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The influence of β-diketones on the induction times for hydrolysis of zirconium(IV) alkoxides

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The influence of low ligand/Zr mole ratios ($\rho = 0$–0.1) of acetylacetone on the hydrolysis of $Zr(OPr^n)_4$ has been examined by investigating its effect on the induction time (t_i) before precipitation commences in the system. A remarkable feature of the data is the large increase in the induction time (reduction in hydrolysis/condensation rate) caused by addition of acetylacetone. This occurs even though only a maximum of one in eighty Zr–OR bonds have reacted with ligand and are no longer available for hydrolysis or further condensation. The effects on t_i of five other β-diketones having varying steric properties (trifluoroacetylacetone, hexafluoroacetylacetone, benzoylacetone, dibenzoylmethane and dipivaloylmethane) are compared with that of acetylacetone, under similar concentration conditions, with $\rho = 0.1$. Each shows a greater effect than acetylacetone, the largest change being caused by dibenzoylmethane which, under the conditions used, increases the induction time by a factor of 26 relative to acetylacetone. A mechanism rationalising the origin of the effect is discussed.

Introduction

Chelating agents, such as β-diketones (*e.g.* acetylacetone, acacH),† have been widely used in sol–gel processing to modify the reactivity of metal alkoxides,[1] and hence, control the processing[2–4] and properties of the final particles or gels.[5,6] A typical nucleophilic reaction between β-diketones and alkoxides such as $Zr(OR)_4$ results in the transfer of an acidic proton from the β-diketone to an alkoxy ligand, yielding the corresponding alcohol and a modified alkoxide precursor:

$$Zr(OR)_4 + x(acacH) \rightleftharpoons Zr(OR)_{4-x}(acac)_x + xROH$$

Depending on the nature of R, $M(OR)_4$ molecules may be associated by alkoxy-group bridging and, hence, their acetylacetone complexes are also likely to be associated.[7] Both monomeric and associated $Ti(OR)_{4-x}(acac)_x$ complexes have been identified, depending on the nature of R,[8] while dimeric structures have been established for the compounds $Sn_2(OPr^i)_6(acac)_2$[9] and $Ce_2(OPr^i)_4(acac)_4$.[10] Sanchez and coworkers[11] used spectroscopic techniques to identify the species formed when acetylacetone reacts with $Ce(OPr^i)_4$ and have shown in an extensive study of the hydrolysis of the acac-modified alkoxide that the ratio $\rho = [acac]/[Ce]$ determines whether the hydrolysate appears as particles, a sol or turbid gel, a clear gel or as the soluble molecular cluster $[Ce_6(\mu\text{-}O)_4(\mu\text{-}OH)_4(acac)_{12}]$,[10] because of the varying quantities of $[Ce_2(OPr^i)_8 \cdot 2HOPr^i]$, $[Ce_2(OPr^i)_7(acac)(HOPr^i)]$, $[Ce_2(OPr^i)_6(acac)_2]$ and $[Ce_2(OPr^i)_4(acac)_4]$ formed as the proportion of ligand increases.

In the case of $Zr(OR)_4$, if a β-diketone is added such that $\rho < 1$, the system will contain unreacted $[Zr(OR)_4]$ and predominantly the complex $[Zr(OR)_3(ligand)]$ (both of which may be associated) in proportion to ρ. The subsequent hydrolysis of such compounds with excess water will produce hydroxo entities, which may be formally represented as $[Zr(OR)_{4-x}(OH)_x]$ and $[Zr(OR)_{3-y}(OH)_y(ligand)]$. Although individual alkoxy groups have been shown to react with water very rapidly, hydrolysis is an equilibrium reaction and complete removal of alkoxide groups is not readily accomplished in the absence of an acidic catalyst.[12] The β-diketonate ligand in such compounds is also very resistant to hydrolysis,[13] even in the presence of a large excess of water. Indeed, the complexes $[Zr_4(\mu\text{-}O)(OPr^n)_{10}(acac)_4]$[14] and $[Ti_{18}(\mu\text{-}O)_{16}(OBu^n)_{26}(acac)_2]$[15] have been characterised as products in the partial hydrolysis of Zr and Ti alkoxide–acetylacetone complexes.

The generally accepted view of particle growth beyond the initial rapid formation of low molecular weight, hydrolysed oligomers is that further association of oligomers initially occurs by hydrogen bonding. Subsequent formation of –O–Zr–O–Zr– bridges within these larger oligomers (which may be termed 'proto-particles') occurs by slow oxolation:

$$Zr\text{–}OH + HO\text{–}Zr \rightarrow Zr\text{–}O\text{–}Zr + H_2O$$

and alkoxolation:

$$Zr\text{–}OR + HO\text{–}Zr \rightarrow Zr\text{–}O\text{–}Zr + HOR$$

reactions, which stabilise the growing particle.[16–19] Molecular units bearing coordinated ligands will also participate in such processes, with associated incorporation of the ligand into growing particles, in an amount proportional to the initial value of ρ. Those Zr-atoms bearing coordinated ligand molecules will possess fewer sites at which association and/or oxolation can occur and, thus, their presence will cause a decrease in the rate of oligomer growth, by reducing the probability of bond-forming collisions occurring.

