

NMR AND IR SPECTROSCOPIC EXAMINATION OF THE HYDROLYTIC STABILITY OF ORGANIC LIGANDS IN METAL ALKOXIDE COMPLEXES AND OF OXYGEN BRIDGED HETEROMETAL BONDS

D. HOEBBEL, T. REINERT, H. SCHMIDT

Institut für Neue Materialien, Im Stadtwald, Geb. 43, D-66123 Saarbrücken, Germany

ABSTRACT

IR and ^{13}C NMR investigations of the hydrolytic stabilities of the saturated and unsaturated β -keto ligands acetylacetonate (ACAC), ethylacetoacetate (EAA), allylacetoacetate (AAA), methacryloxyethyl-acetoacetate (MEAA) of the Al-, Ti- and Zr-butoxide complexes show a strong dependence on the type of the metal alkoxide and the structure of the organic ligands. The hydrolytic stabilities of the ligands decrease in the order Al->Zr->Ti-alkoxide and ACAC>AAA>EAA>MEAA. Sol-gel reactions of complexes having a weak ligand stability leads to a larger water consumption and to larger particle sizes in sols than those with stable ACAC ligands. Heterometal bonds, i.e. Si-O-Al, Si-O-Ti and Si-O-Zr, in the system diphenylsiloxanediol/metal alkoxide (complex) proved by ^{29}Si and ^{17}O NMR are hydrolysed to a different extent depending on the water amount, the type of the Si-O-M bond and the structure of the heterometal species. The degradation of the heterometal bonds leads to a separation of M-O-M and Si-O-Si bonds which can entail a decreased homogeneity of the materials at a molecular level.

INTRODUCTION

Metal alkoxides, their organic derivatives and oxygen bridged heterometal bonds play an important role in the synthesis of advanced inorganic-organic hybrid materials and heterometal polymers via the sol-gel process. These polymeric materials are used for e.g. optical and electronic devices, functional coatings and the preparation of ceramics and glasses [1-4].

A demand on advanced heterometal or hybrid materials is the high homogeneity in the distribution of the material components at a molecular scale, i.e. in the distribution of heterometal atoms and in the links between the organic and inorganic network structures [4,5]. A homogeneous heterometal structure of the materials is influenced by the condensation rate of the different metal alkoxides [6] and by the hydrolytic stability of the heterometal bond in the course of the sol-gel process [7]. Furthermore, the hydrolytic stability of the functional organic ligands of metal alkoxide complexes is a prerequisite for a continuous link of the inorganic and organic network via metaloxo groups [4,8]. So far, only insufficient knowledge exists about the hydrolytic stability of the organic ligands in metal alkoxide complexes (L-M bonds in Fig. 1) and of the heterometal bonds (M-O-M*) during the sol-gel process.

The objective of this work is the examination of the hydrolytic stabilities of reactive and non-reactive β -keto ligands in Al-, Ti- and Zr-alkoxide complexes and of the heterometal bonds, i.e. Si-O-Al, Si-O-Ti and Si-O-Zr, in the system diphenylsiloxanediol/metal alkoxide (complex) by means of IR, ^{13}C , ^{17}O and ^{29}Si NMR spectroscopy with regard to a more controlled sol-gel reaction leading to materials with defined structure and properties.

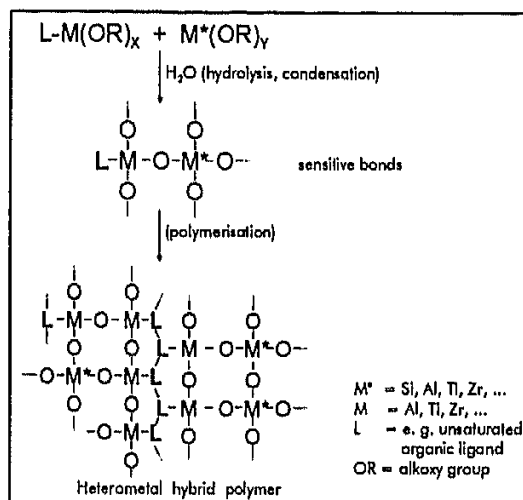


Figure 1. Scheme of the synthesis of a heterometal hybrid polymer by the sol-gel process

