

Comparative Kinetics for the Deposition of Tetra(*neo*-pentyl)- versus Tetra(*tert*-butoxy)-zirconium onto an Oxidized Aluminium Surface. The Effect of the Ligand Type on the Deposition Mechanism

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Kinetics for the deposition of tetra(*tert*-butoxy)zirconium onto oxidized Al have been studied using quartz crystal microbalance techniques. A kinetic isotope effect was measured ($k_H/k_D = 1.6$) and is interpreted in terms of a strongly bound transition state for proton transfer from an –OH of the surface to an :O of the alkoxide. The chemical nature of the ligand lost on deprotonation, not necessarily the basicity of that group, is suggested to have a profound effect on the mechanistic course of that process.

Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

We are interested in studying mechanisms of organometallic complex deposition onto surface-oxidized metals in order to understand molecular parameters of interface synthesis on oxides. In the processes of interest to us, deposition of metal alkyls or alkoxides onto oxides occurs stoichiometrically by proton transfer, but there are no simple reactivity analogs in solution (R–OH) chemistry for the ensemble of hydrogen bonded and isolated surface hydroxyl groups of an oxide to aid our analysis. In particular, we want to learn if bulk (or total) acidity of a surface and the thermodynamic basicity of the depositing organometallic reagent correlate with microscopic phenomena for the deposition process. We have reported^{1,2} a quartz crystal microbalance (QCM)³ technique to measure kinetics for deposition of tetra(*neo*-pentyl)zirconium onto surface-oxidized Al: this QCM methodology lets us probe surface phenomena *directly* and gives accurate rate data, even for our heterogeneous systems and reactions too fast to follow by stoichiometric evolution of products. Surface hydroxylated Al (locally, Bayerite,⁴ 'AlOOH') with –OH group content varying according to surface activation vigor (as inferred from Auger analysis), served as both oscillator electrodes and reactive substrates. Because Auger analysis of variously treated Al showed stoichiometries comparable to the hydrous oxide, we believe these modified metal surfaces are good models for the oxide, itself.

We noted that, surprisingly, *rate constants* for deposi-

tion of tetra(*neo*-pentyl)zirconium onto oxidized Al did not correlate with total –OH content of the surface, but were quantitatively similar over the range of preparation conditions employed and subsequent complex loading (and they did not depend on choice of solution [non-coordinating solvent] or gas-phase reaction conditions). Using (Al)–OH vs. (Al)–OD of comparable surface total acidity, it was found that $k_H/k_D = 8.4$.² Therefore, even though proton transfer might have been thought to be fast for the protolytically labile organozirconium complex based on simple solution observations, this evidently primary isotope effect shows *proton transfer is the rate-determining step* for surface deposition.⁵ The large isotope effect measured may be the result of breaking a strong –OH bond and forming a weak two-electron-three center [Zr(R)(H)] unit in the transition state for Zr–R protolytic cleavage. Overall, deposition occurs via a surface-coordinated metal complex, paralleling protolytic cleavage of coordinatively unsaturated d⁰ and main group organometallics in which coordination of the acid, via its counterion, precedes proton transfer to the metal–carbon bond.⁶

Experimental

The choice of quartz crystals for use as the QCM has been described. A single 2000–2500 Å layer of Al was deposited directly onto the quartz crystal; the electrode overlap area was calculated to be 0.27 cm². The preparation of surface oxidized Al metal electrodes has also been described. A custom oscillator circuit was used for vapor- or solution-

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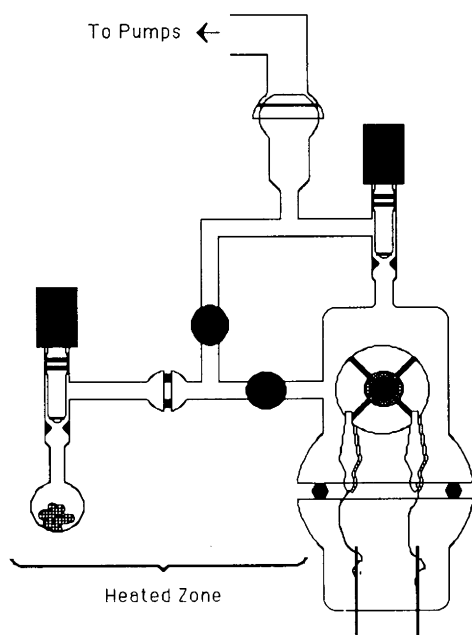


Fig. 1. Apparatus for vapor phase deposition of tetra(*tert*-butoxy)zirconium onto surface-activated Al.

phase deposition of tetra(*tert*-butoxy)zirconium which was powered by a Hewlett-Packard 6234A Dual-Output Power Supply. The crystal frequency was measured using a Hewlett-Packard 5334B Universal Counter and was recorded using a standard laboratory computer.