There have been several studies describing the rate of hydrolysis of Zr alkoxides,[20,21] but only one previous report on the effect of added acetylacetone.[2] That study established that the rate of particle growth up to gelation decreased with increasing concentration of both added ligand and Zr, at the high ratio $\rho = [acacH]/[Zr] = 0.5$. This high value of ρ would have resulted in a large proportion of the $Zr(OPr^n)_4$ being

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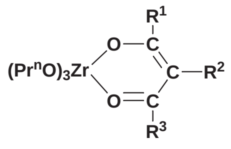
†The commonly used names, corresponding IUPAC nomenclature and ligand anion abbreviations used for the β-diketones are: acetylacetone (2,4-pentanedione)—acac; 1,1,1-trifluoroacetylacetone (1,1,1-trifluoro-2,4-pentanedione)—tfac; 1,1,1-5,5,5-hexafluoroacetylacetone (1,1,1-5,5,5-hexafluoro-2,4-pentanedione)—hfac; benzoylacetone (1-phenyl-1,3-butanedione)—bzac; dibenzoylmethane (1,4-diphenyl-1,3-propanedione)—dbzm; dipivaloylmethane (2,2-6,6-tetramethyl-3,5-heptanedione)—dpvm. The free ligands are abbreviated by the addition of H, *e.g.*, acetylacetone = acacH.



	R^1	R^2	R^3
acacH	CH_3	H	CH_3
tfacH	CF_3	H	CH_3
hfacH	CF_3	H	CF_3
bzacH	C_6H_5	H	CH_3
dbzmH	C_6H_5	H	C_6H_5
dpvm	$C(CH_3)_3$	H	$C(CH_3)_3$

Fig. 1 β-Diketone structure and substituents.

coordinated by acetylacetone. The effect of the acacH/Zr molar ratio on the formation of zirconia particles during acid-catalysed hydrolysis of $Zr(OPr^i)_4$ in ethanol solution, in the presence of added ligand, has been examined by Rinn and Schmidt.[22] They found that the size of the monodispersed particles increased with increasing acetylacetone concentration, with substantial amounts of the ligand present ($\rho=$ [acacH]/[Zr]$=0.3$–0.6 and [Zr]$=1.0$). There have been no investigations into the effect of small quantities of acacH ($\rho<0.1$) on the hydrolytic behaviour of zirconium alkoxide solutions, where a large proportion of the metal will not be coordinated by the ligand. Neither has there been any examination of other β-diketones that might also be expected to influence the hydrolytic process by virtue of their differing substituents. We report a study of the influences of each of these factors on the time before precipitation of a hydrolysis product begins, *i.e.* the induction time, t_i. In the case of acacH, values of t_i have been measured by both simultaneous multi-angle static light scattering and a more convenient spectrophotometric technique. The spectrophotometric technique was shown to give equivalent results to light scattering and was used to obtain data on the effects of a number of other β-diketones. The general structure of a β-diketonate anion coordinated to Zr and the β-diketones investigated, are shown in Fig. 1. These β-diketones are expected to show varying degrees of steric protection to the approach of other zirconium species attempting to bind to the coordinated Zr atom. The size of particles in suspensions of the hydrolysed products has been studied by photon correlation spectroscopy, with subsequent scanning electron microscopic examination of the solids removed by precipitation and centrifugation. A subsequent report will be made on the influence of these β-diketones on the rates of particle precipitation.

Experimental

Materials

Zirconium(IV) *n*-propoxide (Aldrich), an approximately 70 wt.% solution in *n*-propanol, was used as received. The zirconium content was taken as that given by the Aldrich certificate of analysis. Analytical grade *n*-propanol was dried by refluxing with magnesium *n*-propoxide prepared *in situ* by the addition of magnesium metal to the alcohol, followed by distillation. Acetylacetone (BDH), hexafluoroacetylacetone (Aldrich), trifluoroacetylacetone (Aldrich) and dipivaloylmethane (Aldrich) were distilled prior to use. Benzoylacetone (Aldrich) and dibenzoylmethane (Aldrich) were used as received.

Stock solution preparation. Individual stock solutions of alkoxide, water and β-diketone were prepared in *n*-propanol under dry nitrogen, and filtered using 200 nm Millipore membranes. The concentrations were chosen such that the volume ratios of alkoxide : β-diketone : water of 2 : 1 : 1 were used in the final reaction mixtures.