EXPERIMENT

Titanium-*n*-butoxide $\text{Ti}(\text{OBU}^n)_4$, aluminium-*sec*-butoxide $\text{Al}(\text{OBU}^s)_3$ and zirconium-*n*-butoxide $\text{Zr}(\text{OBU}^n)_4$ (84 % in *n*-butanol) were used for the complexation with acetylacetonate (ACAC), ethylacetoacetate (EAA) and the unsaturated β -ketoesters allylacetoacetate (AAA) and methacryloxyethylacetoacetate (MEAA) at a molar ratio metal(M):ligand(L)= 1:1. The metal alkoxide concentration in the solutions was kept at 1 M.

The hydrolysis of the $\text{Ti}(\text{OBU}^n)_3\text{L}$, $\text{Zr}(\text{OBU}^n)_3\text{L}$ and $\text{Al}(\text{OBU}^s)_2\text{L}$ complexes were carried out with a water/*n*-butanol solution at a hydrolysis ratio *h* (molar ratio water/OR)=1.

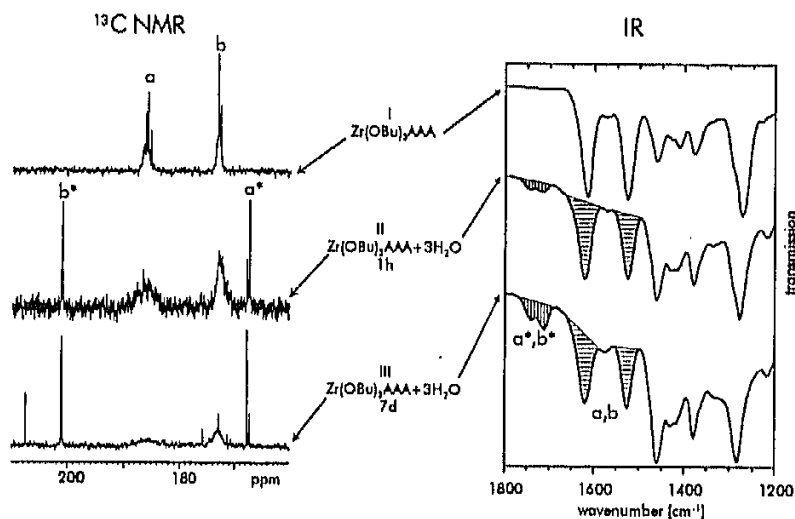


Figure 2. ^{13}C NMR and IR spectra of the $\text{Zr}(\text{OBU})_3\text{AAA}$ complex before and after hydrolysis at $h=1$

Fig.2 describes the changes in the IR and ^{13}C NMR spectra before and after the hydrolysis of the $\text{Zr}(\text{OBU})_3\text{AAA}$ complex. The appearance of IR absorptions at 1740 and 1715 cm^{-1} (a^* , b^*) with increased hydrolysis time indicates that AAA ligands are partially released from the complex by the addition of water. The ^{13}C NMR spectra of the $\text{Zr}(\text{OBU})_3\text{AAA}$ hydrolysate show sharp signals at $\delta=201(b^*)$ and $167\text{ ppm}(a^*)$ for the keto form of AAA which confirm the presence of released AAA. The semi-quantitative determination of the released ligands was made by integration of the respective absorptions bands in the IR spectra.

The Al-sec-butoxide complexes with AAA, EAA and MEAA and the Al-butoxyethoxide complex with ACAC as ligands show a high hydrolytic stability between 95 and 100 % within a reaction time of 7 days. The ACAC ligands of Zr- and Ti-butoxide complexes show a likewise high hydrolytic stability in accordance with the literature [10]. The other ligands of the Ti- and Zr-butoxide complexes (AAA, MEAA and EAA) show a decreased hydrolytic stability. About 15 % of the AAA and MEAA-ligands are released in hydrolysates of Zr-butoxide complexes after 1 day. The AAA-, EAA- and MEAA-ligands at Ti-butoxide complexes are released up to 50 % after the same time.

