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# Reaction between Tetraneopentylzirconium and 2,6-Di-*tert*-butyl-4-methylphenol. A "Homogeneous Analog" of a Metal Complex–Surface Proton Transfer Reaction

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*Summary: The reaction between tetraneopentylzirconium ($[Bu^tCH_2]_4Zr$; neo$_4$Zr) and 2,6-di-tert-butyl-4-methylphenol (BHT-OH) was studied by NMR and proceeds to give BHT-O-Zr(neo)$_3$ plus neopentane. Second order rate constants were measured for reactions using BHT-OH and BHT-OD, and it was found that $k_H/k_D$ = 4.1 (±0.54), interpreted in terms of reversible coordination of BHT-OH to the Zr followed by rate determining proton transfer.*

We recently noted that protolytic deposition of tetraneopentylzirconium ($[Bu^tCH_2]_4Zr$; neo$_4$Zr) onto an hydroxylated Al surface showed a large kinetic isotope effect, $k_H/k_D = 8.5$, and we interpreted this in terms of reversible coordination between the organometallic and a surface OH group followed by rate determining proton transfer (Scheme I).[1] In order to ascertain if this profile were unique to the complex–surface reaction, we examined the protolytic reaction, in solution, between neo$_4$Zr and 2,6-di-*tert*-butyl-4-methylphenol (BHT-OH) which gives BHT-O-Zr(neo)$_3$. In this way, we could examine the effect of switching from an inorganic, hydrophilic, heterogeneous system to an organic, homogeneous, hydrophobic one.

## Experimental Section

**Preparation of 2,6-Di-*tert*-butyl-4-methylphenol-OD.** A solution of 22 g (10 mmol) of BHT-OH (Aldrich) dissolved in 8 mL of dry benzene was placed in a 50-mL Schlenk flask fitted with a magnetic stirring bar under inert atmosphere and was cooled to 0 °C. To this solution was slowly added 10 mL of 1.6 M *n*-butyllithium solution in hexanes (Aldrich). After the addition of *ca.* 2 mL, the solution became cloudy and white BHT-OLi began to precipitate. The resulting slurry was allowed to warm to room temperature, was stirred for 30 min, and then was cooled again to 0 °C. To the slurry was added 0.75 mL of $D_2O$ (CIL, 99.9 atom % D) in three portions. After warming to room temperature, the mixture remained cloudy, so an additional 0.75 mL of $D_2O$ was added, portionwise, whereupon the organic phase cleared. The product was evaporated to dryness under gentle heating (40 °C). The white solid which remained was extracted with 3 × 10 mL of dry toluene and filtered over Celite, and the solvent was removed from the filtrate to leave 20.4 g of BHT-OD (92%). IR: $\nu_{OD}$ 2675 cm$^{-1}$; $\delta_{COD}$ 952 cm$^{-1}$. NMR ($C_6D_6$): $\delta$ 7.03 (s, 2), 4.77 (s, trace), 2.24 (s, 3), 1.37 (s, 18).

**Reaction of BHT-OH with Tetraneopentylzirconium in Benzene.** In the drybox, a measured amount of neo$_4$Zr was dissolved in about 0.4 mL of dry benzene-$d_6$ (CIL, 99.9 atom % D) in a 5-mm NMR tube. The tube was capped with a rubber septum, and the septum was wired in place. Also in the drybox, a measured, equivalent amount of BHT-OH was dissolved in an aliquot of dry benzene in another NMR tube, which was similarly sealed. The NMR spectrum (270 MHz) of each sample was taken separately. The BHT-OH solution was then taken up in a valved, gastight syringe and injected into the tube containing the Zr complex solution. The tube was vigorously shaken for about 5 s and then placed into the spectrometer. Locking the frequency and shimming the magnetic field was performed automatically and generally required about 2 min. Each spectrum recorded was the result of coadding 16 transients which required nearly 1 min to acquire. Spectra were automatically taken 1 min apart for the first 10 min, 10 min apart for the next 1 h, and at hourly intervals thereafter as required. Spectra were not transformed into the frequency domain until all measurements were completed. The product, neo$_3$Zr-O-BHT, was isolated from a pentane solution by solvent evaporation as a thermally labile colorless oil. $^1$H NMR ($C_6D_6$): $\delta$ 7.09 (2), 2.20 (3), 1.56 (6), 1.52 (18), 1.17 (27). $^{13}$C NMR ($C_6D_6$): $\delta$ 160.3, 137.8, 129.3, 126.1, 100.1, 36.3, 34.8, 31.9, 31.0, 21.4. Anal. Calcd for $C_{30}H_{56}ZrO$: C, 68.77; H, 10.77. Found: C, 68.97; H, 10.02.