Reaction mixture preparation. The stock solutions were heated to the reaction temperature prior to preparation of the reaction mixture. Dilute alkoxide–β-diketone–water solutions were then prepared by adding a β-diketone solution to a rapidly stirred aliquot of the alkoxide stock-solution, followed by addition of demineralised water in *n*-propanol. A 'ligand-free' standard solution was prepared by adding pure *n*-propanol alone to alkoxide, followed by a water solution.

Characterisation

Raman (Biorad FT Raman II spectrometer, equipped with a Spectra Physics Nd/YAG diode laser operating at 1064 nm) and Fourier-transform infrared (FTIR) spectroscopy (Biorad FTS-40 spectrometer) were used to study the incorporation of acac into the hydrolysate, while FTIR was used to investigate the residual amounts of acacH in the supernatant fluids.

Static light scattering measurements were made with a Dawn-F multi-angle static light-scattering unit using either an HeNe or Ar^+ laser. The reaction mixtures were measured in one of two ways:

1. The samples were contained in a jacketed vessel maintained at the desired reaction temperature by means of a circulating water bath. Solutions were then circulated through the Dawn-F flow cell for light-scattering measurements.
2. The samples were transferred to clean, dust-free vials and placed in the batch-cell compartment of the Dawn-F light-scattering unit. Solutions were maintained at the desired reaction temperature by means of the Dawn-F variable-temperature attachment.

The mixing time and the time at which data collection was started were noted and the appropriate time correction made to the data prior to analysis. The final stages of the precipitation reactions could not be monitored, due to the effects of detector saturation and multiple scattering. The values of t_i were determined by least squares regression analysis of the straight portions of a scattering intensity–time curve before and after particle precipitation commenced, and extrapolating the regression lines to the point of intersection, t_i.

Turbidity measurements were recorded on a Cary 3 Spectrophotometer fitted with a multiple-cell compartment, allowing the simultaneous measurement of six kinetic runs. Constant temperature (±0.1 °C) was maintained by the Cary Temperature Controller. All stock solutions were preheated to reaction temperature before mixing. Immediately after mixing, samples were transferred to 1 cm cuvettes and inserted into the spectrophotometer, with the block preheated to the reaction temperature. As for the light scattering measurements, the mixing time and time at which data collection commenced were noted, and corrections applied to the data. The percentage transmittance, $\%T$ ($=I_t/I_0\times100$), was recorded as a function of time and converted into a turbidity measurement τ using the relation $\tau=-\ln\,[I_t/I_0]$, I_t and I_0 being the transmitted and incident intensities, respectively (this relationship holds for the experimental cell pathlength of 1 cm).

To determine a suitable wavelength for measuring t_i values, the spectrum of a test solution containing 0.06 M $Zr(OPr^n)_4$, 0.24 M H_2O and 0.003 M acacH in *n*-propanol was measured at room temperature at one minute intervals in the range 300–800 nm. Turbidity data were obtained at 50 nm intervals over this range and used to calculate t_i by least-squares regression analysis of the two linear sections of the turbidity–time curve, similar to the method applied to the light-scattering measurements. The data showed a small, but systematic, increase in t_i with increasing wavelength. In all subsequent experiments, values of t_i were measured at 500 nm, since the value calculated at this wavelength was the mean of the values at the lowest and highest wavelengths examined. The spread of t_i values was $\pm5\%$ of the value at 500 nm. Since this error was larger than the error associated with the determination of

t_i at a single wavelength (typically <2%), an error of ±5% was assumed for each measurement in subsequent data analyses.

Particle size measurements were obtained by photon correlation spectroscopic (PCS) measurements of solutions containing freshly produced particles, which had not yet settled out (a Brookhaven BI-9000AT digital correlator equipped with a He–Ne laser was used to obtain data at a scattering angle of 90°). Scanning electron microscopy (SEM; JOEL JXA-840 instrument) was used to measure the size of residual particles collected by centrifugation of a suspension until the supernatant liquid remained clear when decanted. The particle sample was dried overnight in air and a specimen mounted on an aluminium disc and carbon coated before examination. All solutions used in these experiments contained the same concentration of zirconium (0.06 M) and water (0.24 M). All PCS measurements were performed on samples produced with the same concentration of β-diketone (0.006 M). Samples were diluted to a suitable visible level of turbidity before measurement, except for samples involving dipivaloylmethane where the slow rate of precipitation allowed the initial suspension to be examined without dilution.