The different hydrolytic stability of the ligands at one and the same metal alkoxide is visible at the example of the Ti-butoxide complexes (Fig.4). The ligand stability decreases in the order $ACAC > AAA > EAA \geq MEAA$. Furthermore, the hydrolytic stability of one and the same ligand at different metal alkoxides decreases in the order $Al(OBu^s)_3 > Zr(OBu^s)_4 > Ti(OBu^s)_4$. The results make sure that the hydrolytic stability of the complex ligands is significantly influenced by the structure of the ligands and the type of the metal alkoxide.

A more detailed investigation of the hydrolysates of the metal alkoxide complexes [11] showed that the hydrolytically stable ligands of Al-butoxide complexes and the ACAC ligand of Ti- and Zr-butoxide complexes consume 0.3-0.4 mol water/OR at $h=1$ and complexes with unstable ligands (i.e. MEAA) 0.4-0.7 mol within 1 day. The additional amount of water is required for the splitting off and a partial chemical degradation of the unstable ligands. As consequence, additional OH/OR groups appear at the metal atoms which contribute to more extended condensation reactions of the complexes and to larger particles in the sols. Complexes with the stable ACAC ligand form in their hydrolysates particles with nearly time-independent sizes of about 3-4 nm within 7 d whereas the hydrolysates of unstable Zr/MEAA and Ti/MEAA complexes contain particles between 6 and 10 nm after 1 day hydrolysis.

The results show that only the complexes $Al(OBu^s)_2AAA$, $Zr(OBu^s)_3AAA$ and $Zr(OBu^s)_3MEAA$ have a sufficient hydrolytic stability of their unsaturated ligands. Therefore, these complexes should be suitable precursors for the preparation of sols with a defined particle size and for the synthesis of hybrid polymers with a high homogeneity in the interconnections between the inorganic and organic networks.

Formation and Characterisation of Heterometal Bonds

So far, it has not been sufficiently proved whether or not an optimal homogeneous distribution of the heterometal bonds at a molecular scale exists in the sol-gel derived products [12,13]. Recent NMR investigations [14] have indicated a remarkable degradation of heterometal Si-O-Ti bonds to Si-O-Si and Ti-O-Ti bonds during hydrolysis/condensation reactions. The objective of the second part of this work is to contribute to the detection and identification of heterometal Si-O-Al, Si-O-Ti and Si-O-Zr bonds and to a better characterisation of their hydrolytic stability by means of ^{29}Si and ^{17}O NMR spectroscopy. Diphenylsilanediol (DPSD) has been chosen as model compound because of its high stability towards condensation reactions and its difunctionality, which only allows chain-like or cyclic structures of the homo-condensation products and more simple structures in the hetero-condensation products with metal alkoxides as compared to those of multifunctional alkoxy silanes.

In general, a broad distribution of different siloxanes and heterometal species is detected in mixtures of DPSD with metal alkoxides or their complexes [15]. In the course of our examination of the reactions of DPSD with $Al(OBu^s)_3$, $Ti(OBu^s)_3ACAC$ and $Zr(OBu^s)_3ACAC$ we found special compositions of solutions in which mainly one structural type of Si atoms in the heterometal compounds prevails.

Fig.5-IV, V, VI shows the ^{29}Si and ^{17}O NMR spectra of the chosen systems with a molar

