Examination of Condensation Products of Group 4 Alkoxides with Laser-Induced Liquid Beam Ionization/Desorption Mass Spectrometry

Frank Sobott, Stephan Andreas Schunk, Ferdi Schüth, and Bernhard Brutschy*

Abstract: Group 4 Alkoxides hydrolyzed in methanolic solutions in the presence of stoichiometric amounts of water were investigated with laser-induced liquid beam ionization/desorption (LILBID) mass spectrometry. This soft desorption method produces a minimum of fragmentation products, as analyte ions are desorbed from a thin liquid jet into vacuum by means of an IR laser pulse which has been tuned to a vibrational absorption band of the alcohol. The resulting mass spectra allow insight in the oligomer distribution produced at different degrees of hydrolysis of the alkoxide precursors. In the mass range corresponding to monomeric units, a great variety of species was observed because of ligand exchange with the solvent alcohol or water. Hydrolysis of $[Ti(OR)_4]$ and $[Zr(OR)_4]$ leads to large series of peaks with a spacing which is believed to correspond to TiO_2 and ZrO_2 units, respectively. Depending on the amount of water added to the solution and on the amount of heating prior to analysis, distinctive cluster sizes dominate the continuous oligomer distribution. An impression of the earliest stages of crystallization can be obtained with this new mass spectrometric method.

Keywords: condensation reactions • laser desorption • mass spectrometry • titanium • zirconium

Introduction

Metal alkoxides of the main group and transition metals are well studied inorganic precursors in sol–gel chemistry.[1, 2] A rich polyoxo chemistry has been observed especially for Group 5 and Group 4 elements, where several species coexist depending on solution parameters like concentration and pH.[3] Another system where the existence of oligomeric equilibria has been studied extensively are the silicon alkoxides.[4] In this case the monomeric and oligomeric species that occur in solution can be readily observed and identified by ^{29}Si NMR spectroscopy.[4–6] Although several well-defined oligomers are known for Group 4 alkoxides, which are obtained by quantitative hydrolysis and crystallize readily,[7, 8] the hydrolysis and condensation processes in solution have not been studied to the same extent and are much less understood. For instance, it remains unclear whether structures obtained from single crystals make up the major part of an oligomer distribution in solution as well, or whether they refer to single species that are in an equilibrium with others and can be crystallized preferentially due to a unique symmetry.

For Group 4 alkoxides, it can be assumed in analogy to the neighboring groups that their hydrolysis produces a diversity of condensation products in solution with a rather broad size distribution of oligomers. NMR spectroscopy is not a simple technique for these elements, because the metal nuclei are quadrupolar or do not have a resulting nuclear spin at all. Still, ^{17}O NMR spectroscopy sheds some light on the ongoing condensation processes and the kinetics of condensation, but gives little information on the generation and composition of oligomeric species, as well as on the oligomer distribution resulting from condensation in solution.[9]

Recently, Løver et al. reported the successful use of electrospray ionization (ESI) mass spectrometry for the analysis of Group 4 alkoxides in dry alcoholic solvents under the addition of sodium alkoxides as ionizing agents.[10] They were able to detect series of oligomeric species of the type $[Zr_n(OEt)_{4n+1}]^-$ ($n = 1-5$). These findings correlate very well with the polymeric nature of the compounds that has been reported elsewhere.[2, 4] However, Løver et al. did not examine reactive systems in which water was added to start hydrolysis and condensation reactions. In the present study, mass spectrometry is applied to the analysis of condensation products of Group 4 alkoxides at different degrees of hydrolysis. The major advantage of the mass spectrometric approach is the capability for the simultaneous detection of a complex mixture of species of different size and composition.

We employed the newly developed desorption method called laser-induced liquid beam ionization/desorption

---

[*] Prof. Dr. B. Brutschy, Dipl.-Chem. F. Sobott
Institut für Physikalische und Theoretische Chemie
der Universität Frankfurt
Marie-Curie-Strasse 11, D-60439 Frankfurt am Main (Germany)
Fax: (+49) 69-798-29560
E-mail: brutschy@chemie.uni-frankfurt.de

Prof. Dr. F. Schüth, Dipl.-Chem. S. A. Schunk
Institut für Anorganische Chemie der Universität Frankfurt (Germany)

0947-6539/98/0411-2353 $ 17.50+.25/0

(LILBID)[11] to the mass analysis of condensation products of Group 4 alkoxides. As rather high electrolyte concentrations of 0.1 mol$\,$L^{-1} are used, electrospray would not be a feasible technique for this kind of sample. Furthermore, the addition of ionizing agents as done by Løver et al. might lead to a perturbation of the solution and thus influence the condensation processes.

With LILBID, ions are desorbed by means of an IR laser pulse from a thin liquid jet of analyte solution injected into high vacuum. The liquid phase remains intact in the vacuum for a distance of a few centimeters, until the jet decays into droplets which are frozen out on a cold trap. Previous experiments with different cations in dilute alcoholic and aqueous solutions have proven that specific interactions with the solvent or with coronands are preserved in the mass spectra.[12, 13] Furthermore, labile biomolecules and noncovalently bound complexes can be detected without a considerable amount of fragmentation.[14, 15] LILBID mass spectrometry is applied now for the first time to the analysis of organometallic compounds and their hydrolysis and condensation products.

