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19. In a uniform composition mantle, in the absence of melting we can write,

$$\delta T \approx \frac{(\delta V_s/V_s)}{(\partial \ln V_s/\partial \ln T)_p}$$

where T is temperature and V_s is the seismic shear velocity. Ignoring anelastic contributions to the velocity, which are probably small for cold anomalies in the upper mantle,

$$\delta T \approx \frac{-(\partial \ln \rho/\partial \ln V_s)_p}{\alpha}(\delta V_s/V_s)$$

where ρ is density and α is the coefficient of thermal expansion. Choosing reasonable upper mantle values for α and $(\partial \ln \rho/\partial \ln V_s)_p$, $\delta T \approx -1.0 \times 10^4\, dV_s/V_s$, which for a 2% velocity anomaly corresponds to 200 degrees.

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19 July 2000; accepted 11 October 2000

Direct Condensation of Carboxylic Acids with Alcohols Catalyzed by Hafnium(IV) Salts

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In order to promote atom efficiency in synthesis and to avoid the generation of environmental waste, the use of stoichiometric amounts of condensing reagents or excess substrates should be avoided. In esterification, excesses of either carboxylic acids or alcohols are normally needed. We show that the direct condensation of equimolar amounts of carboxylic acids and alcohols can be achieved with the use of hafnium(IV) salts, such as commercially available hafnium(IV) chloride and hafnium(IV) *tert*-butoxide. The present method can be applied to direct polyesterification and may be suitable for large-scale operations.

The replacement of current chemical processing with more environmentally benign alternatives is an increasingly attractive subject (*1*). Esterification is one of the most fundamental and important reactions in organic synthesis [(*2*), and references cited therein]. Although several methods have been explored and developed [(*2*), and references cited therein], the use of large amounts of condensing reagents and activators should be avoided in order to promote green chemistry and atom efficiency. The direct condensation of carboxylic acids with alcohols using small amounts of catalysts is the most ideal method, but in most cases, large excess amounts of either carboxylic acids or alcohols are used in this condensation to give esters in high yield (*3–18*). We describe highly efficient and direct ester condensation with equimolar amounts of carboxylic acids and alcohols catalyzed by hafnium(IV) chloride and alkoxides (*19–21*).

We first investigated the catalytic activities of various metal salts [10 mole percent (mol%)], which promote the model reaction of 4-phenylbutyric acid (1 equivalent) with benzyl alcohol (1 equivalent) in toluene at reflux with removal of water (calcium hydride in a Soxhlet thimble) for 1.5 hours (condition A in Table 1). Both $HfCl_4$ and $ZrCl_4$ (*15, 16*) were highly effective catalysts for the present reaction. Hafnium(IV) *tert*-butoxide was also effective, whereas $Zr(OEt)_4$ was inert. Although Ti(IV) (*10, 11*) and Sn(IV) (*12–14*) salts are well known to be good esterification catalysts, their catalytic activities were lower than those of Hf(IV) and Zr(IV) salts. Various other metal salts and organometallics such as $3,4,5\text{-}F_3C_6H_2B(OH)_2$ (*22, 23*), BCl_3 (*6, 7*), $AlCl_3$ (*8*), $SiCl_4$ (*9*), $ScCl_3$, $Sc(OTf)_3$ (Tf, OSO_2CF_3) (*24–26*), $FeCl_3$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $GaCl_3$, $GeCl_4$, $SbCl_5$, $LaCl_3$, and $PbCl_2$ were either less active or inert.

Next, to identify esterification catalysts with a high turnover frequency, we reexamined several metal salts, which were suggested by the above screening, for the same reaction as above, but under different conditions [reflux for 12 hours in the presence of 1 mol% of catalysts (condition B in Table 1)]. As expected, $HfCl_4$ and $Hf(Ot\text{-}Bu)_4$ gave the corresponding esters quantitatively, but Zr(IV) and Sn(IV) gave the corresponding esters in low yield. Interestingly, Ti(IV) gave better results than other metal halides and metal alkoxides except Hf(IV). Thus, Hf(IV) was shown to be the most effective metal catalyst for direct esterification.

The commercially available $HfCl_4{\cdot}(THF)_2$ (THF, tetrahydrofuran) is hydrolytically more stable than $HfCl_4$ and is lower in price than the corresponding alkoxides. To optimize the reaction conditions regarding the removal of water and solvents for the esterification of phenylbutyric acid with cyclohexanol in the presence of 0.2 mol% of $HfCl_4{\cdot}(THF)_2$, we evaluated, using ^1H nuclear magnetic resonance (NMR) analysis, the percentage of cyclohexanol condensed with 4-phenylbutyric acid over time (Fig. 1). We found that heating the reaction mixture in toluene under azeotropic reflux conditions to remove water through a Soxhlet thimble with 4 Å molecular sieves gave the best result. However, heating the reaction mixture without solvents at the same temperature as above was less effective, and the reaction rate was reduced after ~2 hours had passed. A similar tendency was observed in control experiments in the absence of any catalysts. These experimental results indicate that not only catalytic activity but also the efficiency of water removal are very important for the present esterification system.

