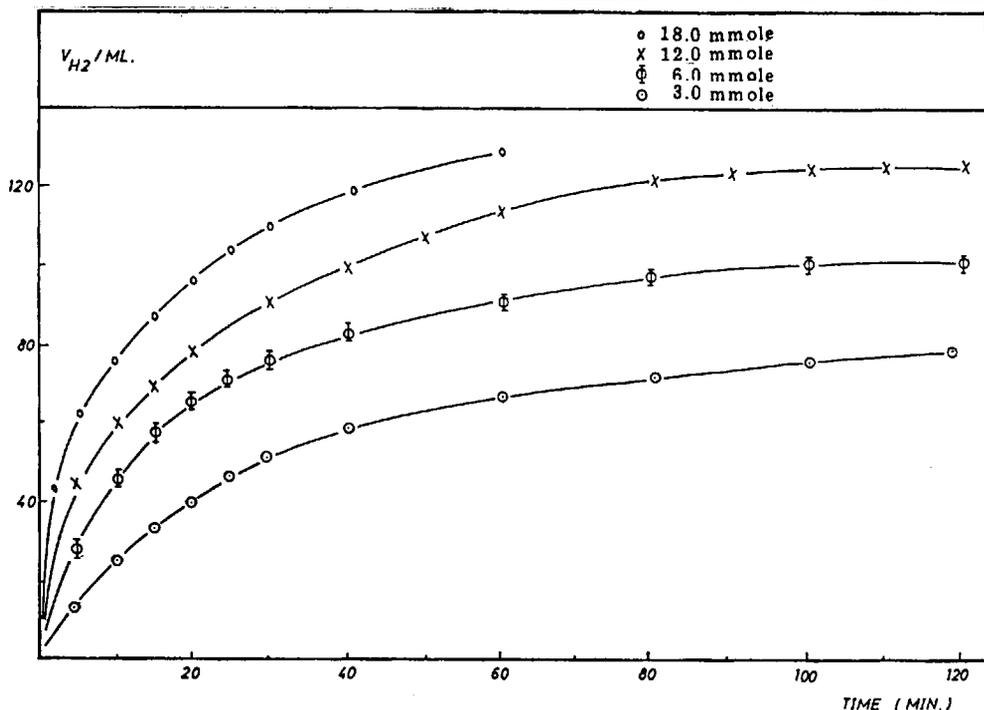
Fig. 4 Effect of the concentration of *EtOH* on the rate of the reaction. All reactions were conducted using *(Co(acac)$_3$)* (0.1 mmole) and *(EtO)$_3$SiH* (6.0 mmole) in toluene.

Proposed mechanism: From (Fig.1), it is apparent the complex *(Co(acac)$_3$)* plays a role in the catalysis of the o-silylation reaction. The mechanism proposed below is one with a quickly established equilibrium, in which activation of the silane occurs. The nature of the activation of the silane is still not fully understood. However, an oxidative-addition step of *Si-H* on *Co* in the *(Co(acac)$_3$)* form like other catalytic systems[6,7] is excluded. This is due to the lack of a vacant site on Co. The remaining step are of similar nature to those suggested for similar reactions[2,6]

$$(Co) + R_3SiH \longrightarrow (HCo(SiR_3)) \qquad (2)$$

$$(HCo(SiR_3)) + R'OH \longrightarrow (H_2Co) + R_3SiOR \qquad (3)$$

$$(H_2Co) \longrightarrow (Co) + H_2 \cdot \qquad (4)$$

V_{H2} /ML.

◇ 18.0 mmole
φ 12.0 mmole
○ 6.0 mmole
✗ 3.0 mmole

Fig.5

TIME (MIN.)
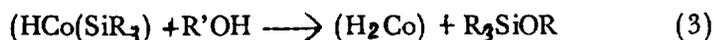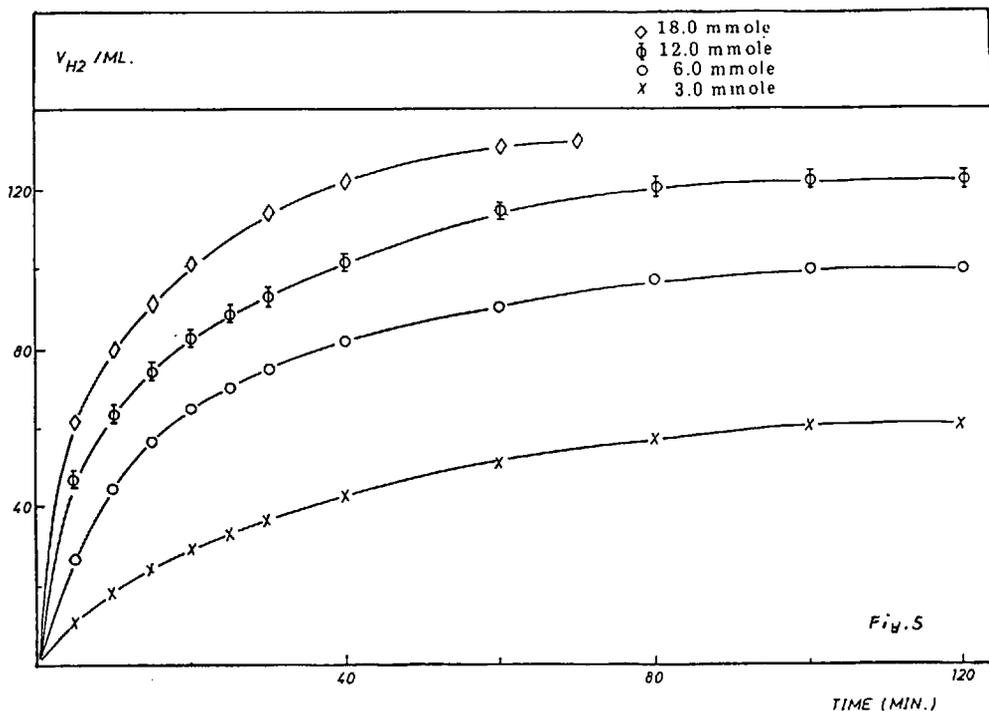
Fig. 5 Effect of varying the concentration of *(EtO)₃ SiH* on the rate of the reaction. All reactions were conducted using *(Co(acac)₃)* (0.1 mmole) and *EtOH* (0.6 mmole) in toluene.

Nucleophilic attack of the alcohol at the activated *Si* atom, (Eq. 3) has been suggested for similar systems using complexes of $Co^{2,}$[6], Rh[7], and Ir[5]. If this is a slow step, then this mechanism would explain the following observation:

a. The raction is first order with respect to the alcohol.

b. The reaction goes faster with *(EtO)₃ SiH* than with *Et₃ SiH*. The electron - withdrawing ethoxy groups would concentrate the partial positive charge on the *Si* atom, thus increase its susceptibility to nucleophilic attack in equation 3.

c. The reaction goes slower if electron-withdrawing or bulky alkyl groups, on the alcohol are used. In either case, the alkyl group would decrease the nucleophilic character of the alcohol.

ACKNOWLEDGEMENT

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