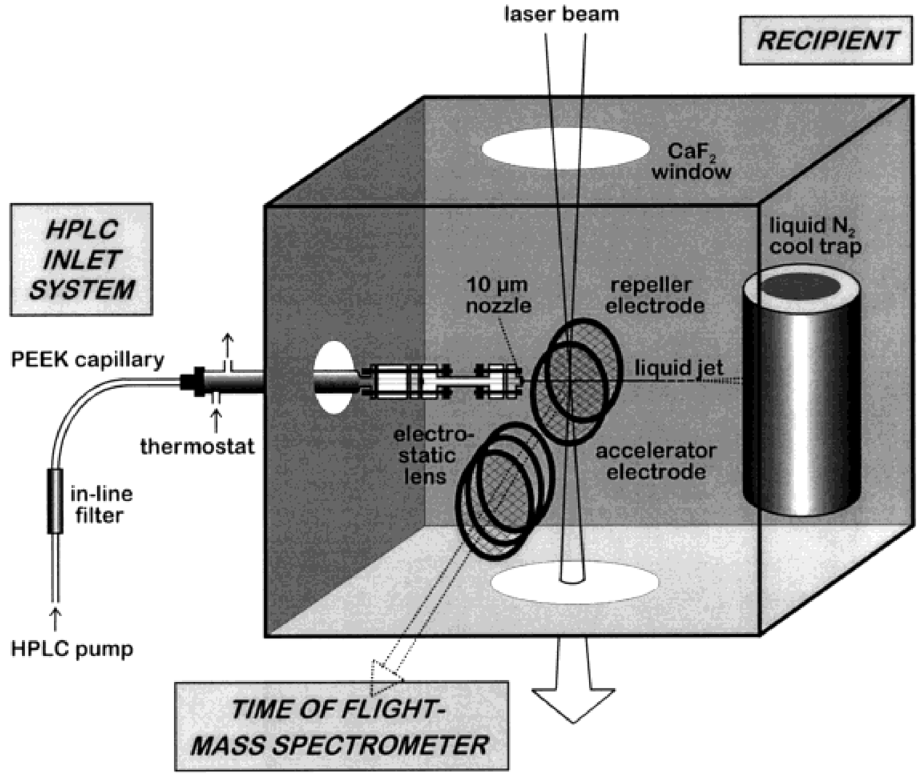


Figure 1. Schematic setup of the LILBID experiment.

Experimental Section

Materials: All solutions were prepared under the usual precautions for the preparation of anhydrous chemicals and kept under a dry inert atmosphere of nitrogen. All alkoxides (the highest available purity grades were used for [Ti(OMe)$_4$], [Ti(OEt)$_4$], [Ti(O*i*Pr)$_4$], [Ti(O*n*Bu)$_4$], [Zr(OEt)$_4$], [Zr(O-*n*Bu)$_4$],(Aldrich), [Zr(O*n*Pr)$_4$], [Zr(O*i*Pr)$_4$] (Dynamit Nobel)) were dissolved in anhydrous methanol (Aldrich, Sure Seal) and stirred for 15 minutes until most of the alkoxide was dissolved. Next millipore water was added and the samples were stirred again for 60 min, and then filtered through a 0.2 µm dry and sterile filtration unit (Nalgene). If samples had to be stored for several hours, they were kept at +6 °C in a refrigerator.

UV/Vis spectroscopy: UV/Vis spectra were recorded in the range of 220–800 nm with a Leica MPV-SP microscopic photometer unit. The samples were placed in a pyrex glass cuvette with a light path of two millimeters. Absorption wavelengths were determined with standard procedures.

Mass spectrometry: A detailed description of the LILBID method and the apparatus has been published previously;[11–15] therefore only a brief outline of the experiment is given here. The sample solution was fed from a glass container through a PEEK capillary at a constant backing pressure of 40–60 bar by using a HPLC pump (Merck-Hitachi L-6000 A). It is then injected through a 10 or 20 µm wide Pt-Ir aperture into high vacuum (Figure 1). There laminar flow is preserved for a few centimeters, until the jet decays into small droplets due to Rayleigh instabilities. The initial temperature of the liquid can be adjusted between −30 and +50 °C with a thermostat. In the vacuum however, evaporative and adiabatic cooling rapidly lower the temperature of the liquid by several tens of degrees. To maintain a high vacuum of some 10^{-6} mbar in the recipient in spite of the presence of a liquid, a large oil diffusion pump (Balzers DIF 320) was used assisted by a liquid nitrogen cooling trap where the jet is frozen out. After entering the vacuum region, the liquid beam is crossed several millimeters behind the nozzle with a pulsed IR laser (CO_2-laser URANIT ML – 104), which was tuned to a vibrational absorption band of the solvent (methanol: 9.66 µm). An energy of 20–30 mJ per pulse, which corresponds to an irradiance of 10^6–10^8 W$\,$cm^{-2}, was typically required for the desorption of ions from the liquid. After absorption of the IR photons by the solvent, the excited molecules undergo a fast vibrational relaxation which entails a rapid heating of the solvent (typically 10^{10} K$\,$s^{-1}). This temperature jump induces the desorption of ions which have been formed in solution by the attachment or loss of protons or cations. Ions in the gas phase were then orthogonally extracted into a reflectron time-of-flight (Re-TOF) mass spectrometer; delayed extraction was used to compensate in part for their initial energy distribution. After passing the field-free drift region, the ions were postaccelerated with 20 kV into an ion/electron converter (Even-cup) coupled to a scintillator and a photomultiplier. Mass spectra are stored with a digital oscilloscope (Le Croy 9410) and read out for further processing with a PC. The mass spectra were internally calibrated by using calibration standards.