**Determination of Second Order Rate Constants.** BHT-OH or BHT-OD was treated with neo$_4$Zr; reactant concentrations were systematically varied (see Table I) to determine the appropriate rate law: $-d[\text{BHT-OH}]/dt = k_{obs}[\text{BHT-OH}] \times [\text{neo}_4\text{Zr}]$. Standard analysis gave second-order rate constants for each run.

Table I

| experiment | $[Zr]_0$ (M) | $[\text{BHT-OH}]_0$ (M) | $[Zr]_0[\text{BHT-OH}]_0$ | $t_{1/2}$ (min) |
|---|---|---|---|---|
| BHT-OH | 0.193 | 0.162 | 0.031 | 8 |
| BHT-OH | 0.092 | 0.112 | 0.010 | 16 |
| BHT-OH | 0.224 | 0.110 | 0.025 | 11 |
| BHT-OD | 0.131 | 0.263 | 0.039 | 21 |
| BHT-OD | 0.141 | 0.127 | 0.027 | 34 |
| BHT-OD | 0.221 | 0.099 | 0.031 | 28 |

## Results and Discussion

BHT-OH was chosen as a reagent to compare with hydroxylated Al surfaces for several reasons. First, it is a relatively moderate Brønsted acid (p$K_a$ = 11.2), as is alumina (p$K_a$ *ca.* 9.2[2]). Second, protolytic reaction between BHT-OH and neo$_4$Zr could proceed sequentially, with a significantly lower rate constant for each additional protonolysis, because both BHT-OH and neopentyl are bulky.[3] This would enable us to probe only a single protonolysis, uncomplicated by any subsequent substitutions. Third, in contrast to the hydroxylated (hydrophilic) Al surface, the ortho *tert*-butyl groups create a sterically crowded, hydrophobic environment about the reactive OH in any putative intermediate association complex (A) and in the reaction products.

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[1] Miller, J. B.; Schwartz, J. *Inorg. Chem.* **1990**, *29*, 4579.

[2] Robinson, McD.; Pask, J. A.; Fuerstenau, D. W. *J. Am. Ceram. Soc.* **1964**, *47*, 516.

[3] This is similar to substitution reactions noted for tri-*tert*-butylmethanol (tritox). See: Lubben, T. V.; Wolczanski, P. T.; Van Duyne, G. D. *Organometallics* **1984**, *3*, 977.

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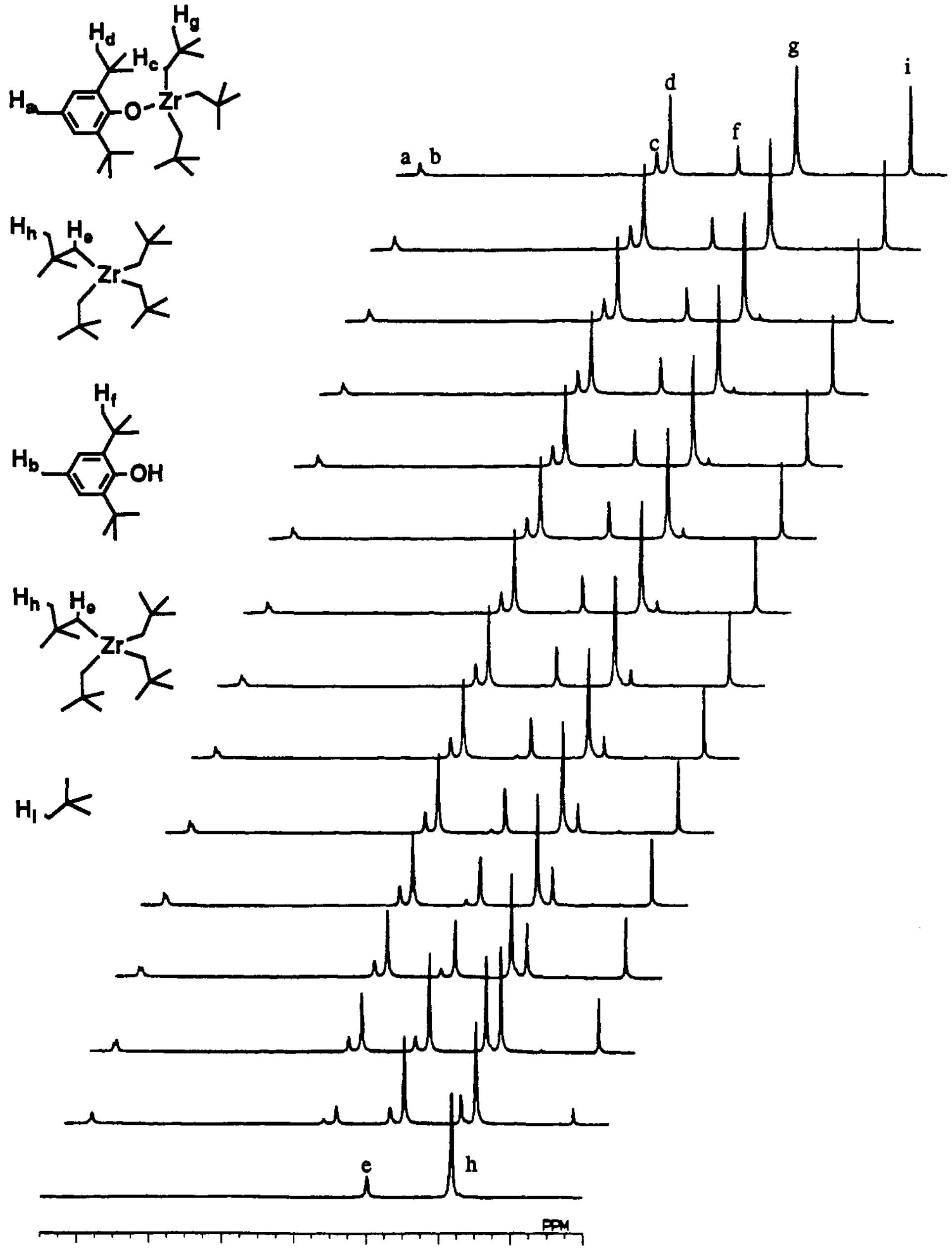
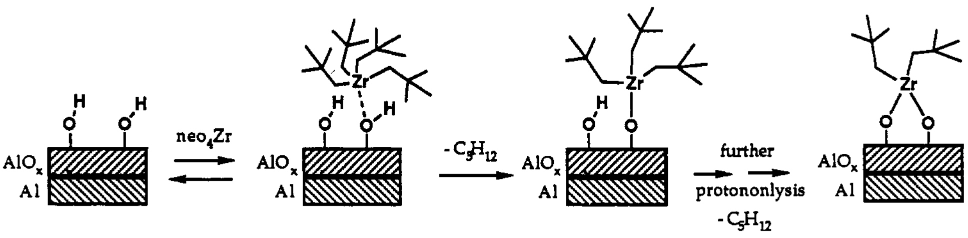