Auger analysis. QCM crystals were placed in an Ultra-High Vacuum chamber; pump-down to a base pressure of $<5 \times 10^{-8}$ Torr was achieved without bakeout to eliminate contamination of the samples. The chamber, which is more fully described elsewhere,⁷ was equipped with a Perkin-Elmer Φ 15-255GAR double-pass cylin-

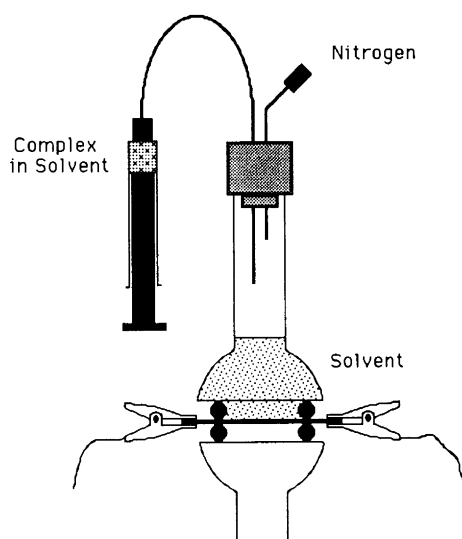


Fig. 2. Apparatus for deposition of tetra(*tert*-butoxy)zirconium from solution onto surface-activated Al.

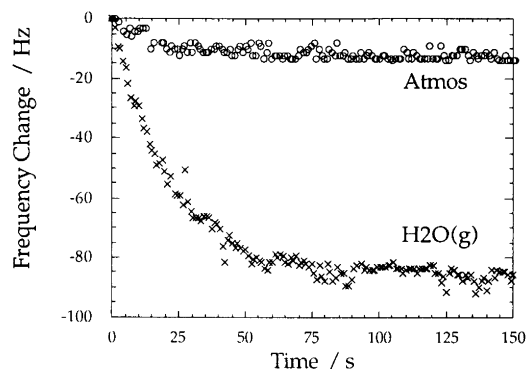


Fig. 3. QCM kinetics for vapor phase deposition of tetra(*tert*-butoxy)zirconium onto surface-activated Al.

drical mirror analyzer with an integral electron gun controlled by a Perkin-Elmer Φ 11-010 Electron Gun Control. The primary electron energy was 2 kV with an emission current of 1.2 mA. Care was taken to ensure that the sample current was constant, at 3.2 μ A, and consistent. Spectra were obtained in the first-derivative mode $[dN(E)/dE]$ with a peak-to-peak modulation of 3 eV. The signal was detected with a Princeton Applied Research model 128A lock-in amplifier at a sensitivity of 1 mV and the data were collected by laboratory computer. Spectra were measured twice at three different positions on the crystal electrode surface and individual results averaged. The crystals were bombarded with a focused 3 kV Ar^+ beam, generated using a Varian 981-2043 Ion Bombardment gun, and the elemental ratios were monitored as a function of bombardment.

Vapor phase deposition of tetra(tert-butoxy)zirconium onto surface-activated Al. Tetra(*tert*-butoxy)zirconium (ca. 500 mg) was placed in the small vial of the reactor depicted in Fig. 1. The reagent vial was immersed in an oil bath and the delivery tube wrapped with heating tape. Insulation was not necessary. The heated zone was warmed to 75–80°C under vacuum (10^{-2} Torr); the temperature was monitored via a thermocouple or

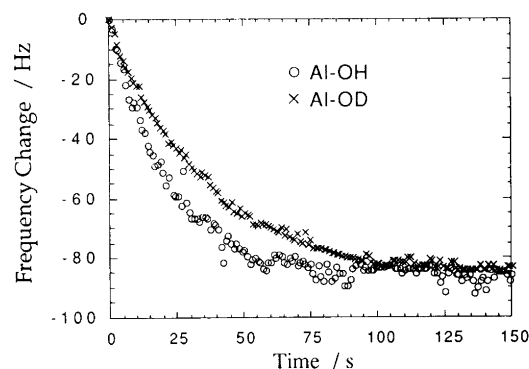


Fig. 4. QCM kinetics for isotopic study of vapor phase deposition of tetra(*tert*-butoxy)zirconium onto surface-activated Al.

Table 1. QCM-derived rate constants for R₄Zr deposition onto oxidized aluminium.

Complex R ₄ Zr	Deposition medium	Hydroxylation method ^a	Rate constant/10 ⁻³ s ⁻¹	k _H /k _D	Loading (ng/cm ²)	Concentration (nmol/cm ²) ^b
c	Pentane	Steam	4.5		4700	20
c	Gas phase	'Atmosphere' (1.4)	4.2		1300	6
c	Gas phase	Steam (1.9)	3.7	8.4	4800	21
c	Gas phase	D ₂ O steam	0.44		5000	21
d	Gas phase	Steam	41	1.6	4200	18
d	Gas phase	D ₂ O steam	26		4200	18

^a Corrected Auger ratio O:Al (for Al₂O₃, 1:5; for 'AlOOH,' 2.0); ^b for the surface ligated fragment ZrR₂; ^c R = *neo*-pentyl; ^d R = *tert*-butoxy.

thermometer. After a short time (3–5 min), the vapor of the zirconium reagent was introduced into the crystal-containing chamber while the crystal frequency was monitored (1 Hz sampling rate). The crystal chamber was continuously evacuated using only a mechanical pump during and after exposure. The crystal frequency was periodically monitored, even after exposure, to ensure that mass changes observed were due to the deposition reaction and not simply to condensed overlayer formation.