Results and Discussion

Titanium alkoxides: The quantitative hydrolysis of titanium alkoxides was performed by dissolving the respective alkoxide in anhydrous methanol and then adding stoichiometric quantities of water. The condensation reaction can be monitored by UV/Vis spectroscopy, as the onset of absorption is red-shifted with an increasing amount of water added. Figure 2 shows the shift of the absorption threshold as obtained from the extinction spectra. This red shift can be interpreted in terms of the formation of titanium oligomers with a decreased HOMO/LUMO distance;[16, 17] this already takes place to a certain extent at very low water contents by condensation of the alkoxide. For a

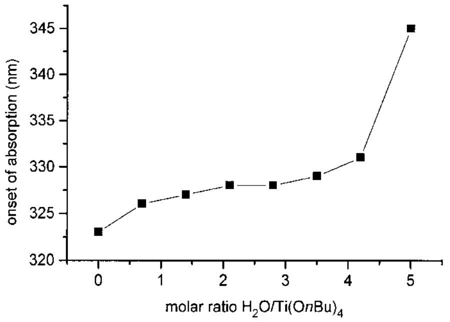


Figure 2. The onset of UV absorption is plotted vs. the molar ratio of H_2O/Ti.

H_2O/Ti ratio of 0 to 4, only a slight red shift of a few nanometers can be observed, but it increases dramatically for higher ratios. From a solution with a H_2O/Ti ratio of 4, we obtained a white precipitate which proved to be X-ray amorphous and transforms into anatase upon heating at 300 °C.

Different water contents also have a strong influence on the LILBID mass spectra, leading to a dramatic change in the peak pattern. For samples with no water added to the solution, hardly any high mass signals for titanium oligomers were detected. Figure 3 A shows a mass spectrum of a $[Ti(OMe)_4]$ solution (molar ratio Ti/MeOH = 1/550) at 25 °C with no water added, and Figure 3 B shows the same solution after it had been heated to 65 °C. Here a multitude of peaks for masses up to $m/z = 1200$ can be seen, some of them with a regular spacing of $m/z = 80$. This change in the mass spectrum is attributed to the fact that even under standard precautions for the preparation of anhydrous chemicals, minimum amounts of water (H_2O/Ti less than 0.1) are present in the hydrophilic samples. When the solution is heated, the alkoxide molecules may exceed the activation barrier for the start of condensation reactions. Under these conditions, most alkoxide species in the solvent are not charged and thus cannot be detected, except when ionizing agents are added.[10]

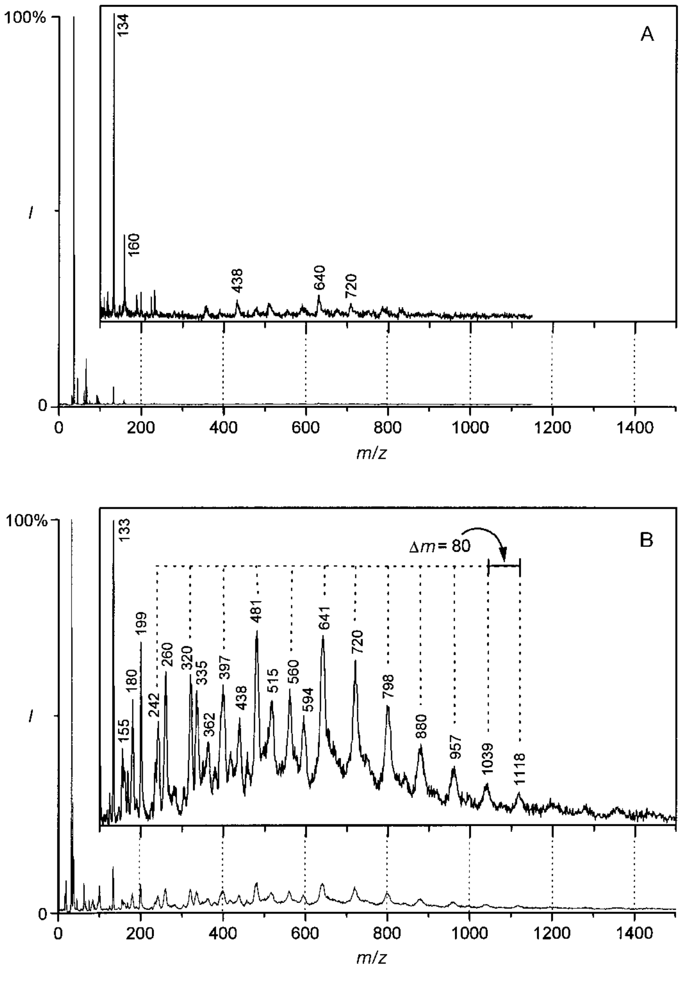


Figure 3. A) LILBID anion spectrum of a $[Ti(OMe)_4]$ solution (molar ratio Ti/MeOH = 1/550) in methanol at 25 °C with no water added to start the condensation reaction. B) Spectrum of the same solution as in Figure 3 A after it has been heated to 65 °C for one hour. I = relative intensity.