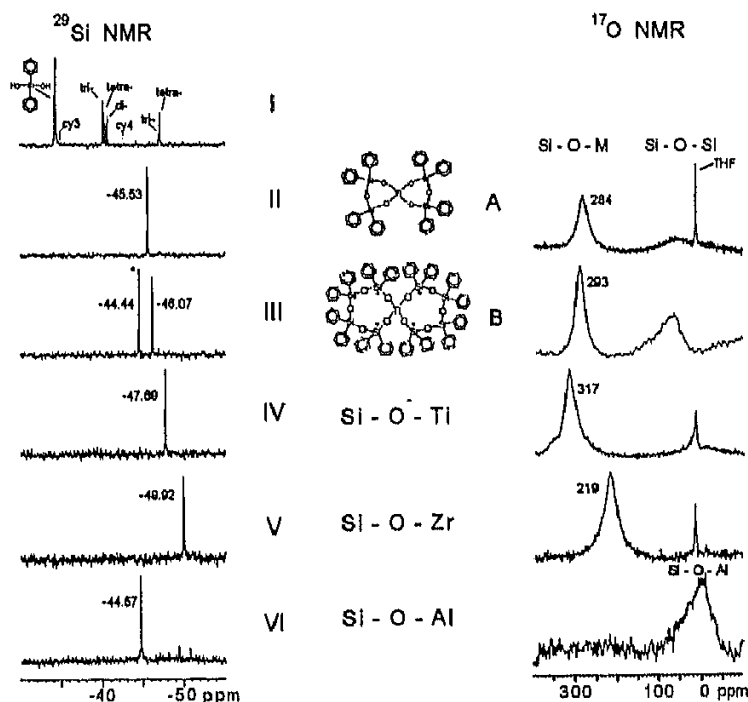


Figure 5. ^{29}Si and ^{17}O NMR spectra of a condensed DPSD solution (I), the spirocyclic titanosiloxanes A and B (II,III), and the reaction products of DPSD with $\text{Ti}(\text{O}^n\text{Bu}^n)_3\text{ACAC}$ (IV), $\text{Zr}(\text{O}^n\text{Bu}^n)_3\text{ACAC}$ (V) and $\text{Al}(\text{O}^n\text{Bu}^n)_3$ (VI) at a molar ratio 1:0.75.

ratio DPSD/0.75 metal alkoxide (complex) in THF solution. Two heterometal compounds of known structure, the spirocyclic titanosiloxanes $\text{Ti}[\text{O}_3\text{Si}_2(\text{C}_6\text{H}_5)_4]_2$ (A) and $\text{Ti}[\text{O}_5\text{Si}_4(\text{C}_6\text{H}_5)_8]_2$ (B), are included in the series. The structures of the monomolecular compounds in the solutions IV-VI are still unknown. For comparison in Fig.5-I the ^{29}Si spectrum of a condensed DPSD solution is shown. Practically, all expected signals of the condensation products (chain-like di-, tri- and tetrameric phenylsiloxanediol) are visible in the spectrum [15]. Additionally, the positions of the chemical shifts of the cyclic tri- (cy3) and cyclic tetrameric phenylsiloxanes (cy4) are marked in the spectrum. The ^{29}Si NMR spectra IV-VI show mainly a single signal with chemical shifts between $\delta = -44.4$ and -49.9 ppm. The chemical shift of the signals does not correspond with those of the condensed siloxanes in Fig.5-I. From this it can be concluded that the silicon atoms are bonded in monomolecular, probably, heterometal species.

Additionally, ^{17}O NMR spectra were recorded from the solutions II-VI to confirm the existence of heterometal bonds (Fig.5). The spectra of the ^{17}O labelled DPSD/ $\text{Ti}(\text{O}^n\text{Bu}^n)_3\text{ACAC}$ and DPSD/ $\text{Zr}(\text{O}^n\text{Bu}^n)_3\text{ACAC}$ solutions show intensive signals at $\delta = 317$ and 219 ppm, resp., which confirm the presence of Si-O-Ti and Si-O-Zr bonds [14] (Fig.5-IV,V). The chemical shift of the oxygen atoms in Si-O-Al bonds is expected in the region $\delta = 30$ to 80 ppm [16]. The detected broad signal in the spectrum of the DPSD/ $\text{Al}(\text{O}^n\text{Bu}^n)_3$ solution between $\delta = 0$ - 70 ppm overlaps with the region in which the signals of the oxygen atoms in Si-O-Si and Si-OH bonds appear. Therefore, an exact identification of the Si-O-Al bond cannot be made.

Hydrolytic Stability of the Heterometal Bonds

Fig.6 shows as an example the ^{29}Si and ^{17}O NMR spectra of the ^{17}O labelled spirocyclic compound A before and after hydrolysis in THF solution at $\text{H} = 9$.

