# Kinetics and Mechanisms of Thermally Induced Alkane Eliminations from Silica-Supported Bis(alkyl)chromium(IV) and -vanadium(IV) Complexes

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**Abstract:** Silica-supported bis(alkyl) complexes of Cr(IV) and V(IV), $(\equiv SiO)_2M(CH_2R)_2$, undergo surprisingly clean thermal transformations to generate supported alkylidene complexes, $(\equiv SiO)_2M{=}CHR$, with concurrent liberation of $RCH_3$. The reactions are quantitative and kinetically first order, suggesting that all surface organometallic complexes possess or can access very similar coordination environments. Isotope-labeling and kinetics experiments support a mechanistic assignment of intramolecular α-H elimination. In the case of the Cr complexes, the temperature dependences of the first-order rate constants give nonlinear Eyring plots that are concave downward. A two-step mechanism of reversible (alkyl)(alkylidene)$Cr^{VI}$ hydride formation followed by reductive elimination of alkane is proposed. This mechanism is not accessible for V(IV), therefore concerted α-H elimination is considered more likely. The activation parameters for the thermolysis of $(\equiv SiO)_2V(CH_2SiMe_3)_2$, obtained from the linear Eyring plot, are $\Delta H^{\ddagger} = (11.0 \pm 1.0)$ kcal/mol and $\Delta S^{\ddagger} = (-43 \pm 3)$ cal K$^{-1}$ mol$^{-1}$. The large negative value of $\Delta S^{\ddagger}$ is suggestive of surface assistance for α-H elimination.

## Introduction

Predicting and designing the surface chemistry of complex organometallic fragments are goals with major implications for heterogeneous catalysis.[1,2] Reactivity studies on conventional solid catalysts rarely yield clear mechanistic conclusions due to the inherent heterogeneity of active sites. However, if the oxygen atoms of oxide surfaces can be considered as donor atoms of a supporting ligand[3,4] (since the bonds on covalent oxide surfaces such as that of silica are fairly localized),[5] then useful analogies may be made with molecular organometallic chemistry.[4]

Well-defined supported organometallic complexes may be obtained by reaction of molecular precursors with an oxide surface when the grafting conditions are mild and rigorously clean (dry and anaerobic).[2] Most studies of such systems focus on spectroscopic characterization of surface structures.[6,7] Quantitative equilibrium measurements,[3] or kinetic studies of catalytic reactivity,[8−10] are uncommon and usually predicated on analyses of product ratios. In this report, we present the first kinetic study of stoichiometric surface reactions in a series of supported organometallic complexes which form alkylidenes.

Alkylidene complexes of first-row transition metals are rarely stable enough to be isolated, although evidence for their participation in C−H activation[11,12] and chemical vapor deposition of metal carbide films[12] has rekindled interest in their synthesis. We[13] and several others[14−19] have suggested that such species may play a role in heterogeneous α-olefin polymerizations catalyzed by oxide-supported first-row metals, but their origin is not known. In an elegant model reaction, the photoinduced transformation of coordinated ethylene to ethylidene was recently described on a W(IV) calix[4]arene complex.[20] We recently reported the generation of stable silica-supported Cr(IV) alkylidenes by α-H elimination from bis(alkyl) complexes.[21] The kinetics of alkyl → alkylidene transformations are often difficult to monitor because one of the two forms is not stable.[12,22−25] The stabilization of both forms by im-

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mobilization and, consequently, site isolation on the silica surface has allowed us to observe this transformation directly.

## Experimental Section

Tetraalkyl (neopentyl and trimethylsilylmethyl) complexes of Cr[26,27] and V[28] were synthesized according to published procedures and purified by sublimation. $Cr(D_2CMe_3)_4$ (90% α-$D_2$, 10% α-$H_2$) was synthesized from the isotopically labeled Grignard reagent, prepared from the labeled neopentyl bromide that was obtained by a literature method.[29] HCl (Matheson, 99% anhydrous) and DCl (Cambridge Isotopes, 98% enriched) were used as received. Styrene was distilled under reduced pressure from $CaH_2$ and stored over molecular sieves.

All IR experiments were performed in sealed glass high-vacuum reactors, equipped with KCl windows for in situ infrared spectroscopy. A nonporous fumed silica (Degussa Aerosil-200, 200 $m^2/g$) was used as the oxide support in all experiments. To begin the experiment, the silica (either pressed into a self-supporting disk or pressed then ground into a finely divided powder) was partially dehydroxylated under dynamic vacuum at 200 °C. This treatment does not change the surface area of the silica, but it standardizes the number of surface hydroxyl groups at 2.6 OH/$nm^2$ or 0.86 mmol of OH/g.[30] Deuterated silica was obtained by treating this partially dehydroxylated silica with several cycles of 50 Torr of DCl(g) followed by evacuation, until the IR spectrum showed ca. 90% deuteration of surface hydroxyl groups (as judged by the decrease in intensity of the $\nu$(SiO−H) mode at 3747 $cm^{-1}$). DCl is readily contaminated with HCl by exchange on glass walls or in the presence of grease. Labeling studies were therefore performed by using deuterated glass reactors and vacuum lines and perfluorinated grease (Krytox).

The organometallic complexes were sublimed in vacuo at room temperature from a breakseal onto the silica, with the aid of a liquid $N_2$ bath. After several hours of reaction at room temperature, the unreacted material was desorbed to a liquid $N_2$ trap. Each of the grafted species described below is stable in vacuo at room temperature but is highly air-sensitive. Therefore all manipulations, including kinetic studies, were performed in situ without exposing the samples to solvents or inert gases at any time during the experiment. The experimental protocol has been described in detail previously.[13]

Gases were analyzed qualitatively and quantitatively by in situ IR, or transferred cryogenically for GC and GC/MS analyses. In experiments where they were the sole volatile product, neopentane and tetramethylsilane were quantified by integration of the intensity in the $\nu$(C−H) region of the gas-phase IR absorption spectrum. If HCl or DCl were also present, the gas phase was first condensed with liquid $N_2$ into a separate bulb containing powdered NaOH, which quantitatively removes the acid prior to analysis of the hydrocarbon. GC analyses were performed on a Hewlett-Packard 5710A gas chromatograph with a Porasil packed column and an FID detector. GC/MS analyses were performed on an HP 5890 Series II gas chromatograph with a Kratos mass selective detector using Concept 1H and a J&W DBI column (30 m long, 0.2 mm i.d, 0.33 $\mu$m film). The deuterium content of labeled neopentanes was calculated from the corrected relative intensities of the *tert*-butyl fragment peaks at *m*/*e* 57, 58, 59, 60.[12,31]