To explore the generality and scope of the above Hf(IV)-catalyzed esterification, we examined the reaction with various structurally diverse carboxylic acids and alcohols. (Table 2). Less than 0.2 mol% of $HfCl_4{\cdot}(THF)_2$ was

Table 1. Direct esterification of 4-phenylbutyric acid and benzyl alcohol for different conditions. The esterification of 4-phenylbutyric acid (1 mmol) and benzyl alcohol (1 mmol) in toluene (5 ml) was carried out in a flask fitted with a pressure-equalized addition funnel (containing a cotton plug and ~1 g of calcium hydride and acting as a Soxhlet extractor) surmounted by a reflux condenser under argon. *i*-Pr, isopropyl. For condition A, the reaction mixture was heated under reflux conditions in the presence of 10 mol% of catalyst for 1.5 hours. For condition B, the reaction mixture was heated under reflux conditions in the presence of 1 mol% of catalyst for 12 hours.

Catalyst	Yield (%)	
	A	B
$SnCl_4$	34	48
$TiCl_4$	28	73
$Ti(Oi\text{-}Pr)_4$	34	82
$ZrCl_4$	77	–
$ZrCl_4{\cdot}(THF)_2$	84	38
$Zr(OEt)_4$	0	–
$HfCl_4$	83	–
$HfCl_4{\cdot}(THF)_2$	82	>99
$Hf(Ot\text{-}Bu)_4$	82	>99
HfO_2	<5	–

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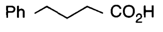
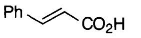
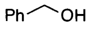
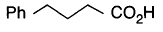
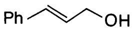
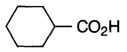
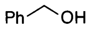
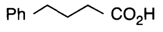
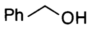
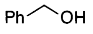
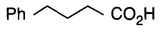
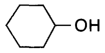
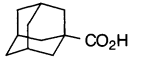
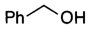
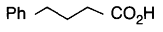
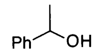
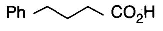
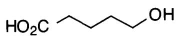
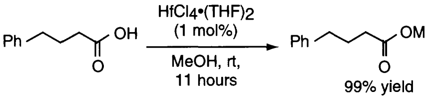
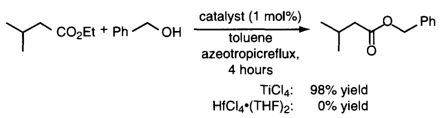
Table 2. Direct esterification of carboxylic acids with alcohols catalyzed by $HfCl_4{\cdot}(THF)_2$. Unless otherwise noted, the esterification of carboxylic acid (10 mmol) with alcohol (10 mmol) in toluene (2 ml) was carried out in a flask fitted with a pressure-equalized addition funnel [containing a cotton plug and ~1.5 g of 4 Å molecular sieves (pellets) and acting as a Soxhlet extractor] surmounted by a reflux condenser under argon. Additional entries are available at *Science* Online as supplementary material (*30*).

RCO_2H	ROH	$HfCl_4{\cdot}(THF)_2$ (mol%)	Time (hours)	Yield (%)	RCO_2H	ROH	$HfCl_4{\cdot}(THF)_2$ (mol%)	Time (hours)	Yield (%)
	$Ph-\!\equiv\!-CH_2OH$	0.2	6	97			0.2	10	92
		0.2	24	92			0.2	7	96
		0.1	18	>99*	$PhCO_2H$		0.2	15	92
		0.2	5	94†			0.2	10	92
		0.2	13	>99	$PhCO_2H$	$3{,}5\text{-}Me_2C_6H_3OH$	1.0	24	95§
	PhOH	0.2	36	91‡			0.2	10	96‖

*Toluene (5 ml) was used. †For the uncatalyzed reaction, yield was 36%. ‡*o*-Xylene (2 ml) was used. §1.3.5-Mesitylene (2 ml) was used. ‖Yield of lactones is indicated.



Reaction 1



Reaction 2

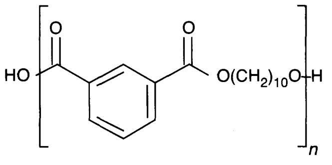
suitable for condensing various carboxylic acids with not only primary alcohols but also with sterically hindered secondary alcohols. However, esterification with tertiary alcohols did not proceed. Although aromatic substrates such as benzoic acid and phenol were less reactive than aliphatic substrates, their reactions proceeded very well by increasing the amount of $HfCl_4{\cdot}(THF)_2$ to 1 mol%.