**Figure 1.** Aliphatic region of the NMR spectrum shown at various times during the course of reaction between BHT-OH and neo$_4$Zr.

**Scheme I. Reaction between Tetraneopentylzirconium and a Hydroxylated Aluminum Surface**



The $^{13}$C NMR spectrum of neo$_4$Zr has been the subject of some discussion: It has been claimed[4] that all of the carbons cannot be observed. However, we note the expected three carbon resonances (in CD$_2$Cl$_2$) for which assignments were easily made on the basis of a $^1$H–$^{13}$C coupled spectrum. A noteworthy feature is that the methylene carbon is further downfield ($\delta$ 102; $^1J_{CH}$ = 104.9 Hz) than might be anticipated, *prime facie*, on the basis of the chemical shift of the methylene protons ($\delta$ 1.45); prediction of $^{13}$C chemical shifts is not always straightforward,[5] particularly for carbon attached to transition metals.[6]

Reactions between BHT-OH and neo$_4$Zr (at 27 °C) were monitored in C$_6$D$_6$ by $^1$H and $^{13}$C NMR. Assignments

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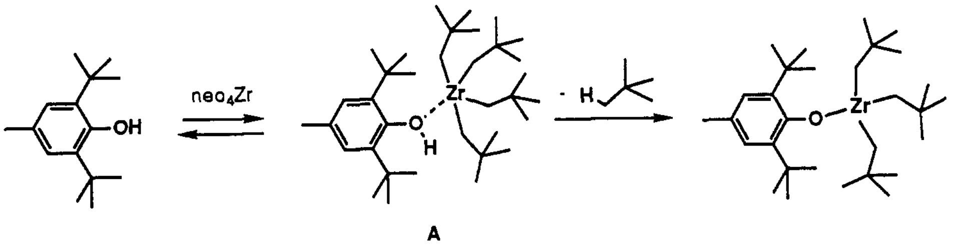
(4) Quignard, F.; Lecuyer, C.; Bougault, C.; Lefebvre, F.; Choplin, A.; Olivier, D.; Basset, J.-M. *Inorg. Chem.* **1992**, *31*, 928.