Results and discussion

Variation in induction time

(a) Acetylacetone. If pure liquid water is added to an alcoholic solution of a Zr(IV) alkoxide, the immediate formation of a hydrolysis product is observed. However, if a water–alcohol solution is added, there is a period, the 'induction time' (t_i), before precipitation commences, as marked by the appearance of a faint turbidity, which increases until major precipitation commences. We have previously demonstrated that this occurs when such a water–alcohol solution is added to a solution of $Zr(OPr^n)_4$ in *n*-propanol, such that the final H_2O/Zr mole ratio is in the range 4–6.[21] In the present investigation, the addition of a β-diketone, such as acacH, to the Zr(IV) alkoxide solution prior to the water–alcohol mixture has been found to result in substantial increases in t_i. This effect is clearly highlighted in Fig. 2, which shows plots of the static intensity of light scattered at 90° by solutions of $Zr(OPr^n)_4$ containing fixed proportions of Zr and water and varying concentrations of acacH, such that ρ (=[acacH]/[Zr]) ranges from 0 to 0.1. The dependence of t_i on [acacH] at 30 °C is shown in Table 1. A preliminary account of our initial studies in this area has been communicated.[23] It is clear that the presence of quite low proportions of acacH can increase t_i substantially. It was also found that the induction time for a given concentration of acacH increased when $Zr(OPr^n)_4$ solutions containing acacH were left standing for periods ranging from a few days to weeks prior to addition of water and induction time measurement. Accordingly, all solutions were prepared by the standard procedure outlined in the Experimental section. The values reported for t_i are thus to be considered as relevant only to the experimental conditions defined.

Table 1 Induction time for varying initial acetylacetone concentrations, [Zr] = 0.06 M, $[H_2O]$ = 0.24 M, ρ = [ligand]/[Zr] and T = 30 °C

[acacH]/M	ρ	10^{-3} Induction time[a]/s	10^{-3} Induction time[b]/s
0	0	3.2 (±0.2)	3.25 (±0.03)
0.001	0.017	4.0 (±0.2)	4.0 (±0.2)
0.002	0.033	5.2 (±0.3)	5.2 (±0.1)
0.003	0.050	7.5 (±0.4)	7.5 (±0.1)
0.004	0.067	9.8 (±0.5)	9.8 (±0.2)
0.005	0.083	13.1 (±0.7)	13.1 (±0.1)
0.006	0.10	18.6 (±0.9)	18.6 (±0.1)

[a] Error set at 5%. [b] With calculated area.

Raman and IR spectra of the precipitates revealed that acacH was still bound to Zr in the final solid material; bands in the Raman spectra attributable to coordinated acac[24] occur at 1190 cm^{-1} [δ(C–H)] and 1280 and 1360 cm^{-1} (ν_{as} of the delocalised C–O bond). The intensities of the Raman bands attributable to coordinated acac increase with the increasing amount of initially added acacH (Fig. 3). This is clearly highlighted by the change in intensity of these bands relative to a constant intensity band found at 1450 cm^{-1}, considered to be due to a C–H deformation mode of coordinated alkoxo or alcohol species. Infrared analysis of the supernatant liquors from the various experiments showed only trace amounts of free acacH and there was no variation in intensity with concentration of ligand added, indicating that nearly all of the ligand had been incorporated into the precipitates. The hydrolytic resistance of acac coordinated to metal alkoxides has been previously noted.[10–13]

(b) Other β-diketones. The effects of several other β-diketones on the hydrolysis of $Zr(OPr^n)_4$ have been examined using the turbidometric technique, following confirmation (using acacH) that this technique gave values of t_i that were within experimental error of those determined by the light scattering method. A comparison of the two techniques under the same conditions of [Zr] (0.06 M), $[H_2O]$ (0.24 M) and [acacH] (0.006 M) gave induction times of 1.86 (±0.09) × 10^4

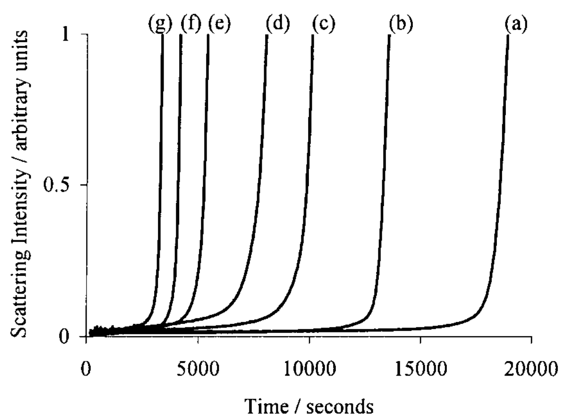


Fig. 2 The time dependence of the intensity of scattered light for hydrolysing solutions of Zr *n*-propoxide containing varying concentrations of added acetylacetone. [Zr] = 0.06 M, $[H_2O]$ = 0.24 M, T = 30 °C, [acacH] = 0.006 M (a); 0.005 M (b); 0.004 M (c); 0.003 M (d); 0.002 M (e); 0.001 M (f); 0.0 M (g).