Furthermore, $HfCl_4{\cdot}(THF)_2$ was highly effective for the esterification of carboxylic acids with volatile alcohols such as methanol (MeOH) (reaction 1). The reaction proceeded in alcohols at room temperature (rt; reaction 1) without removal of water.

Titanium(IV) salts are known to be good catalysts for the transesterification of esters with alcohols (*27*). Surprisingly, $HfCl_4$ did not catalyze the transesterification at all (reaction 2). The catalysis for esterification is essentially different between Hf(IV) and Ti(IV). These experimental results can be understood by assuming that the active intermediates that are generated in esterification are Hf(IV) carboxylate and Ti(IV) alkoxide, respectively. However, their roles are still not clear.

To demonstrate the effectiveness of Hf(IV) salts as esterification catalysts, we synthesized polyesters by polycondensing ω-hydroxycarboxylic acids or equimolar amounts of aliphatic dicarboxylic acids and

Table 3. Direct polyesterification catalyzed by $HfCl_4{\cdot}(THF)_2$. Unless otherwise noted, the polyesterification was carried out in the presence of 0.2 mol% of $HfCl_4{\cdot}(THF)_2$ for 1 day. See (*19*) for procedure. Two linear TSK-gel-GMH_{XL} gel permeation chromatography (GPC) columns (Tosoh, Japan) were used to determine the number-averaged molecular weight M_n and the weight-averaged molecular weight M_w. The polymers were run at 0.2 weight % in THF at 40°C with a polystyrene standard. The average polymerization degrees (DP) and M_n values in brackets were determined by ^1H NMR.

Polyester	Isolated yield (%)	DP	$M_n \times 10^4$	$M_w \times 10^4$
$HO[CO(CH_2)_9O]_nH$	95	>200	1.82 [>3.40]	3.40
$HO[CO(CH_2)_{11}O]_nH$	97 (88)*	>200 (45)	2.77 [>3.96] – [(0.89)]	7.24 –
$HO[CO(CH_2)_2CO_2(CH_2)_6O]_nH$	98	>200	2.24 [>4.00]	3.87
$HO[CO(CH_2)_7CO_2(CH_2)_{10}O]_nH$	97	>200	2.69 [>6.52]	5.83
	96†	>200	1.34‡ [>6.09]	6.51‡

*Data in parentheses are for the uncatalyzed thermal polyesterification. †The reaction was carried out in the presence of 1 mol% of $HfCl_4{\cdot}(THF)_2$ for 4 days. ‡GPC (the polymer was run at 0.3 weight % in THF at 23°C).

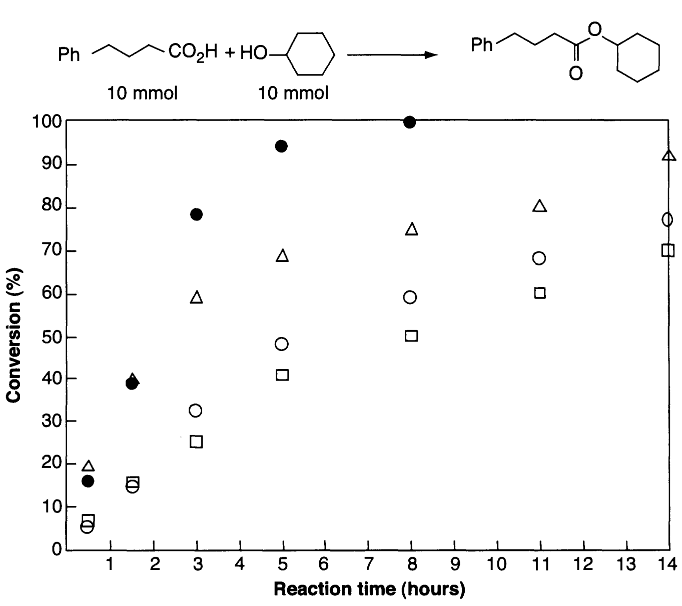


Fig. 1. Conversion versus time at 120°C. Ph, phenyl. Solid circles represent 0.2 mol% of $HfCl_4{\cdot}(THF)_2$ and reflux with 2 ml of toluene-d_8; triangles represent 0.2 mol% of $HfCl_4{\cdot}(THF)_2$ with no solvent; open circles represent no catalyst and reflux with 2 ml of toluene-d_8; and squares represent no catalyst and no solvent.

aliphatic diols in the presence of 0.2 mol% of $\mathrm{HfCl_4{\cdot}(THF)_2}$ in *o*-xylene with the removal of water for 1 day (*28, 29*). In most cases, polycondensation proceeded quantitatively (Table 3). Although no polycondensation of aromatic dicarboxylic acids and aromatic diols occurred because of the insolubility of aromatic carboxylic acids for *o*-xylene and less nucleophilicity of aromatic diols, the polycondensation to semiaromatic polyesters successfully proceeded.