The amount of chemisorbed metal was determined by quantitative extraction at the end of each experiment. For Cr, a 100 mg sample was stirred with 10 mL of 5 M NaOH to extract the metal from the silica. One mL of 30% $H_2O_2$ was added to oxidize the metal to Cr(VI), and the yellow solution was boiled for 5 h, then diluted with water to 50 mL. Cr was analyzed as $CrO_4^{2-}$ by its absorbance at 374 nm.[32] For V, the metal was extracted in boiling 1 M $H_2SO_4$ followed by addition of 30% $H_2O_2$ and spectrophotometric detection of the vanadium(V) peroxo complex at 462 nm.[33]

Magnetic susceptibility measurements were made on ca. 70 mg samples sealed in vacuo inside quartz tubes. Data collection was performed in the temperature range 4−300 K on a Quantum Design SQUID magnetometer operating at 5 T, using a 3 cm Reciprocating Sample Option scan at 1 Hz with iterative regression, 10 cycles per measurement, and 5 measurements per average. The reference was the same quantity of unmodified silica. After subtraction of the background due to silica, nonlinear curve fits were performed with the equation $\chi_M^{corr} = C/(T + \theta)$.[34]

For kinetics studies, approximately 100 mg of compacted (pressed then reground in a mortar) silica was partially dehydroxylated at 200 °C in the bottom of an in situ IR cell. After reaction with $M(CH_2R)_4$ and evacuation of volatile products and unreacted starting material, the IR cell was aligned in the IR spectrometer, so that the beam sampled only the gas phase above the solid sample. A preheated tube furnace equipped with a thermocouple (±1 K) was placed around the bottom of the IR cell where the modified silica was located. The gas-phase IR absorbance spectrum was recorded at regular time intervals, without moving the IR cell, until the reaction was complete. The relative amount of product in the gas phase was evaluated by performing an integration of the $\nu$(CH) spectral region, 3200−2800 $cm^{-1}$, to give the values of absorbances ($A_t$) in the figures. Nonlinear least-squares fits were performed with three variable parameters ($A_0$, $A_\infty$, and $k$), in the first-order integrated rate equation $A_t = A_0 + ((A_\infty - A_0)(e^{-kt})$, using the program Kaleidagraph (Abelbeck Software). Activation parameters were derived from a straight line fit to a plot of $\ln(k/T)$ vs $T^{-1}$, and errors in the parameters were calculated according to an error propagation formula.[35]

## Results

**Characterization of Surface Organometallic Complexes.** The number of surface hydroxyl groups on a nonporous silica surface, when the latter is pretreated in vacuo at 200 °C, has been measured by various methods to be 0.86 mmol of OH/g, or 2.6 OH/nm,[2,30] of which a small fraction are inaccessible depending on the size of the probe molecule.[5] The subsequent gas−solid reactions of volatile $M(CH_2R)_4$, where M = Cr or V and R = ${}^tBu$ or $SiMe_3$, with this surface at room temperature produce solely bis(alkyl) surface complexes, eq 1.

$$\begin{array}{lll} 2{\equiv}\mathrm{SiOH} + \mathrm{M(CH_2R)_4} \rightarrow & ({\equiv}\mathrm{SiO})_2\mathrm{M(CH_2R)_2} & + 2\mathrm{RCH_3} \\ & \mathbf{1},\ \mathrm{M = Cr;\ R = {}^{\mathit{t}}Bu} & \\ & \mathbf{2},\ \mathrm{M = Cr;\ R = SiMe_3} & \\ & \mathbf{3},\ \mathrm{M = V;\ R = SiMe_3} & \end{array} \tag{1}$$

During the grafting reactions, the initially white silica acquired the color characteristic of the molecular precursor (**1** orange; **2** pink; **3** green) and, after desorption of unreacted $M(CH_2R)_4$,

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**Table 1.** Mass Balances for Bis(alkyl) Surface Organometallic Complexes Obtained by Grafting $M(CH_2R)_4$ on Silica Partially Dehydroxylated at 200 °C[a]

| M | R | wt % M on silica[b,c] | mmol M (per g silica) | M per surface hydroxyl[d] | $RCH_3$/M formed in grafting | $RCH_3$/M formed in reaction with HCl |
|---|---|---|---|---|---|---|
| Cr | $^t$Bu | 1.94 ± 0.04 (48) | 0.374 (48) | 0.43 (48) | 1.93 ± 0.02 (48) | 1.88 ± 0.02 (25) |
| Cr | $SiMe_3$ | 1.92 ± 0.04 (22) | 0.372 (22) | 0.43 (22) | 1.90 ± 0.01 (22) | 1.90 ± 0.01 (14) |
| V | $SiMe_3$ | 2.0 ± 0.1 (12) | 0.39 (12) | 0.46 (12) | 2.1 ± 0.1 (12) | 1.95 ± 0.10 (11) |

[a] Numbers in parentheses refer to the number of independent experiments used to calculate the average and the standard deviation. [b] Measured by UV−vis spectrophotometry after quantitative extraction of metal from the solid. [c] Values correspond to maximum loading of the organometallic complex on silica. At less than maximum loading, the ratio M/surface hydroxyl group is lower, but the ratios $RCH_3$/M formed in grafting and in reaction of the surface complex with HCl remain 2 in all cases. [d] Based on the hydroxyl content of silica treated at 200 °C, 0.86 mmol OH/g.[30]