In the mass spectra for a H_2O/Ti ratio of 3, which corresponds to a much higher degree of hydrolysis, signals in the mass range up to several thousands could be detected (Figure 4). While some peaks are present in the spectra with

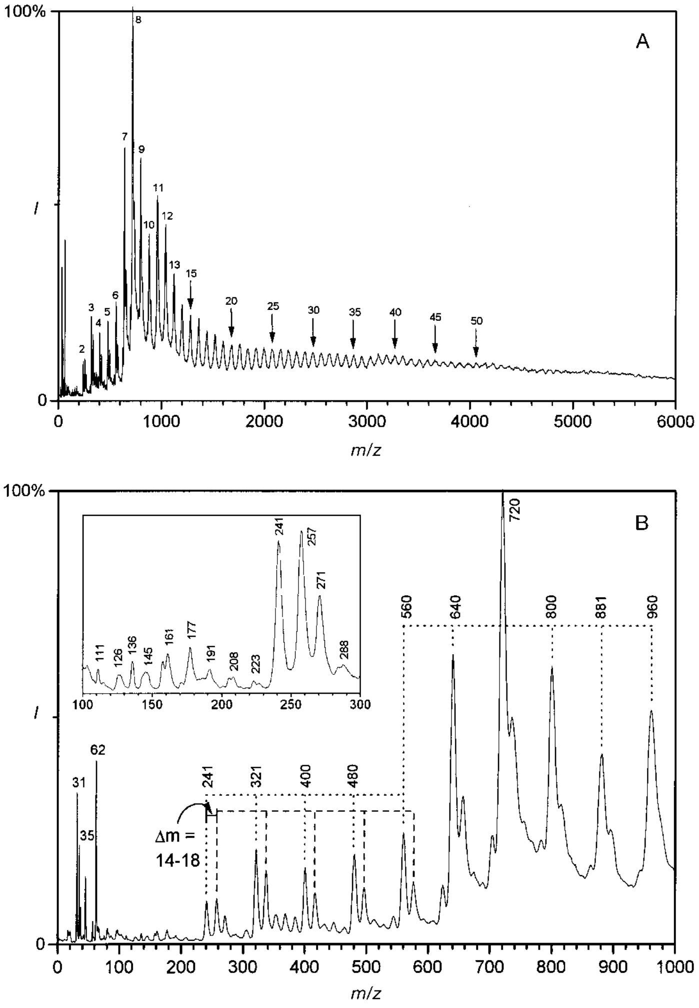


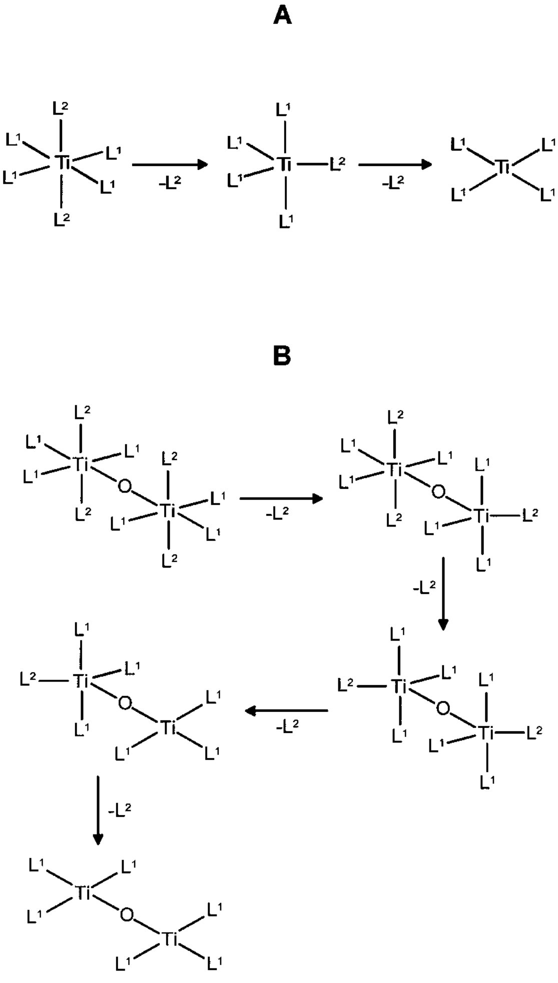
Figure 4. A) LILBID anion spectrum of a methanolic solution of $[Ti(OMe)_4]$ with water added (molar ratio $Ti/H_2O/MeOH = 1/3/550$), showing a continuous peak series with a spacing of $\Delta m/z = 80$ corresponding to TiO_2 units. The number of titanium atoms in the oligomeric unit is given for each peak. B) Expanded section of the same spectrum in the mass range $m/z = 0–1000$ (inset: mass range $m/z = 100–300$). Two peak series are marked wich are shifted by $\Delta m/z = 14–18$ in relation to each other. $m/z = 31$ corresponds to the methanolate ion, $m/z = 35$ to one chlorine isotope. I = relative intensity.