Deposition of tetra(tert-butoxy)zirconium from solution onto surface-activated Al. The crystal was clamped between two 7 mm O-ring connectors under dry, oxygen-free N₂, and 1–2 ml dry solvent were placed on the crystal. A 0.5 ml aliquot of 0.05 M Zr(OC₄H₉)₄ in the solvent was added via syringe (see Fig. 2). For depositions onto hydroxylated aluminum powder, an aliquot of a Zr(OC₄H₉)₄ solution in ether was added to the metal powder. The resulting slurry was stirred for several hours, the organic materials were distilled and the 2-methyl-2-propanol yield was measured (1.9 equivs.).

Results and discussion

As the organometallic deposition reagent became more basic (thermodynamically), or as the site for kinetic protonation of the complex changed (for example, for Zr

alkyls vs. alkoxides), or as the acidity of surface hydroxyl groups increased, essential features of proton-transfer dynamics might also change, as could surface deposition site selectivity and coverage. We now report that, in fact, some dramatic contrasts in deposition chemistry, but also some similarities, exist for reaction between (*tert*-butoxy)₄Zr vs. tetra(*neo*-pentyl)zirconium and (Al)–OH when deposition kinetics were probed by QCM. Even though (*tert*-butoxy)₄Zr is *less basic* overall (thermodynamically) than is tetra(*neo*-pentyl)zirconium (with *tert*-butoxy and *neo*-pentyl groups similar in size), the alkoxide complex reacted with (Al)–OH *more rapidly* (but with slightly lower loading) than did the alkyl one. Significantly, the kinetic isotope effect for the alkoxide was found to be small compared with that measured for the alkyl (k_H/k_D = 1.6) (Table 1).

For tetra(*neo*-pentyl)zirconium, the metal center is d⁰ and all ligands are alkyl; there are no alternative sites than the metal–carbon bond, itself, for competitive protonation by the surface hydroxyl groups. Thus k_H/k_D is large because k₋₁ > k₂. For the d⁰ alkoxide (*tert*-butoxy)₄Zr, kinetic protonation at an alkoxide oxygen 'lone' electron pair could occur (each O contains two formally 'lone pairs,' but π-donation to the metal exists⁸). We suggest that proton transfer from (Al)–O:H to RÖ(Zr) in the alkoxide is also rate determining in a process with a tightly bound four-electron, three-center transition state.

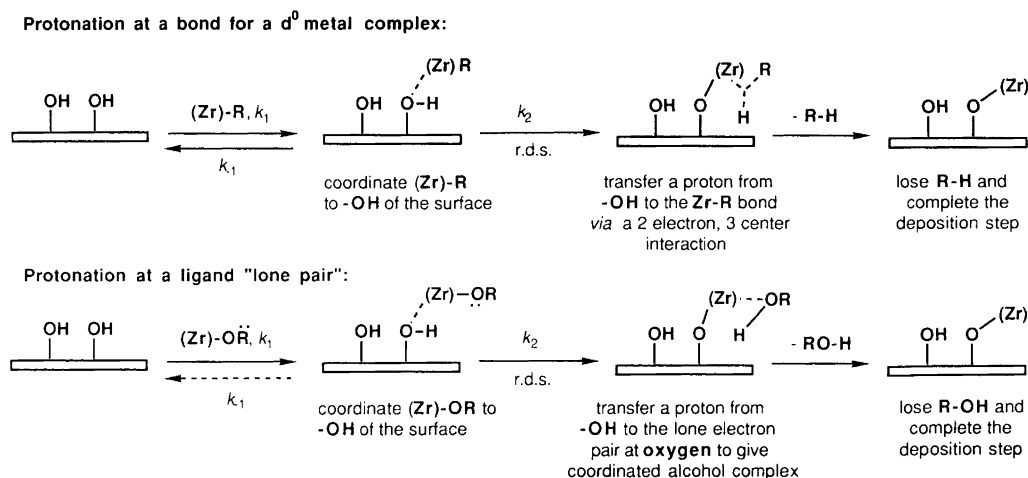


Fig. 5. Protonation at the bond or at a 'lone' electron pair of a ligand in a d⁰ complex.

(The observed kinetic isotope effect is primary and relatively small: $k_{-1} < k_2$; see Fig. 5). These results show that it is the chemical nature of the ligand lost on deprotonation, and not necessarily the basicity of that group, which has the most profound effect on the mechanistic course of that process. Furthermore, they underscore the importance of deposition kinetic studies done from the perspective of the surface to elucidate even the ostensibly simple reaction of proton transfer between a surface functional group and a 'reactive' organometallic complex.

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