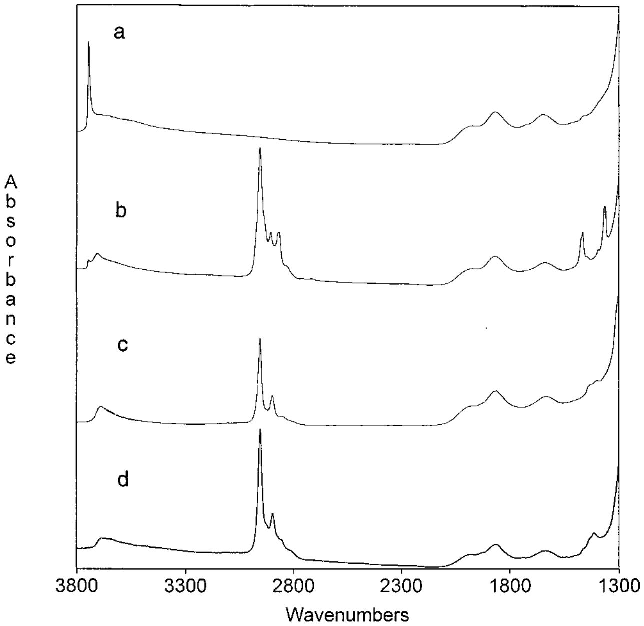

**Figure 1.** IR spectra of (a) silica pellet partially dehydroxylated at 200 °C, (b) after reaction with excess $Cr(CH_2{}^tBu)_4$, (c) after reaction with excess $Cr(CH_2SiMe_3)_4$; and (d) after reaction with excess $V(CH_2SiMe_3)_4$. Unreacted (physisorbed) metal complexes were removed by desorption to a cold trap before these spectra were recorded.

each solid contained a maximum of 2% metal by mass, Table 1. When $M(CH_2R)_4$ was present in excess, the non-hydrogen-bonded surface hydroxyl groups were >90% consumed in the reaction, as judged by in situ IR spectroscopy, Figure 1. The ratio of the number of surface hydroxyls initially present to the number of chemisorbed metal complexes is 2:1 when maximum loading is achieved, according to the stoichiometry shown in eq 1. The grafting reaction generated $RCH_3$ as the only gaseous product detectable by GC, in an amount that corresponds to twice the number of moles of chemisorbed metal (Table 1), regardless of whether maximum loading was attained or not.

The temperature-dependent magnetic susceptibilities of surface complexes **1** and **3** exhibit simple Curie behavior above 8 K. The effective magnetic moments are 2.68 and 1.57 $\mu_B$ per metal atom for **1** and **3**, respectively, consistent with their formulation as mononuclear $d^2$ and $d^1$ surface organometallic complexes.

Each of the grafted species liberated 2 equiv of $RCH_3$ per chemisorbed metal atom when exposed to a low pressure of anhydrous HCl(g) (typically 50 Torr), eq 2 and Table 1.

$$(\equiv SiO)_2M(CH_2R)_2 + 2HCl \rightarrow \text{“}(\equiv SiO)_2MCl_2\text{”} + 2RCH_3 \quad (2)$$

**Thermolysis of Supported Bis(alkyl) Complexes.** When surface complex **1** was heated, typically at 69 °C, in a vacuum for 10 h, 1 equiv of neopentane was evolved (Table 2) and was the only volatile product detected by GC. Heating for a further 10 h at this temperature failed to effect any other spectral change or further release of gas, implying that the product, **4**, is a stable surface complex, eq 3.

**Table 2.** Quantitative Analyses for *in Vacuo* Thermolysis Reactions of $(\equiv SiO)_2M(CH_2R)_2$[a]

| M | R | thermolysis temp (°C) | % loss of surface $\nu$(CH)[b] | $RCH_3$/M formed upon thermolysis[c] |
|---|---|---|---|---|
| Cr | $^t$Bu | 62−110 | 51 ± 2 (55) | 0.89 ± 0.03 (55) |
| Cr | $SiMe_3$ | 60−190 | 50 ± 3 (31) | 0.91 ± 0.04 (31) |
| V | $SiMe_3$ | 50−70 | 51 ± 2 (20) | 0.95 ± 0.10 (10) |

[a] Numbers in parentheses refer to the number of independent experiments used to calculate the average and standard deviation. [b] Based on *in situ* integration of the IR spectrum of the silica pellet in the $\nu$(CH) region, 3200−2800 $cm^{-1}$, which is proportional to the number of alkyl ligands present on the surface. [c] The liberation of 1 equiv of $RCH_3$ per grafted metal was always observed regardless of whether maximum surface coverage by the supported organometallic fragment was achieved. The average values in this column include data from experiments with metal loadings ranging from 10−100% of the maximum value shown in Table 1.

$$\underset{\mathbf{1}}{(\equiv SiO)_2Cr(CH_2{}^tBu)_2} \xrightarrow{69\ °C} \underset{\mathbf{4}}{(\equiv SiO)_2Cr(C_5H_{10})} + CMe_4 \quad (3)$$

Concurrently with the evolution of neopentane, the intensity of IR bands on the silica pellet in the $\nu$(CH) stretching region decreased by (51 ± 2)%, Table 2. The magnetic moment of **4** is 2.77 $\mu_B$/Cr, Figure 2a, consistent with retention of mononuclear $d^2$ Cr(IV) sites during the transformation **1** → **4**. Thus, the oxidation state of Cr does not change during the reaction, nor do the grafted metal complexes aggregate upon heating.

Treatment of **4** with 50 Torr of HCl(g) liberated (0.9 ± 0.1) equiv of $CMe_4$ as the only gaseous product. Reaction of **4** with DCl(g) formed predominantly (71%) $C(CH_3)_3(CD_2H)$. (The rest is neopentane-$d_1$ and -$d_0$, presumably due to isotopic dilution of DCl during its transfer.) On the basis of these results and reactivity tests, we previously suggested that **4** is a chemisorbed mononuclear Cr(IV) neopentylidene complex, $(\equiv SiO)_2Cr{=}CH{-}{}^tBu$.[21]

*In vacuo* thermolysis of **2**, typically at 150 °C, produced 1 equiv of $SiMe_4$ as the only gaseous product, Table 2, and a new surface complex **5** with (50 ± 3)% of the $\nu$(CH) intensity on the silica remaining, eq 4.

$$\underset{\mathbf{2}}{(\equiv SiO)_2Cr(CH_2SiMe_3)_2} \xrightarrow{150\ °C} \underset{\mathbf{5}}{(\equiv SiO)_2CrC_4SiH_{10}} + SiMe_4 \quad (4)$$

Finally, when **3** was heated at 58 °C in vacuo, 1 equiv of $SiMe_4$ was liberated quantitatively, Table 2, while the intensity of the $\nu$(CH) region in the IR spectrum of the solid decreased by