and without added water, the dominating feature is now a peak series with constant spacing starting from $m/z = 240$ (Figure 4 A). Basically similar peak series are found for the clusters in the negative- and positive-ion mode. From this we conclude that the majority of the clusters are neutral and thus cannot be detected with mass spectrometry. Charged species show a distribution mainly from $+1$ to -1, which is due to the attachment or removal of charge carriers like protons or methanolate ions present in the solvent (for methanol at 20 °C, $\mathrm{p}K_a = 16$, for water $\mathrm{p}K_a = 15.7$[18]). This certainly leads to a difference between observed species in the mass spectra and species present in solution, as only the charged species can be seen. Here, we want to restrict our further discussion to the neutral and negatively charged species.

Peaks in the low m/z range between 115 and 221 (inset in Figure 4B) can be explained in terms of negatively charged, partially hydrolyzed titanium methylate monomers as shown in Table 1. The most interesting fact is that nearly all the species that are likely to exist under these conditions can be detected. All monomer masses which could be found in the negative-ion LILBID spectra are highlighted in the matrix (Table 1). These findings indicate that all kinds of partially hydrolyzed species coexist in solution. While six-coordinate titanium would be expected,[2] we observed monomeric units with coordination numbers of 4, 5, and 6 simultaneously. It seems reasonable to assume that during the desorption from the liquid, titanium complexes may lose solvent molecules which do not compensate for the charge of the ion and are rather loosely bound in the coordination sphere. As a rather high laser energy of 30 mJ per pulse was chosen to obtain good spectra, and the methanolate ligands in the complex are in resonance with the desorption laser wavelength as well, some of the observed species will be partially desolvated. In Scheme 1 the process of ligand loss for neutral titanium species with a subsequent change of the coordination geometry is illustrated for a monomeric (Scheme 1 A) and a dimeric (Scheme 1 B) unit, with L^1 as a charge-compensating and L^2 as a neutral ligand.

Additional fragments appearing at $m/z = 80, 97$, and 111 are interpreted as $[TiO_2]^-$, $[TiO_2(OH)]^-$, and $[TiO_2(OMe)]^-$, respectively. Since their intensity is quite low, fragmentation of laser desorbed species in the gas phase which would lead to the loss of TiO_2 units does not seem to play a major role.

The monomeric species with the highest possible mass lies at $m/z = 221$. Higher masses thus correlate with condensation products of the hydrolyzed alkoxide. Above $m/z = 240$, we observe a regular spacing of $m/z = 80$ which corresponds to a neutral TiO_2 unit (M = 79.9). Several series appear which are shifted by $m/z = 14$ or 18 relative to each other, but all of these, with the exception of the first series, vanish in the background signal around at $m/z = 1000$ (Figure 4B). While the addition of one water molecule leads to $\Delta m/z = 18$, a mass shift of 14 can be attributed to the exchange of a OHMe or $(OMe)^-$ ligand for a OH_2 or $(OH)^-$ ligand as shown in Scheme 2A. The same mass difference of 14 can be expected for a condensation reaction where the preferential leaving group is either water or methanol (Scheme 2B).

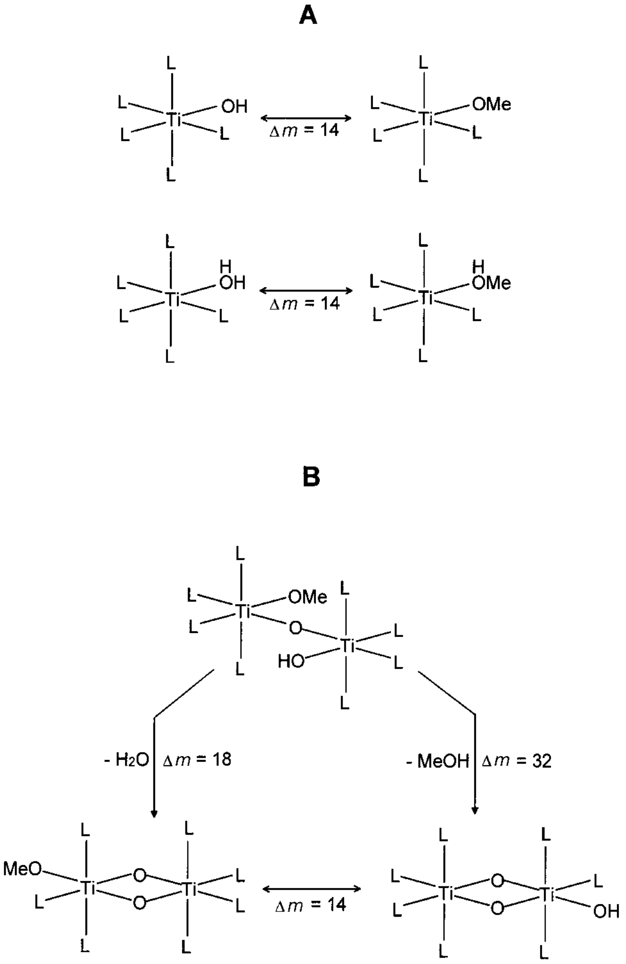


Scheme 1.