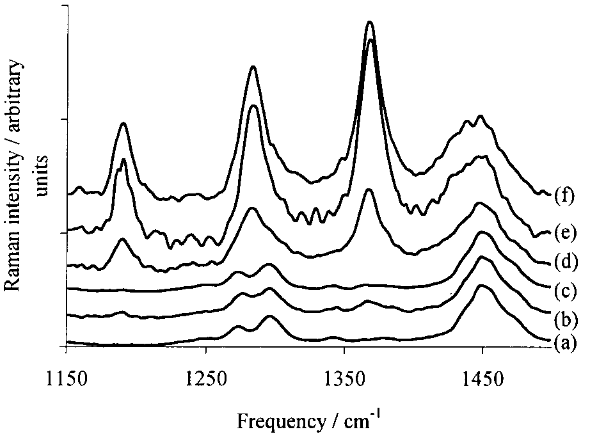


Fig. 3 Variation in FT Raman spectra of precipitates isolated from hydrolysed Zr solution with concentration of added acetylacetone. [acacH] = 0 M (a); 0.001 M (b); 0.002 M (c); 0.003 M (d); 0.005 M (e); 0.006 M (f).

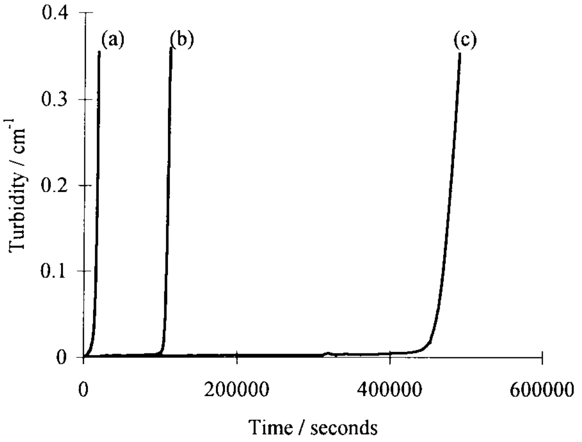


Fig. 4 Comparison of the effect of three β-diketones on the induction time profiles, obtained from turbidometric measurements, on hydrolysing solutions of Zr *n*-propoxide. [Zr] = 0.06 M, [H_2O] = 0.24 M, [β-diketone] = 0.006 M, $T = 25\,°C$, (a) acacH; (b) tfacH; and (c) dbzmH.

s and 1.76 (±0.09) × 10^4 s for light-scattering and turbidometric measurements, respectively.

A comparison of the relative effects of acacH, hfacH and dbzmH on the induction time profiles obtained using turbidometric measurements under the same experimental conditions is shown in Fig. 4. The variations in t_i caused by the various β-diketones, including acacH, with comparable [Zr], [ligand]/[Zr] and hydrolysis ratio ([H_2O]/[Zr]) are summarised in Table 2, and clearly demonstrate the notable dependence of t_i on β-diketone addition, even at the low concentration of ligand studied. For example, the induction times in the presence of acacH and dbzmH are 55 and 1400 times greater, respectively, than in their absence.

Effect on final particle size

Final particle sizes were determined using PCS for systems after the induction time, before substantial deposition of precipitate had occurred. Solids deposited by sedimentation or centrifugation, were examined by SEM. The results are summarised in Table 3.

There were generally only minor differences in the aggregate size of the products formed by hydrolysis of a solution of Zr(OPr^n)$_4$ in *n*-propanol in the absence of any β-diketone and the solids prepared in the presence of acacH, hfacH, bzacH and dpvmH. The aggregates were essentially spherical, with diameters of *ca.* 1000 nm. There was no significant change in the size of the aggregates in any of the systems upon dilution, indicating that dissolution/deaggregation of particles did not occur. Similarly, no variations in aggregate size were observed when the precipitates were left in contact with solution for several days before removal. The sizes measured in suspension by PCS were generally in good agreement with the SEM measurements, except that smaller species, *ca.* 500 nm in diameter, found in the ligand-free system by SEM examination, were not always detected by PCS measurements. This may be due to the stronger scattering from the larger particles obscuring that from the smaller particles. Alternatively, the smaller species might be produced during a secondary nucleation event occurring after the initial particle precipitation.

Table 2 A comparison of induction times for the hydrolysis of Zr(OPr^n)$_4$ in the presence of various β-diketones and their stability constants for coordination to Cu(II); [Zr] = 0.06 M, [H_2O] = 0.24 M and [β-diketone] = 0.006 M

β-Diketone	10^{-4} Induction time/s	log K_1 {Cu(II)}
No added ligand	0.40(±0.02)	
Acetylacetone	1.76 (±0.09)	11.30,[a] 11.57[b]
Hexafluoroacetylacetone	2.1 (±0.1)	4.30[a]
Trifluoroacetylacetone	9.4 (±0.5)	8.60[a]
Dipivaloylmethane	9.5 (±0.5)	13.91[b]
Benzoylacetone	10.0 (±0.5)	11.51[a]
Dibenzoylmethane	46 (±2)	12.50[a]

N.B. Induction times have been averaged over a number of experiments. [a]Ref. 28. [b]Ref. 29.