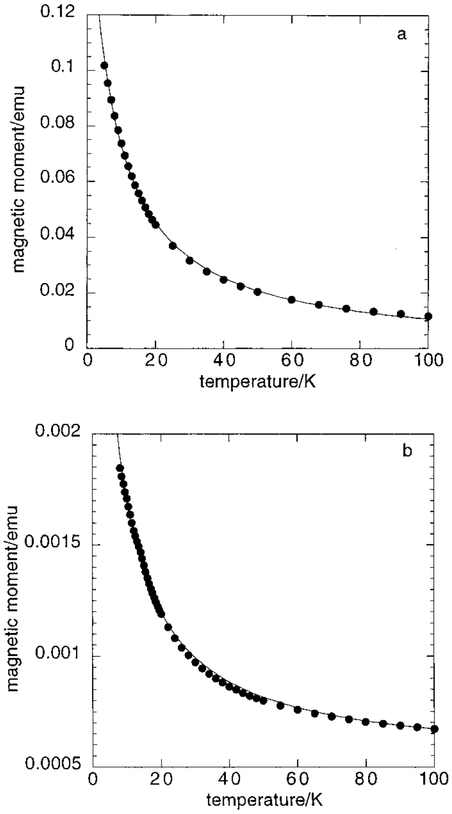

**Figure 2.** Temperature-dependent magnetic susceptibility of (a) $(\equiv SiO)_2Cr{=}CH^tBu$ (**4**) and (b) $(\equiv SiO)_2V{=}CHSiMe_3$ (**6**). The solid lines are curve fits to the Curie−Weiss law.

(51 ± 2)%, eq 5.

$$\underset{\mathbf{3}}{(\equiv SiO)_2V(CH_2SiMe_3)_2} \xrightarrow{58\ °C} \underset{\mathbf{6}}{(\equiv SiO)_2VC_4SiH_{10}} + SiMe_4 \quad (5)$$

The product **6** has a magnetic moment of 1.63 $\mu_B$/V, Figure 2b, consistent with its formulation as a mononuclear $d^1$ V(IV) surface complex, as shown in eq 5.

**Deuterium-Labeling Experiments.** When the silica hydroxyl groups were labeled with deuterium (ca. 90% $\equiv$Si*OD*, estimated by IR) prior to reaction with $M(CH_2R)_4$, the hydrocarbon released during grafting contained a single deuterium atom, $RCH_2D$, in each case ((80 ± 2)% $C(CH_3)_3(CH_2D)$ for **1**, (83 ± 2)% $Si(CH_3)_3(CH_2D)$ for **2**; 82% $Si(CH_3)_3(CH_2D)$ for **3**).[36] When **1**−**3** were grafted onto deuterated silica and then thermolyzed at the temperatures shown in eqs 3−5, the $EMe_4$ (E = C, Si) liberated was 100% undeuterated in each case.

The reaction of $Cr(CD_2(C(CH_3)_3)_4$ (90% α-$D_2$) with 85% deuterated silica-200 generated 2 equiv of $CMe_4$, which was 79% $C(CH_3)_3(CD_3)$, eq 6.

$$2{\equiv}SiOD + Cr(CD_2C(CH_3)_3)_4 \rightarrow \underset{\mathbf{1}\text{-}\alpha D_4}{(\equiv SiO)_2Cr(CD_2C(CH_3)_3)_2} + 2C(CH_3)_3(CD_3) \quad (6)$$

The infrared spectrum of **1**-α$D_4$ contains two low-intensity peaks at 2163 and 2103 cm$^{-1}$, assigned to $\nu_{as}(CD_2)$ and $\nu_s(CD_2)$, respectively. Upon thermolysis, both peaks decreased in intensity until they disappeared into the baseline noise, while $CMe_4$ was produced, which was (71 ± 1)% $C(CH_3)_3(CD_3)$, consistent with α-D abstraction,[37] eq 7.

$$\underset{\mathbf{1}\text{-}\alpha D_4}{(\equiv SiO)_2Cr(CD_2C(CH_3)_3)_2} \xrightarrow{69\ °C} \underset{\mathbf{4}\text{-}\alpha D}{(\equiv SiO)_2Cr{=}CDC(CH_3)_3} + C(CH_3)_3(CD_3) \quad (7)$$

Finally, reaction of **4**-αD with either HCl or DCl caused the evolution of 0.9 ± 0.1 equiv of $CMe_4$. In the case of reaction with HCl, the product was 73% $C(CH_3)_3(CH_2D)$ (the rest being unlabeled neopentane), whereas with DCl the product was (78 ± 2)% (average of four independent experiments) of the isotopomer $C(CH_3)_3(CD_3)$ (expected yield 81%, the rest being neopentane containing less deuterium), eq 8.

$$\underset{\mathbf{4}\text{-}\alpha D}{(\equiv SiO)_2Cr{=}CDC(CH_3)_3} + HCl/DCl \rightarrow \text{“}(\equiv SiO)_2CrCl_2\text{”} + C(CH_3)_3(CH_2D)/C(CH_3)_3(CD_3) \quad (8)$$

Although similar labeling studies were not feasible for **2** and **3** (due to the unavailability of the selectively labeled $Me_3SiCD_2$ ligand), their behavior is so similar to that of **1** in all other respects (vide infra) that we propose analogous alkylidene formulations for **5** and **6**.

**Kinetic Studies.** The kinetics of each of the thermolysis reactions in eqs 3−5 were investigated. A sample of **1** was heated in vacuo at 69 °C in an in situ IR cell, and the spectrum of the gas phase above the sample was recorded periodically. By integration of the $\nu$(CH) region of the gas-phase IR spectrum (i.e., the product $CMe_4$), we were able to monitor the progress of the surface reaction, since neopentane is not adsorbed on the silica surface. The result is shown in Figure 3a. A single exponential (first-order) curve fit yielded $k(69\ °C) = 0.0046 \pm 0.0002$ min$^{-1}$. A second experiment with a independently prepared sample of **1** gave $k(69\ °C) = 0.0046 \pm 0.004$ min$^{-1}$. The data are displayed as a semilog plot in Figure 3b, showing its linearity over four half-lives.