This possible variance in the ligand composition should be highlighted as it shows clearly that the broad peaks occurring in the spectra are not exclusively a result of a poor mass resolution of the spectrometer. Instead we are convinced that the relatively broad signals are composed of a peak pattern of closely standing peaks of similar intensities that presently cannot be resolved.

Table 1. Possible monomeric species present in a solution of partially hydrolyzed titanium alkoxides.

Number of methyl groups hydrolyzed	Coordination number [m/z] 4	5	6
1	$[TiO(OMe)_3]^-$ **[157]**	$[TiO(OMe)_3(MeOH)]^-$ **[189]**	$[TiO(OMe)_3(MeOH)]^-$ **[221]**
2	$[TiO(OH)(OMe)_2]^-$ **[143]**	$[TiO(OH)(OMe)_2(MeOH)]^-$ **[175]**	$[TiO(OH)(OMe)_2(MeOH)_2]^-$ **[207]**
3	$[TiO(OH)_2(OMe)]^-$ [129]	$[TiO(OH)_2(OMe)(MeOH)]^-$ **[161]**	$[TiO(OH)_2(OMe)(MeOH)_2]^-$ [193]
4	$[TiO(OH)_3]^-$ [115]	$[TiO(OH)_3(MeOH)]^-$ **[147]**	$[TiO(OH)_3(MeOH)_2]^-$ **[179]**
(5)	–	$[Ti(OH)_5]^-$ **[133]**	$[Ti(OH)_5(MeOH)]^-$ [165]



Scheme 2.

The first series starts with a peak between $m/z = 240$ and 242 (Figure 4B) that we attribute to a dimeric unit. A conceivable composition formula for this species would be $[Ti_2O_2(OH)_3(OMe)_2]^-$, but an unambigious assignment is not possible. The overall coordination number of this starting unit is found to be rather low for the reasons mentioned above. Of greater interest concerning the process of oligomer growth is the size distribution of the peak series, which shows a distinctive maximum around $m/z = 720$. Following the assignment in Figure 4A, this peak belongs to an oligomeric unit containing eight titanium atoms. Lower condensation products up to hexamers have a much smaller intensity, but heptamer and nonamer signals are strong as well. Apparently units composed of a backbone with ten titanium atoms appear much less frequently than the neighboring nonamer and undecamer. For higher degrees of condensation, a decrease in intensity can be seen until the peaks vanish in the underlying background signal.

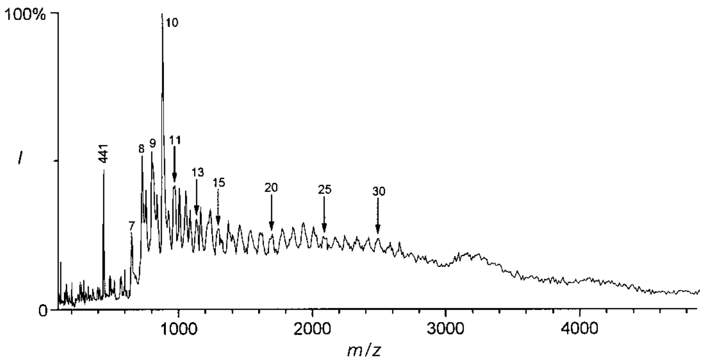


Figure 5. LILBID anion spectrum of the same solution as in Figure 4 after several hours of storage in the sample container. I = relative intensity.

When the same titanium alkoxide solution with a H_2O/Ti ratio of 3 is kept for several hours at 37 °C, ongoing condensation reactions could be followed visually when clear solutions turned opaque. Accordingly, characteristic features of the mass spectra change as well (Figure 5). For example, the maximum of the oligomer distribution is shifted to $m/z = 880$, which corresponds to a decameric unit. In addition, the signal intensity in the mass range up to $m/z = 600$ is now much lower, except for a prominent peak at $m/z = 441$ which could possibly be the doubly charged decamer. We attribute this change to an increased degree of hydrolysis which is accompanied by the preferential formation of larger oligomeric units. The overall peak intensity in the low mass range correlates well with the postulate of increasing hydrolysis (Figures 3B, 4, and 5), as the solution becomes more and more depleted in small oligomers. We were not able to examine solutions with a H_2O/Ti ratio higher than 3, because the nozzle was easily blocked by the precipitation of TiO_2 particles.