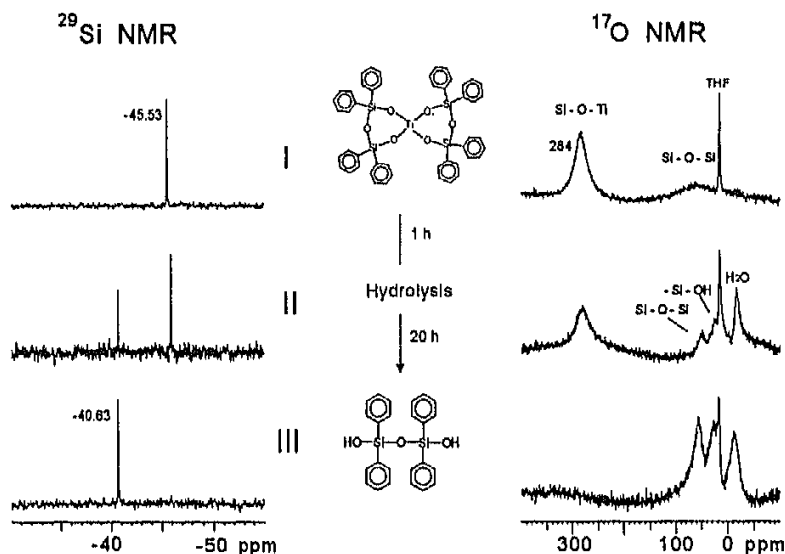


Figure 6. ^{29}Si and ^{17}O NMR spectra of the spirocyclic titanasiloxane A before and after hydrolysis at $H=9$

It follows from the ^{29}Si spectra that the spirocyclic structure is degraded to the tetraphenyl-disiloxanediol within about 20 h. The typical signal of Si-O-Ti bonds at $\delta=285$ ppm disappears in the ^{17}O spectrum after 24 h in favour of signals caused by oxygen atoms in Si-O-Si and SiOH bonds of the disiloxanediol.

The results of the examination of the hydrolytic stability of the Si-O-Al, Si-O-Ti and Si-O-Zr bonds at molar ratio $H=1$ and 6 by means of ^{29}Si and ^{17}O NMR are summarised in Fig. 7.

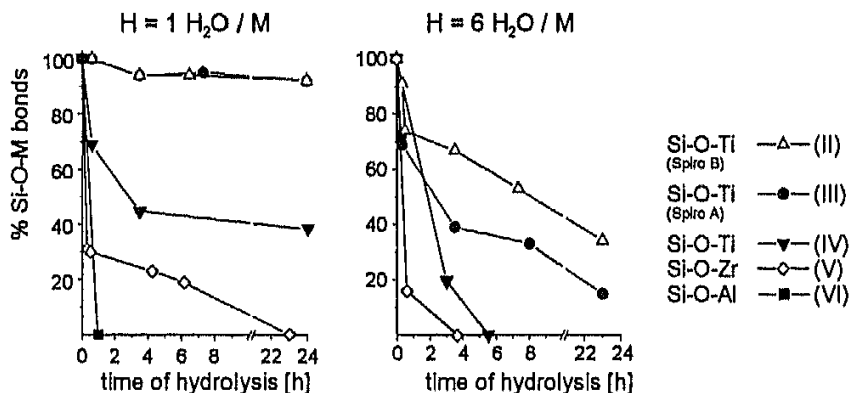


Figure 7. Hydrolytic stability of the Si-O-M bonds in the spirocyclic titanasiloxanes (A,B) and in solutions of DPSD/0.75{Ti(OBuⁿ)₃ACAC (IV) or Zr(OBuⁿ)₃ACAC (V) or Al(OBuⁿ)₃ (VI)} at $H=1$ and 6

The results show that already at $H=1$ a complete hydrolysis of the Si-O-Al bonds occurs within 1 h. At the same time of hydrolysis about 70 % of the Si atoms in Si-O-Zr bonds and 30 % in Si-O-Ti bonds are hydrolysed. The spirocyclic titanasiloxanes A and B show in contrast to the Si-O-Al, Si-O-Ti and Si-O-Zr species in the solutions IV-VI a high hydrolytic stability of its Si-O-Ti bonds. A larger water amount ($H=6$) leads to significantly stronger degradation reactions. The Si-O-Ti and Si-O-Zr bonds in the solutions IV and V are completely hydrolysed within 5 h. The Si-O-Ti bonds of the spirocyclic structures A and B are hydrolysed to 60 and 40 %, resp., after 5 h. A complete hydrolysis of the Si-O-Ti bonds in the compound (A) only occur at $H=9$ after 20 h (see Fig.6). The results show a decreased stability of the Si-O-M bonds in the solutions IV-VI in the order Si-O-Ti>Si-O-Zr>Si-O-Al. Furthermore, the

results show that the heterometal Si-O-Ti bonds in the spirocyclic structures are considerably more stable towards hydrolysis than those of the solution IV.