The rate constant for thermolysis of $(\equiv SiO)_2Cr(CD_2C(CH_3)_3)_2$, **1**-α$D_4$, was obtained in a similar fashion. Thermolysis of **1**-α$D_4$ is first order but significantly slower than thermolysis of **1**, Figure 3, consistent with a substantial primary kinetic isotope effect. The rate constant at 69 °C is 0.00165 ± 0.0004 min$^{-1}$ (average of two independent experiments), giving $k_H/k_D$ = 2.8 *at 69* °C.

Kinetics experiments with **1** were performed at various temperatures between 62 and 110 °C, Figure 4. At each temperature, 1 equiv of $CMe_4$ was the exclusive gaseous product of thermolysis. Each kinetic curve was fitted with a single-exponential function; the rate constants are given in Table 3. The Eyring plot in Figure 5a was constructed with these results; it is not linear. In light of this behavior, the primary kinetic isotope effect was redetermined at a higher temperature. Thermolysis of **1**-αD at 110 °C gave 1 equiv of $CMe_4$ as 70% $C(CH_3)_3(CD_3)$ with $k = 0.0096 \pm 0.0001$ min$^{-1}$, yielding $k_H/k_D = 1.2$ at 110 °C. Reaction of **4**-αD formed at 110 °C with HCl(g) liberated 73% $C(CH_3)_3(CH_2D)$, as before.

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[36] The remaining $CMe_4$ or $SiMe_4$ was unlabeled, presumably due to the presence of a small amount of protonic impurity. When the silica was only 63% deuterated, we obtained 56% neopentane-$d_1$ and 44% unlabeled neopentane upon grafting of **1**. We previously erroneously reported that the incorporation of deuterium into the neopentane liberated by grafting $Cr(CH_2{}^tBu)_4$ onto silica was not quantitative.[13]

[37] The other neopentane isotopomers present contained less that three deuteriums. The expected yield of neopentane-$d_3$ is 81%, based on the preference for C−H vs C−D cleavage in incompletely (90%) α-deuterated **1**. The slightly lower yield than expected may be attributed to a small amount of $\gamma$-H elimination that becomes competitive[12] with slow $C_\alpha$−D cleavage in the labeled surface complex.

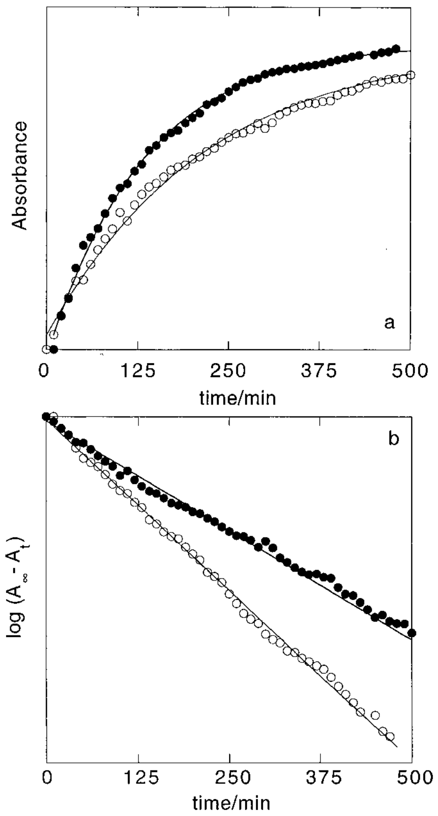

**Figure 3.** Time-resolved evolution of $CMe_4$ from $(\equiv SiO)_2Cr(CH_2{}^tBu)_2$ (filled circles) and $(\equiv SiO)_2Cr(CD_2{}^tBu)_2$ (open circles) at 69 °C: (a) absorbance of in situ gas-phase IR spectra, as a function of time; (b) semilog plots of data from (a). The solid lines are (a) nonlinear and (b) linear fits to the first-order integrated kinetic rate equation.

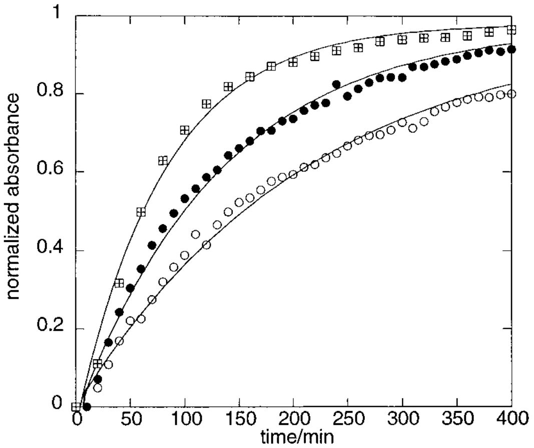

**Figure 4.** Time-resolved evolution of $CMe_4$ from $(\equiv SiO)_2Cr(CH_2{}^tBu)_2$ at 69 (open circles), 75 (filled circles), and 110 °C (squares). Absorbances have been normalized to show all data on the same scale. Solid curves are three-parameter single-exponential fits to the first-order integrated kinetic rate equation.

**Table 3.** First-Order Rate Constants for Loss of $RCH_3$ from $(\equiv SiO)_2M(CH_2R)_2$

| surface complex | temp/°C | $k$/min$^{-1}$ [a] |
|---|---|---|
| $(\equiv SiO)_2Cr(CH_2{}^tBu)_2$ | 62 | $0.0023 \pm 0.0004$ |
| | 69 | $0.0046 \pm 0.0002$ |
| | 69 | $0.0046 \pm 0.0004$ |
| | 71 | $0.0054 \pm 0.0003$ |
| | 75 | $0.0073 \pm 0.0002$ |
| | 82 | $0.0083 \pm 0.0002$ |
| | 90 | $0.0099 \pm 0.0002$ |
| | 110 | $0.0123 \pm 0.0040$ |
| $(\equiv SiO)_2Cr(CD_2C(CH_3)_3)_2$ | 69 | $0.0015 \pm 0.0004$ |
| | 69 | $0.0018 \pm 0.0004$ |
| | 110 | $0.0096 \pm 0.0001$ |
| $(\equiv SiO)_2Cr(CH_2SiMe_3)_2$ | 60 | 0.0011[b] |
| | 100 | $0.0073 \pm 0.0002$ |
| | 130 | $0.015 \pm 0.002$ |
| | 150 | $0.020 \pm 0.001$ |
| | 190 | $0.029 \pm 0.003$ |
| $(\equiv SiO)_2V(CH_2SiMe_3)_2$ | 50 | $0.0038 \pm 0.0003$ |
| | 58 | $0.0062 \pm 0.0002$ |
| | 58 | $0.0057 \pm 0.0002$ |
| | 58 | $0.0060 \pm 0.0002$ |
| | 70 | $0.0112 \pm 0.0006$ |

[a] Errors are from nonlinear least-squares fit to the single-exponential rate law, using data from at least four half-lives. [b] Estimated from the first two half-lives.