Different titanium alkoxides basically did not lead to changes in the spectra, as the peak pattern and the typical masses remain the same for all the studied alkoholates (methylate, ethylate, isopropylate, *n*-butylate). This is not a very surprising result, as it is known that metal alkoxides are highly reactive and the solvent alcohol ROH is easily exchanged for the alkoholate (R′O)-M group within short times.[19] Again this is in good agreement with the results obtained with ESI-MS.[10] Thus the prominent peak series with $\Delta m/z = 80$ represents oligomeric units of partially hydrolyzed titanium alkoxide, with a lowered coordination number due to partial ligand loss during the desorption process. These oligomeric units therefore do not necessarily exist in solution with the observed number of ligands and the respective coordination number, but the titanium oxide backbone and oligomer size distribution are preserved and should allow insight into the condensation process.

Zirconium alkoxides: In the mass spectra of solutions of $[Zr(OiPr)_4]$ in methanol (molar ratio Zr/MeOH = 1/550) in the presence of water, again peak series are found which extend beyond $m/z = 3000$, but they now show a regular mass spacing of $\Delta m/z = 123$ (Figure 6). This difference is in good agreement with the mass of a ZrO_2 unit ($M_r = 123.2$). In comparison to titanium, the variation in the ligand composition of zirconium oligomers is observed to be much smaller, as continuous distributions with a $\Delta m/z = 14$ spacing only play a minor role up to a mass of 600. In this case, the chemically favored clusters can be identified more easily as the atomic weight of the metal atom is much higher and therefore mass differences are bigger between the possible cluster species. In the low mass range, fragmentational clusters appear again at $m/z = 123$, $[ZrO_2]^-$, and 140 $[ZrO_2(OH)]^-$ (Figure 6B). The isotope-split signals around $m/z = 158$ and 172 correspond to

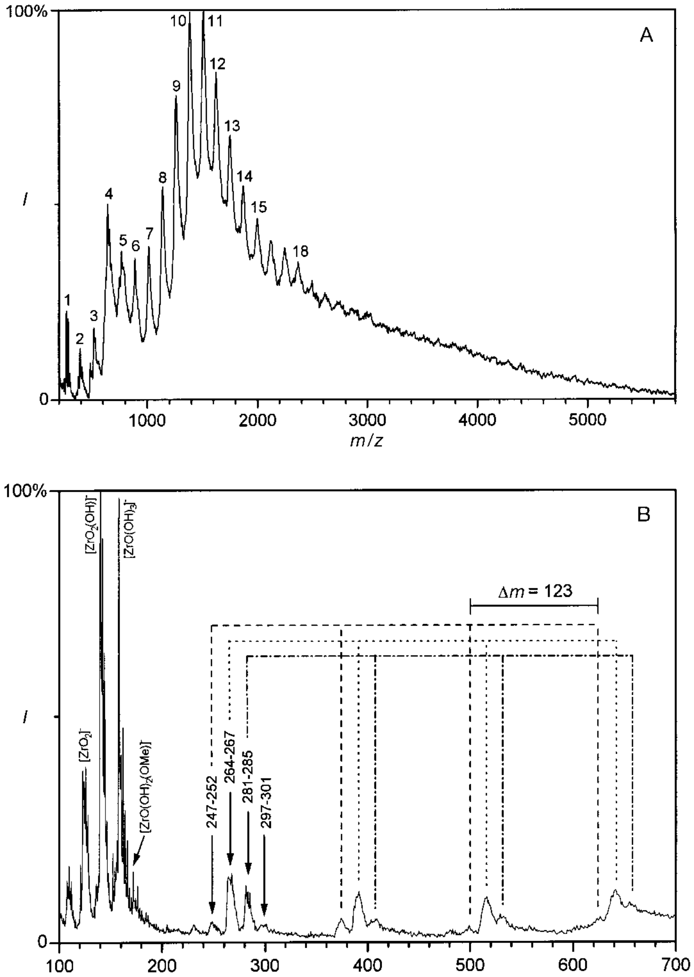


Figure 6. A) LILBID anion spectrum of a methanolic solution of $[Zr(OiPr)_4]$ at 25°C (molar ratio $Zr/H_2O/MeOH = 1/3/550$) in the mass range $m/z = 200-5800$. B) Expanded section of the same spectrum in the mass range $m/z = 100-700$. I = relative intensity.

the low-coordinate monomeric species $[ZrO(OH)_3]^-$ and $[ZrO(OH)_2(OMe)]^-$, respectively. As said above, no isopropylate-containing species are found due to a rapid ligand exchange with solvent molecules which are present in large excess. The group of signals in the range from $m/z = 250$ to 300 can be interpreted in terms of six- to eight-coordinate zirconium monomers with the proposed compositions $[ZrO(OH)(OMe)_2(OHMe)_2]^-$ ($M_r = 250.4$), $[ZrO(OMe)_3(OHMe)_2]^-$ ($M_r = 264.4$), $[ZrO(OH)(OMe)_2(OHMe)_3]^-$ ($M_r = 282.4$) and $[ZrO(OH)_2(OMe)(OHMe)_4]^-$ ($M_r = 300.4$). Following this interpretation, the mass spectra reflect the tendency of zirconium for higher coordination numbers than titanium.