The degree of turbidity produced in the presence of dpvmH was noticeably less than when other ligands were present. This effect, which was presumably due to similarities in the refractive indices of the precipitate and the solvent, prevented a particle size distribution analysis by PCS, because of the poor signal-to-noise in the correlation function. SEM measurements of precipitates from solutions containing 0.003 M dpvmH showed them to be of approximately the same size (1100 nm) as those from solutions containing 0.006 M dpvmH, but having a more regular appearance. Thus, it appears that dpvmH has little effect on the final aggregate size, but the aggregates tend to be more irregular when formed at high ligand concentration. The very small amounts of precipitate formed initially suggest that dpvmH is enhancing the solubility of the final particles and this effect may well explain the apparently anomalous position of that ligand in the overall series (see later discussion). The enhanced solubility may be due to the presence of the *tert*-butyl groups, which have an increased affinity for the bulk solvent.

In contrast, the presence of the ligands tfacH and dbzmH did appear to influence the final aggregate size. The PCS data indicated that, for systems containing these ligands, *ca.* 90% of the hydrolysate consisted of notably smaller species (*ca.* 400 nm) than obtained in the absence of ligand or the presence of acacH, hfacH, bzacH or dpvmH. The balance of the material consisted of aggregates of comparable size to those forming the main part of the precipitate obtained in the presence of the other ligands.

Mechanism of inhibition of particle growth

The light scattering study of the period that follows the end of the induction time for a Zr(OPr^n)$_4$ system, both with and without acacH, showed a rapid increase in the static intensity of light scattered due to nucleation of insoluble colloidal particles as precipitation begins. At the end of the induction period, the colloids were *ca.* 50 nm in diameter, increasing in size to *ca.* 200 nm within a few minutes,[21] and finally forming *ca.* 500–1000 nm particles. The method of Amal *et al.*[25] was used to analyse the variations in light intensity as a function of scattering wavevector (q), over nine discrete values of q. The colloids produced were found to have fractal dimensions of 3.0 ± 0.1, suggesting that the particles were 'dense'. Such types of particles have been shown to grow by a 'reaction-limited monomer-cluster aggregation' (RLMCA) mechanism,[16] implying that particle growth occurs by the preferential reaction of small oligomeric species with larger oligomers or particles, rather than small oligomers with other small oligomers or large clusters with other large clusters. Davies *et al.*[17] have explained the formation of spherical zirconia particles by hydrolysis of a zirconium alkoxide using such a model based on the mechanism of particle formation suggested by Barrett and Thomas.[18] This assumes that the alkoxide initially reacts with water to form low molecular weight oligomers, *i.e.* associated 'monomer' units [Zr(OR)$_{4-x}$(OH)$_x$]$_n$, reacting initially by mutual condensation to form 'proto-particles' which can subsequently react with further oligomers to form larger units which grow until a point in time where insoluble colloids are formed,[17] *i.e.* at the end of the induction period. The 'proto-particles' will be further stabilised through the formation of –O–(Zr–O–Zr)$_n$–O– three-dimensional networks by slow oxolation and alkoxolation processes.

Table 3 Final particle size data for the hydrolysate of $Zr(OPr^n)_4$ in the presence of various β-diketones $[Zr]=0.06$ M, $[H_2O]=0.24$ M and $T=25$ °C

	Particle size/nm and notes	
β-Diketone	PCS	SEM
No added ligand	1160 (1020–1290)	1000 (spherical) smaller number at 500
acacH	1100 (800–1400) some at 370	1000 (800–1000) some at 370
dpvmH	900	1000 (900–1100)
hfacH	1200 no smaller particles	1000 some smaller particles
tfacH	430 (200–510) (90% of sample) 1200 (10% of sample)	700–900 and some small (0.003 M) no particles obtained (0.006 M)
bzacH	1000 (700–1000)	1000 (irregular) and some small 0.003 M particles less irregular than 0.006 M
dbzmH	400 (300–500) (80–90% of sample) 1200 (900–1400) (10–20% of sample)	Most 400, some 1000 (0.006 M) 700–900 (0.003 M)

Hydrolysed Zr species with coordinated ligands attached, $[Zr(OR)_{3-x}(OH)_x(\text{ligand})]_n$, will also participate in the condensation processes, but will represent only a small fraction of the hydroxy Zr-species available for incorporation in the growing particles at low [ligand]/[Zr] ratios. The general ability of the various ligands to influence the value of t_i even when present in such low concentrations relative to Zr means that the ligands must be interfering with the rate of growth of the 'proto-particles'. Dramatic inhibition of particle growth has been achieved even though, at the highest concentrations of added ligands used in this study, a maximum of only one in forty Zr–OR bonds have reacted with ligand and are no longer available for hydrolysis and cannot act as centres for further condensation.