The evolution of $SiMe_4$ from **2** and **3** was monitored in the same way as for **1** and was, in both cases, first order. The kinetics of thermolysis of **2** were also studied at several different temperatures, from 60 to 190 °C. The rate constants, Table 3, were used to construct a Eyring plot, which is also nonlinear, Figure 5b. A similar variable-temperature study (50−70 °C) of the thermolysis of **3** led to the rate constants in Table 3 and the linear Eyring plot in Figure 5c, yielding $\Delta H^\ddagger = 11.0 \pm 1.0$ kcal/mol and $\Delta S^\ddagger = -43 \pm 3$ cal $K^{-1}$ mol$^{-1}$. Although the temperature range is unfortunately small, kinetics experiments with **3** at higher temperatures were not feasible, because **6** is not stable above 70 °C and undergoes further loss of hydrocarbons from the surface.

**Reaction of Supported Alkylidenes with Styrene.** **1**−**3** do not react with styrene at room temperature. However, when **1**−**3** were exposed to excess styrene vapor at their typical thermolysis temperatures, or when **4**−**6** were exposed to excess styrene at room temperature, neohexene (from **1**/**4**) or trimethylvinylsilane (from **2**/**5** and **3**/**6**) was formed. The initial reaction is formulated as a metathetical exchange, eq 9.

$$(\equiv SiO)_2M{=}C(H)EMe_3 + PhCH{=}CH_2 \rightarrow (\equiv SiO)_2M{=}C(H)Ph + CH_2{=}C(H)EMe_3 \quad (9)$$

M is Cr, V; E is C, Si

However, the surface benzylidenes were not isolated. They react further with styrene to produce polystyrene.

## Discussion

Various crystal faces of quartz, $\beta$-cristobalite, and $\beta$-tridymite have been suggested as models for the silica surface.[38−41] Partial dehydroxylation leads to rows of isolated hydroxyl groups on some crystal faces, and pairs of hydroxyl groups (geminal and/or vicinal) on others. The surface of amorphous silica has been described as a heterogeneous assortment of small crystalline domains, representing these different crystal faces.[42] Nevertheless, it has often been assumed that hydroxyl groups are randomly distributed on the silica surface,[43] so that their reaction with an organometallic complex $MR_4$ may occur with a variety

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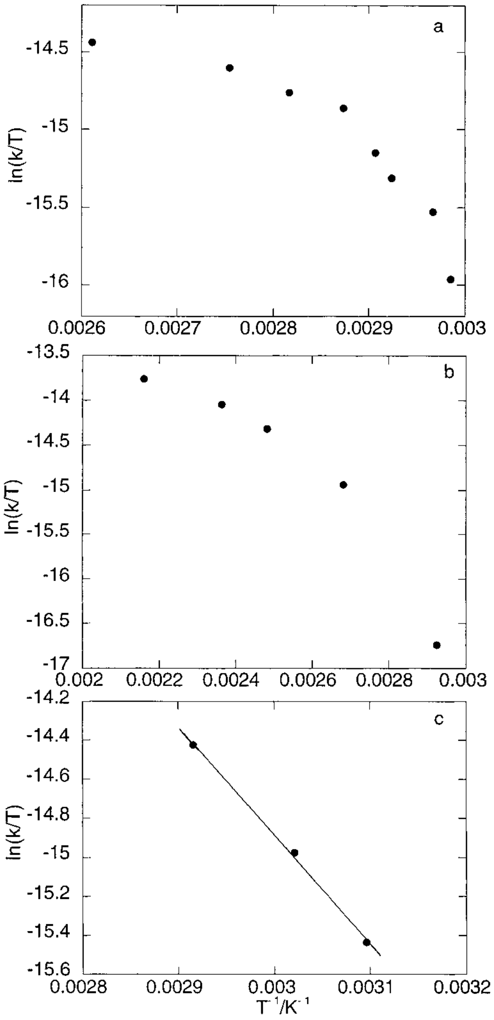

**Figure 5.** Eyring plots of the temperature dependence of rate constants for the thermolyses of $(\equiv SiO)_2M(CH_2R)_2$: (a) **1**; (b) **2**; and (c) **3**. Data are given in Table 3.

of reaction stoichiometries, eq 10, where $1 \leq n \leq 3$.

$$n\equiv SiOH + MR_4 \rightarrow (\equiv SiO)_nMR_{4-n} + (4-n)\ RH \quad (10)$$

Some authors report that, if the silica is partially dehydroxylated above 450 °C, the surface hydroxyls are essentially all isolated, and consequently a 1:1 reaction takes place. For example, grafting of $MR_4$ to give $(\equiv SiO)MR_3$ has been reported for M = Ti,[44] Zr,[45] Hf,[46] and Cr.[13] On silica-200, an *average* grafting stoichiometry of $n = 2$, giving $(\equiv SiO)_2MR_2$, has been reported for M = Zr[47,48] and Cr.[13] However, it has also been suggested that the Group IV surface complexes are mixtures of mono-, bis-, and tris(alkyl)metal fragments.[44,49]

In the present study, we confirm that the average value of $n$ is indeed 2 for the reactions of homoleptic metal tetraalkyls with an amorphous silica surface partially dehydroxylated at 200 °C. In addition, the kinetic behavior of each surface organometallic fragment during thermolysis implies that *all* the surface structures are bis(alkyl), since they undergo elimination of alkane quantitatively and with a single first-order rate constant. Rates of reactions on surfaces are extremely sensitive to small changes in bonding of surface species,[50] therefore the reproducible single exponential behavior of these thermolysis reactions is not consistent with the presence of widely different coordination environments at the surface metal atoms. We propose that the formulation of the surface complexes **1**−**3** given in eq 1 is exact, i.e., $n = 2$ at the microscopic as well as the macroscopic level. Indeed, the coordination geometry of the surface complexes, which is determined by the separation between each member of a pair of reacting surface hydroxyls, must be very similar in all cases.