The recorded peak distributions show a sharp increase in intensity from $m/z = 642-645$ onwards, followed by a decrease up to $m/z = 1140$ (Figure 6A). From there on the peak intensity rises dramatically and has its maximum in the range of $m/z = 1250$ to 1750. For samples which turned opaque during the measurement, another broad maximum usually with poor peak resolution could be found from $m/z = 3000$ up to 5000 (not shown). With the assignment made above for the monomers around $m/z = 250-300$, the maxima in the peak distribution correspond to a tetramer and to a decamer or undecamer, respectively.

An interesting fact is that in most of the experiments no peaks are supposed to belong to clusters with a charge higher than plus or minus one. From a colloidal point of view, this finding makes sense as the alcoholic solvent would less readily shield the highly charged ionic species which would then have increased probability of collision with countercharged species, resulting in precipitation of a solid product. This result is also in good agreement with structural chemistry, as small oligomers like tetramers would not readily carry a high charge in solution, because this would result in strong repulsion of the charge carriers which could easily lead to depolymerization.

Conclusion

For the first time it has been possible to analyze an evolving series of clusters under controlled hydrolysis conditions by applying a new mass spectrometric technique that allows the observation of weak interactions of molecules and ions in solution. In addition, it has been shown that controlled hydrolysis produces continuous series of clusters from monomers up to oligomers with a maximum weight of several thousand mass units. Distinctive maxima are observed in these peak series, which correspond to preferential cluster sizes in solution. However, the amount of energy transferred to the probe during the process of desorption is found to be sufficient to partly desolvate the oligomeric species.

When no water is added to the alkoxide solution, only small oligomers appear with low intensity. Samples with higher water contents showed aging effects which could be followed visually as clear solutions turned opaque. Accordingly, higher masses could then be detected in the spectra and lower masses disappeared. Mass spectrometric techniques are envisaged that allow the analysis of the desorbed oligomers in the gas phase (CID, MS^n), as well as structural modeling studies on the basis of these data and the possible compositions. Future experiments will show whether better mass resolution is possible through intermediate ion storage. We also believe that with the new mass spectrometric technique applied here, deeper insight into the earliest stages of crystallization is possible, and experiments with this aim are in progress.

Acknowledgments: We want to thank Dr. Jevgeni Avdiev and Dr. Wolfgang Kleinekofort for their contributions towards the development of LILBID, and Dipl.-Chem. Andreas Wattenberg for his collaboration. Financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Herrmann-Willkomm-Stiftung is gratefully acknowledged.

Received: March 25, 1998 [F 1065]

---

[1] D. C. Bradley, R. C. Mehrotra, D. P. Gaur, *Metal Alkoxides*, Academic Press, New York, **1978**.
[2] J. Livage, M. Henry, C. Sanchez, *Prog. Solid State Chem.* **1988**, *18*, 259.
[3] C. F. Baes, R. E. Mesmer, *The Hydrolysis of Cations*, Wiley, New York, **1976**.
[4] C. J. Brinker, G. W. Scherer, *Sol-Gel Science*, Academic, Boston, **1990**, p 99.
[5] H. Schmidt, H. Scholze, J. Kaiser, *J. Non-Crystalline Solids*, **1984**, *63*, 1.

[6] L. W. Kelts, N. J. Armstrong in *Better Ceramics Through Chemistry III* (Eds.: C. J. Brinker, D. E. Clark, D. R. Ulrich), Mat. Res. Soc. **1986**, p 27.

[7] V. W. Day, T. A. Eberspacher, W. G. Klemperer, C. W. Park, *J. Am. Chem. Soc.* **1993**, *115*, 8469.

[8] R. Schmid, A. Mosset, J. J. Galy, *Chem. Soc. Dalton Trans.* **1991**, 1999.

[9] J. Blanchard, S. Barboux-Doeff, J. Maquet, C. Sanchez, *New J. Chem.* **1995**, *19*, 929.

[10] T. Løver, W. Henderson, G. A. Bowmaker, J. M. Seakins, R. P. Cooney, *J. Mater. Chem.*, **1997**, *7*, 1553.

[11] F. Sobott, A. Wattenberg, W. Kleinekofort, A. Pfenninger, B. Brutschy, *Fresenius J. Anal. Chem.* **1998**, *360*, 745.

[12] F. Sobott, W. Kleinekofort, B, Brutschy, *Anal. Chem.* **1997**, *69*, 3587.

[13] A. Wattenberg, H.-D. Barth, B. Brutschy, *J. Mass Spectrom.* **1997**, *32*, 1350.

[14] W. Kleinekofort, J. Avdiev, B. Brutschy, *Int. J. Mass Spectrom. Ion Processes* **1996**, *152*, 135.

[15] W. Kleinekofort, A. Pfenninger, T. Plomer, C. Griesinger, B. Brutschy, *Int. J. Mass Spectrom. Ion Processes* **1996**, *156*, 195.

[16] M. Grätzel, *Acc. Chem. Res.* **1981**, *14*, 376.

[17] C. Kormann, D. W. Bahnemann, M. R. Hoffmann, *J. Phys. Chem.* **1988**, *92*, 5196.

[18] K. Schwetlick, *Organikum*, Deutscher Verlag der Wissenschaften, Berlin, **1990**, p 442.

[19] J. A. Ibers, *Nature* **1963**, *197*, 2947.