**Scheme II. Reaction of BHT-OH with Tetraneopentylzirconium**



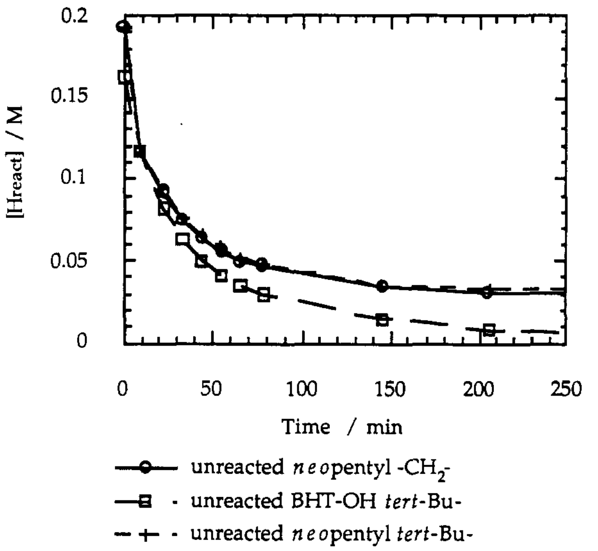


**Figure 2.** Normalized reactant $^1$H NMR intensities plotted *vs* time.

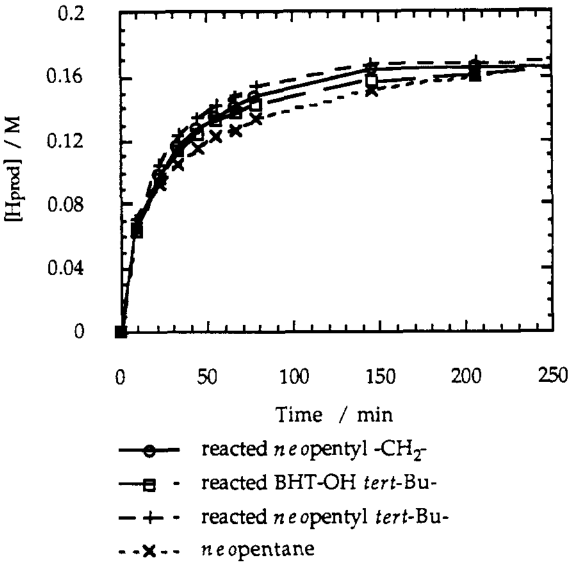


**Figure 3.** Normalized product $^1$H NMR intensities plotted *vs* time.

were made on the basis of analysis of spectra for reaction products and by comparison with starting materials.[7] A stacked plot of the aliphatic region of the NMR spectrum taken at various times during the course of reaction is shown in Figure 1, and peak intensity changes (normalized to the appropriate number of protons) for the reaction in Scheme II are shown in Figures 2 and 3. To elucidate mechanistic details, rates for reaction of neo$_4$Zr with BHT-OH and BHT-OD were compared, and second order rate constants were determined: $k_H = 0.54\ (+0.05, -0.16)\ mol^{-1}\ s^{-1}$; $k_D = 0.13\ (+0.04, -0.03)\ mol^{-1}\ s^{-1}$; $k_H/k_D = 4.1\ (\pm 0.54)$.

## Conclusions

The large kinetic isotope effect observed in the reaction of BHT-OH with neo$_4$Zr indicates that proton transfer must be the rate-limiting step, as was found for the complex–surface reaction; if coordination of BHT-OH to the metal center were rate-limiting, then only a small, secondary isotope effect would exist. Although the acidities of the types of proton donor are similar for the heterogeneous and homogeneous cases studied, most of the other aspects of interaction between the metal complex and the Brønsted acid are quite different. It appears, then, that the course of protonolysis may be largely determined by the nature of the proton acceptor, which, for neo$_4$Zr, is a kinetically unfavorable Zr–C $\sigma$-bonding orbital.

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**Supplementary Material Available:** Five NMR spectra and four figures concerning reaction rate calculations (9 pages). Ordering information is given on any current masthead page.

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(5) Mason, J. *J. Chem. Soc. A* **1971**, 1038.

(6) A systematic framework for predicting $^{13}$C chemical shifts for carbons attached to transition metals has not yet been developed. A discussion of shifts found in $\pi$-bonded systems may be found in: Evans, J.; Norton, J. R. *Inorg. Chem.* **1974**, *13*, 3042. For a similar discussion of $^{13}$C shifts of transition-metal carbonyls, see: Buchner, W.; Schenk, W. A. *J. Magn. Reson.* **1982**, *48*, 148.

(7) It is interesting to note that, on forming BHT-O-Zr(neo)$_3$, the phenolic carbon has shifted significantly downfield, while the methylene carbons attached to Zr have shifted upfield. Perhaps electron density is transferred from the oxygen, *via* the zirconium, to the methylene carbons, through $\pi$-type donation to the metal by oxygen, as has been observed crystallographically for several zirconium alkoxide complexes.[8,9]

(8) Clarke, J. F.; Drew, M. G. B. *Acta Crystallogr.* **1974**, *B30*, 2267.

(9) Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1989**, *28*, 1769.