There are several possible ways that such uniformity in local surface environments might arise. First, we may consider that the surface hydroxyl groups on partially dehydroxylated amorphous silica are not randomly distributed, but that they occur in well-ordered pairs. Such an ordering was proposed for silicas treated below 450 °C; above this temperature the pair structure was thought to be lost.[48] IR spectroscopy[51] and NMR techniques[52] have long been applied to the problem of characterization of surface hydroxyls on a variety of silicas. The proportion of geminal pairs is constant[53] or even increases[54,55] with the dehydroxylation temperature, according to $^{29}Si$ NMR studies. However, vicinal and isolated hydroxyls are indistinguishable by solid-state NMR, and all three kinds of non-hydrogen-bonded hydroxyls are indistinguishable by vibrational spectroscopy (geminal and vicinal pairs are not capable of internal hydrogen bonding).[56,57] The IR spectrum of silica-200, Figure 1, shows two kinds of surface hydroxyls, a sharp peak at 3747 $cm^{-1}$ corresponding to isolated/vicinal/geminal hydroxyls, and a broad band to lower wavenumbers corresponding to hydrogen-bonded hydroxyls.[58] We believe that it is unlikely that unmodified amorphous silicas possess the unique kind of paired hydroxyl surface structure that would be required to produce the uniform surface organometallic complexes shown in eq 1.

A second possible way to attain uniformity in surface structure is by reorganization of the surface during or after grafting.[59] This could be achieved either by migration of surface hydroxyl groups or migration of singly bound surface organometallic fragments $\equiv SiOMR_3$. We previously showed that a 200 $m^2$/g silica surface is fully covered by tris(neopentyl)chromium(IV) fragments when the metal content reaches ca. 0.37 mmol of Cr/g.[13] On silica-200, this loading is achieved when slightly less than half of the surface hydroxyls have been consumed. Since full surface coverage leaves little room for mobility of surface organometallic fragments, we believe that it is more likely that unreacted surface hydroxyl groups migrate until they reach the optimal position for reaction with an already-grafted tris(alkyl)metal fragment. This mechanism is depicted in Scheme 1, where the most stable surface environment is suggested to

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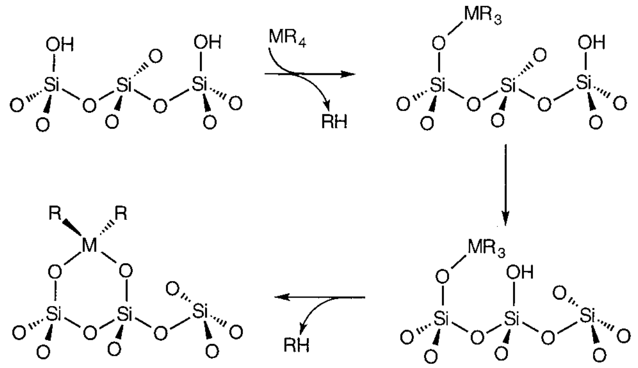
**Scheme 1**



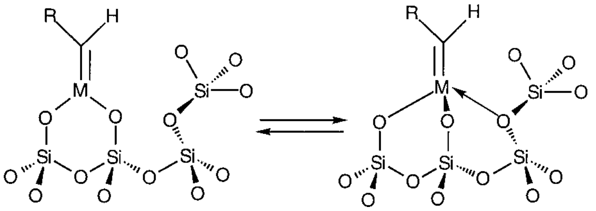
occur when the metal occupies a position in a six-membered siloxane ring. A third possibility, which may operate in addition to the mechanism shown in Scheme 1, is that grafting occurs on a variety of hydroxyl pairs, but that the surface is flexible enough to allow the resulting surface organometallic complexes to achieve the optimum transition state geometry for α-H elimination via molecular vibration.

Substitution of alkyl ligands on organometallic complexes by siloxo "ligands" derived from the silica surface tends to enhance their thermal stability. For example, (≡SiO)(≡SiOH)-Rh($\eta^3$-allyl)$_2$[60] and (≡SiO)Ni($\eta^3$-allyl)[61] are more stable than Rh($\eta^3$-allyl)$_3$ and Ni($\eta^3$-allyl)$_2$ with respect to reduction to metallic forms. Also, (≡SiO)ZrR$_3$[62] and (≡SiO)CrR$_3$[13] are thermally more robust than either $ZrR_4$ or $CrR_4$. This phenomenon can be ascribed to increased metal−ligand bond strengths due to the inductive effect of the electron-withdrawing silica "ligand". Similar effects have been remarked in mixed alkyl/halide complexes: for example, $CrRCl_2$ is thermally more stable than $CrR_3$.[63] Therefore the facility with which silica-supported bis(alkyl)metal fragments undergo thermolysis was surprising considering that tris(alkyl)chromium(IV) fragments on silica do not show this reactivity.[13] It appears that the second substitution by a siloxo "ligand" on an organometallic fragment does not enhance the stabilizing effect of the first substitution.[64]

Deuterium-labeling experiments with (≡SiO)$_2$Cr(CH$_2{}^t$Bu)$_2$ and (≡SiO)$_2$Cr(CD$_2{}^t$Bu)$_2$ confirm that the thermolytic transformation is an α-H elimination to give a supported alkylidene complex, (≡SiO)$_2$Cr═C(H/D)$^t$Bu, **4**. In addition, the metathetical reaction of styrene, eq 9, with **4**−**6** is characteristic of alkylidene complexes. Several mechanisms are possible for the formation of metal alkylidenes: intramolecular α-H abstraction by the metal or by an adjacent neopentyl ligand, intermolecular α-H abstraction, or M−C bond homolysis followed by H abstraction by the neopentyl radical.[23] Thermolyses of **1**−**3** are first order, ruling out intermolecular reactions; as well, the magnetic moments of the products **4** and **6** support mononuclear formulations for the alkylidenes, therefore the mobility of surface organometallic complexes required for intermolecular reactions is unlikely. $CrR_xCl_{3-x}$, where R is a tertiary alkyl, readily decompose by metal−carbon bond homolysis,[63] whereas Cr complexes with primary alkyl ligands generally do not.[65] The absence of radical coupling products and the sizable primary kinetic isotope effect both support a mechanistic assignment of intramolecular α-H elimination.[66]