CONCLUSIONS

1. The significant differences in the hydrolytic stability of the organic ligands (β -diketone and β -ketoester) in Al-, Ti- and Zr-butoxide complexes are to be taken into consideration for more controlled syntheses of sols with a defined particle size, of organically modified polymers and of inorganic-organic hybrid polymers. A highly hydrolytically unstable ligand is connected with additional condensation reactions of the MOR/OH groups and leads to larger particle sizes in the sols. Furthermore, the instability of unsaturated ligands can lead to incomplete connections between inorganic and organic networks in the hybrid polymers.

2. The heterometal Si-O-Al, Si-O-Ti and Si-O-Zr bonds in co-condensation products of diphenylsilanediol with Al-butoxide and Ti- and Zr-butoxide complexes are already degraded to a great extent at low water amounts ($H=1$). The Si-O-Ti bonds in spirocyclic titanasiloxanes show a considerably higher hydrolytic stability at identical hydrolysis conditions. The results lead to the conclusion that the hydrolytic stability of the Si-O-Ti bonds is strongly influenced by the structure of the heterometal compounds. The instability of heterometal bonds can lead to a separation of Si-O-Si and M-O-M bonds rich regions, which lowers the homogeneity of the materials at a molecular scale.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Volkswagen-Stiftung and the Fonds für die Chemische Industrie for the financial support and thank Prof. E. Arpac, Akdeniz-University Antalya, Turkey, for helpful discussions, Ms S. Carstensen for preparative work and Dipl.-Chem. M. Nacken for NMR measurements.

REFERENCES

1. R.C. Mehrotra, Chemistry, Spectroscopy and Applications of Sol-Gel Glasses, edited by R. Reisfeld, C.K. Jorgensen (Springer-Verlag, Berlin, Heidelberg, 1992).
2. C.J. Brinker, D.E. Clark, D.R. Ulrich, Better Ceramics Through Chemistry, (Elsevier Science Publishers, New York, 1984).
3. H. Schmidt, *J. Non-Cryst. Solids* **100**, 51-64 (1988).
4. U. Schubert, N. Hüsing, A. Lorenz, *Chem. Mater.* **7**, 2010-2027 (1995).
5. C.J. Brinker and C.W. Scherer, Sol-Gel Science, (Academic Press, New York, 1990).
6. P.J. Dirken, M.E. Smith, H.J. Whitfield, *J. Phys. Chem.* **99**, 395 (1995).
7. J. Jonas, A.D. Irwin and J.S. Holmgren, in Ultrastructure Processing of Advanced Materials, edited by D.R. Uhlmann and D.R. Ulrich (J. Wiley, 1992) pp. 303-314.
8. C. Sanchez, F. Ribot, *New J. Chem.* **18**, 1007-1047 (1994).
9. V.A. Zeitler and C.A. Brown, *J. Am. Chem. Soc.* **79**, 4618-4621 (1957).
10. P. Toledano, M. In, C. Sanchez, *C.R. Acad. Sci. Paris* **313**, 1247 (1991).
11. D. Hoebbel, T. Reinert, H. Schmidt, E. Arpac, to be published (1996).
12. H. Schmidt and B. Seiferling, *Mat. Res. Soc. Symp. Proc.* **73**, 739-750 (1986).
13. C.L. Schutte, J.R. Fox, R.D. Boyer and D.R. Uhlmann, in Ultrastructure Processing of Advanced Materials, edited by D.R. Uhlmann and D.R. Ulrich (J. Wiley, 1992) pp. 95-102.
14. F. Babonneau, *Mat. Res. Soc. Symp. Proc.* **346**, 949-960 (1994).
15. D. Hoebbel, T. Reinert, H. Schmidt, *J. Sol-Gel Sci. Technol.* in press (1996).
16. G.A. Pozarnsky, A.V. McCormick, *J. Non-Cryst. Solids* **190**, 212-225 (1995).