In direct esterification, the catalytic use of inorganic salts is quite practical because of its simplicity and applicability to large-scale operations. Hafnium(IV) salts, which are hydrolytically more stable than Ti(IV) salts, are extremely active catalysts for direct esterification and polycondensation to polyesters. This catalytic system should be useful as an environmentally and industrially ideal condensation in the near future.

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29. The typical procedure of polycondensation is as follows. A flame-dried, 5-ml, single-necked, round-bottomed flask that is equipped with a Teflon-coated magnetic stirring bar and a 5-ml pressure-equalized addition funnel [containing a cotton plug and 4 Å molecular sieves (~1.5 g)] surmounted by a reflux condenser was charged with α,ω-hydroxycarboxylic acid (10 mmol) or α,ω-dicarboxylic acid (10.0 mmol) and α,ω-diol (10.0 mmol) as substrates and $\mathrm{HfCl_4(THF)_2}$ (0.200 mmol) as a catalyst in *o*-xylene (2 ml). The mixture was brought to reflux with the removal of water. After 1 day, the resulting mixture was cooled to ambient temperature, dissolved with chloroform, and precipitated with acetone or methanol to furnish pure polyester as a white solid in quantitative yield.
30. Web table 1, a more extensive version of Table 2, is available at www.sciencemag.org/feature/data/1054771.shl.

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Solar Wind Record on the Moon: Deciphering Presolar from Planetary Nitrogen

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Ion microprobe analyses show that solar wind nitrogen associated with solar wind hydrogen implanted in the first tens of nanometers of lunar regolith grains is depleted in ^{15}N by at least 24% relative to terrestrial atmosphere, whereas a nonsolar component associated with deuterium-rich hydrogen, detected in silicon-bearing coatings at the surface of some ilmenite grains, is enriched in ^{15}N. Systematic enrichment of ^{15}N in terrestrial planets and bulk meteorites relative to the protosolar gas cannot be explained by isotopic fractionation in nebular or planetary environments but requires the contribution of ^{15}N-rich compounds to the total nitrogen in planetary materials. Most of these compounds are possibly of an interstellar origin and never equilibrated with the ^{15}N-depleted protosolar nebula.

Solar system objects such as terrestrial planets, meteorites, and interplanetary dust particles (IDPs) exhibit up to a factor of 3 variation in their $^{15}\mathrm{N}/^{14}\mathrm{N}$ ratios [see, e.g. (*1–7*)]. These variations may reflect the heterogeneous distribution of isotopically distinct N components in the protosolar nebula. However the N isotopic composition of the sun, a potential reference for the nebular composition, is still unknown. The lunar regolith, irradiated by the solar wind (SW) and solar energetic particles (SEPs), contains information on the elemental and isotopic abundances of volatile elements in the SW and the sun.

Rare gas studies (*8–11*) have shown that the lunar regolith records the history of SW irradiation of the moon. In the case of N, however, the SW component has not been identified because of several contrasting interpretations of the 30% variability in the N isotopic composition found in lunar regoliths. One interpretation attributes the variation to secular variation of the isotopic composition of the SW (*8–10*). Lunar samples that are considered to have been irradiated >1 billion years ago (Ga) tend to be depleted in ^{15}N relative to samples that were exposed more recently. Alternatively, the variation could be due to a mixture in different proportions of solar and nonsolar N sources, such as meteorites, comets, or the fractionated terrestrial atmosphere (*12–14*). This interpretation is supported by 3- to 10-fold excesses of N relative to the SW heavy rare gases in lunar regolith samples.

Because SW-derived isotopes are implanted at shallow depths, characteristic of SW ion energies (*15*), knowledge of the distribution of N isotopes in the surface layers of lunar regolith grains should explain the nature of surface-correlated N components. We used further improvements of the shallow-depth profiling technique, developed for the extraction of SW Li from bulk lunar regolith samples (*16*), to characterize with a depth resolution of 10 nm the isotopic composition of N sitting in individual lunar grains (*17*). Relatively large mineral grains, 500- to 1000-μm-sized ilmenite, pyroxene, or olivine, from two Apollo 17 samples (79035 and 71501) have been analyzed. The 79035 breccia is thought to have been irradiated by the SW at 1 to 2 Ga, whereas the 71501 soil is thought to have been irradiated at 100 million years ago (Ma) (*11*). Previous analyses by conventional methods have shown that the

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