The magnitude of the kinetic isotope effect for thermolysis of **1** at 69 °C, $k_H/k_D = 2.8$, is similar in magnitude to those reported for other α-H eliminations. Kinetic isotope effects of about 3 were reported for α-H elimination from $TaR_5$ (R = Me, CH$_2$Ph, CH$_2{}^t$Bu),[23,31] in reactions later confirmed to be intramolecular and first order.[22,24] However, at 110 °C the kinetic isotope effect for reaction 3 is severely attenuated, $k_H/k_D = 1.2$. The slope of the Eyring plot gradually decreases as the temperature increases, implying that $\Delta H^\ddagger$ is not constant. However, the reaction remains kinetically first order, producing only neopentane, whose isotopomer distribution (predominantly $(CH_3)_3CCD_3$ from **1**-α$D_4$) suggests that the overall mechanism has not changed. These observations are consistent with a mechanism consisting of two consecutive reactions, where the apparent activation enthalpy contains contributions from both steps.[67] Each step is intramolecular but must have a different kinetic isotope effect. A mechanism that is consistent with all these observations and available to Cr(IV) is reversible intramolecular α-H elimination to form a (neopentyl)(neopentylidene)-Cr$^{VI}$ hydride, followed by reductive elimination of neopentane, Scheme 2. We associate formation of the hydride complex with the higher kinetic isotope effect and a moderate activation barrier. Reductive elimination of alkane is associated with the lower kinetic isotope effect and a lower activation barrier. Kinetic isotope effects for reductive eliminations of alkane may be small or even inverse.[68]

Finally, α-H elimination is probably surface assisted, via coordination of an additional surface oxygen "ligand". Base-assisted alkane elimination has precedent in the formation of a benzylidene complex from [Cp*Nb(NR)(CH$_2$Ph)$_2$(PMe$_3$)].[69] The alkylidenes **4**−**6** may maintain a pseudo-tetrahedral coordination environment by increasing the number of interactions with surface siloxane oxygens, eq 11. This additional coordination is probably reversible, so that an incoming olefin could readily displace the siloxane oxygen. The ability of the silica surface to stabilize coordinatively unsaturated species and then regenerate them to permit substrate binding has already been proposed.[70]



(11)

The Eyring plot for thermolysis of **2** is also concave downward, as for **1**, and is suggestive of a similar mechanism. In contrast, the Eyring plot for thermolysis of **3** appears to be linear (albeit over a smaller temperature range). The two-step

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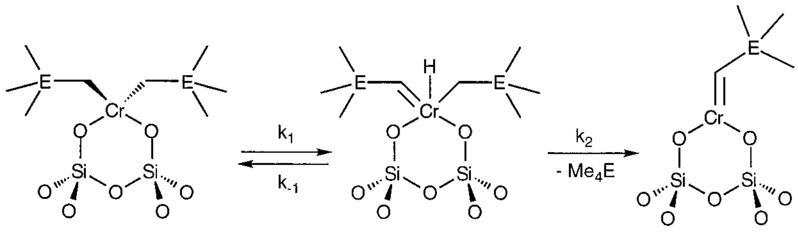
**Scheme 2**



metal hydride pathway (Scheme 2) is not accessible to V(IV) without an energetically prohibitive charge separation.[31] The modest value of $\Delta H^{\ddagger}$, 11.0 ± 1.0 kcal/mol, is in the range of other reported values for concerted α-H elimination,[12,22,71] while the large negative $\Delta S^{\ddagger}$, $-43 \pm 3$ cal $K^{-1}$ $mol^{-1}$, is consistent with surface assistance in the rate-determining step.[69]

The α-H elimination reaction in $d^2$ bis(alkyl)metal complexes is generally favorable when the metal is known to form stable $d^0$ alkylidene complexes.[72] One example of a stable Cr(VI) neopentylidene has now been reported.[11] The driving force for alkylidene formation from bis(alkyl)metal complexes has been described as both enthalphic as well as entropic,[73] where the enthalpic term contains contributions from both steric and electronic effects. Coordination to two electron-withdrawing silica siloxo "ligands" increases the electrophilicity of the metal, favoring the alkylidene over the bis(alkyl) form.[71] At the same time, the second siloxo "ligand" forces the metal closer to the silica surface compared with the monosubstituted analogue $(\equiv SiO)MR_3$. The latter is free to adopt a larger Si−O−M angle to relieve steric strain. The consequent increased crowding at the metal center in $(\equiv SiO)_2MR_2$ may cause the $M-C_\alpha-C_\beta$ angle to increase, enhancing the rate of α-H elimination. Greater thermal stability of **2** compared to **1** is consistent with lower steric crowding in **2** due to the larger size of Si, which causes the methyl groups to be further from the metal. This effect has previously been noted for $Ta(CH_2EMe_3)_5$ (E is C or Si).[22] However, **3** is much less stable than **2** despite the larger size of V(IV) compared to Cr(IV).[74] It is likely that electronic effects also contribute to the stability trends, since metal−carbon bonds tend to be stronger in trimethylsilylmethyl complexes compared to their neopentyl analogues.[75,76]

Finally, the ability of the alkylidene surface complexes **4**−**6** to undergo metathesis with styrene and catalyze its polymerization suggests that these single-site catalysts may perform using the Green-Rooney alkylidene mechanism.[77] A similar mechanism was proposed for supported Cr alkylidenes which polymerize ethylene,[21] and has been demonstrated a Ta(V) neopentylidene hydride ethylene polymerization catalyst.[72] The reversible transformation of a metal alkylidene complex to a metallacycle, as required for metathesis and/or polymerization, was reported to be enthalphically nearly neutral.[73]

## Conclusion

Kinetic studies, isotope labeling experiments, and mass balances demonstrate that silica-supported bis(alkyl)metal complexes are transformed to alkylidenes by thermal α-H elimination in reactions which resemble homogeneous phase chemistry. This unexpected result suggests that, although the unmodified silica surface is amorphous, the surface organometallic complexes are uniform. In this context, the objective of preparing well-defined active sites for catalysis seems plausible. The surface alkylidene complexes undergo metathesis and catalyze styrene polymerization. The details of the polymerization mechanism by silica-supported alkylidenes are currently under investigation.

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