The subsequent formation of uniform *ca.* 1 µm 'particles' from such 'proto-particles' has been investigated by Look and Zukovski,[26] who developed a model describing the effects of parameters such as reactant concentration, solvent dielectric constant, surface potentials, *etc*, on the morphology of precipitates obtained by alkoxide hydrolysis. This work demonstrated that aggregation of stable 'proto-particles' is a primary growth pathway which is controlled by the inter-particle pair potential, consisting of an attractive, van der Waals component and a repulsive component, involving contributions from electrostatic and short-range steric potentials. The latter operate over *ca.* 1 nm and can involve contributions from solvation/hydration forces and steric repulsion due to surface alkoxy or ligand, such as those present in the current system.

Previous workers studying the effect of acetylacetone in reducing the rate of gelation of hydrolysed alkoxides of Zr(IV)[3] and Ti(IV)[27] have suggested that the reason lies in the segregation of ligand molecules on the surface of the growing 'proto-particle'. This would reduce the rate of association of small oligomers to produce larger species, because the number of sites around metal atoms in the surface layers of growing 'proto-particles' at which further association can occur is decreased. The characterisation of the spherical molecular species $Ce_6(\mu\text{-}O)_4(\mu\text{-}OH)_4(acac)_{12}$[10] which has acac ions on the surface supports this hypothesis. The reason for this build up would plausibly be related to the restriction placed on coordinated Zr atoms to link to other colliding Zr–hydroxy species at all potential bonding positions, because two sites at each coordinated Zr atom will be occupied by a chelating ligand which is difficult to replace. Hence, a 'proto-particle' will grow 'away' from the side of Zr atoms bearing a ligand molecule, thus leading to isolation of ligand on the outer surface of a growing particle. As the [ligand]/[Zr] ratio increases, although still remaining small, the growth of 'proto-particles' becomes more restricted since a greater number of ligand molecules lie on the particle surface and further restrict the binding of low nuclearity hydroxy species (Scheme 1). The concept is thus in qualitative agreement with the observed increase in induction times with increasing ligand to metal mole ratio.

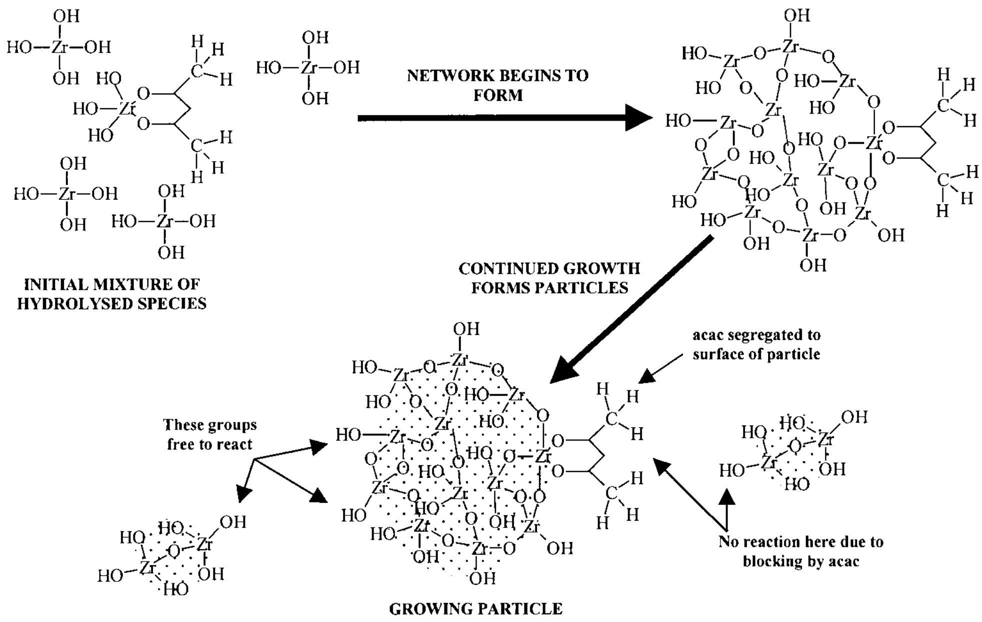
Such steric blocking of a particle surface suggests that the differences between the induction times found with the various β-diketones should be in the order of the size of substituents R and R′ on the R–CO–CH–CO–R′ ligand anions. The 'bulkiness' of the ligands examined is presumed to increase in the order acac < tfac < hfac < bzac < dpvm < dbzm. While this order is followed in general (Table 2) there are departures from the expected trend. Thus, hfac and tfac are individually placed in the order expected with respect to other members in the series, but their effects with respect to each other are reversed.

There also exists the possibility that the stability constants for the reaction,

$$Zr(OPr^n)_4 + \text{ligand H} \rightleftharpoons Zr(OPr^n)_3(\text{ligand}) + HOPr^n$$

vary substantially from ligand to ligand and that this might result in varying concentrations of $[Zr(OPr^n)_3(\text{ligand})]$ being formed and contributing to the differences in induction times. Although values for the stability constants of such reactions are not available for the β-diketone ligands, constants for the coordination of various β-diketones to Cu^{2+} have been determined (see Table 2).[28,29] Calculations based on the values of the stability constants for binding of acac, tfac, dpvm, dbzm and bzac to Cu^{2+} clearly indicate that vanishingly small amounts of ligand would remain uncoordinated. In going from Cu^{2+} to the Zr(IV) *n*-propoxide system, a dramatic decrease in these constants (10^7–10^{12} depending on the ligand) will be required before uncoordinated ligand will be found in the alcohol solution. Thus, for these ligands, complete coordination of ligand can be assumed to have occurred. The situation for hfacH is somewhat different since the stability constant for coordination to Cu^{2+} is much smaller ($\log K_1 = 4.30$) than for the other ligands used in the current study. For this ligand, a drop in K_1 from Cu(II) to Zr(IV) of only two orders of magnitude would lead to significant amounts of free β-diketone and hence a lowering of the concentration of Zr atoms bearing coordinated ligand. This may explain the reversal of the order of induction time for hfacH and tfacH.

The influence of dpvmH is not easily reconciled with either steric or stability arguments, because on either ground it should show an effect similar to, or greater than, dbzmH. However, as reported above, the degree of turbidity first observed with dpvmH present was notably less than when using other ligands, and hence, t_i values were derived from the precipitation of smaller amounts of hydrolysate than in other cases. Possibly, coordination of dpvm anions can cause 'proto-



Scheme 1

particles' with attached ligand to grow more slowly (because of combined steric and stability constant effects) than other particles which can form more quickly from predominantly $[Zr(OR)_{4-x}(OH)_x]$ units and this latter material precipitates more readily than the bulk (yielding a measured t_i smaller than anticipated). A further investigation of this ligand's effects is clearly required.

Although it is implied in this description that the β-diketonate ions remain bound to the same surface site indefinitely, this is probably not the case. The Zr(IV) centre is expected to be sufficiently labile to allow a dynamic equilibrium to exist between the very small amount of free ligand still in solution and its anions coordinated in 'proto-particles'. This will result in continual exchange of ligand molecules in the 'proto-particle' with 'free' ligand H molecules in solution. The likely result of such exchange processes is that a given ligand will become coordinated to zirconium sites other than that to which it was attached initially. Hence, there will be a 'movement' of the sites occupied by an individual ligand across the surface of the 'proto-particle' over time. This periodic movement of occupied sites allows for formation of spherical species, as no one site is actually occupied indefinitely. The 'single-step' nucleation of these spherical, growing 'proto-particles' then causes precipitation to occur at a time when all particles have been growing for the same period resulting in a relatively monodisperse sample of particles being obtained. The presence of lesser amounts of smaller particles, as observed in some instances, is likely to be due to a secondary nucleation event.

Conclusion

The influence of low ligand/Zr mole ratios ($\rho = 0$–0.1) of acetylacetone on the hydrolysis of $Zr(OPr^n)_4$ has been examined by investigating the effect of ρ on the induction time (t_i) before colloidal particle precipitation commences in the system. The addition of β-diketones (acacH, hfacH, tfacH, bzacH, dbzmH, dpvmH) causes a large increase in t_i (reduction in hydrolysis/condensation rate), even though only a maximum of one in forty Zr–OR bonds have reacted with ligands, and hence, are no longer available for hydrolysis or further condensation. Comparable final size particles (*ca.* 1000 nm) are obtained in the presence of the majority of the ligands examined, although tfac and dbzm do appear capable of influencing the final particle size.

The relative effects on t_i of the other β-diketones (which have varying steric properties) are compared with that of acacH, under similar concentration conditions, with $\rho = 0.1$. Each shows a greater effect than acacH, with the largest change being caused by dbzmH, which increased t_i by a factor of 26 relative to acacH.

The fractal dimensions of the colloidal hydrolysate particles ($d_f = 3.0$) indicated that the particles are 'dense', and hence, are predicted to grow by a 'reaction limited monomer-cluster aggregation' process. A proposed mechanism rationalising the origin of the effect involves segregation of β-diketone molecules on the surface of growing particles. The presence of the coordinated ligand on the surface of the growing particle reduces the number of Zr sites at which potential Zr–O–Zr growth can occur. The relative abilities of the β-diketones to influence t_i appear to be generally related to the degree of steric hindrance that each ligand can exert on the approach and attachment of small hydrolysed 'monomers' to the larger, growing 'proto-particles'.

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