

# ULTRASTRUCTURE PROCESSING OF ADVANCED CERAMICS

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## A PREDICTIVE MODEL FOR INORGANIC POLYMERIZATION REACTIONS

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### 1. INTRODUCTION

The sol-gel process offers new approaches to the preparation of glasses and ceramics. Starting from molecular precursors comprising a sol, a solid network is obtained through hydroxylation-condensation reactions. One of the main advantages of this method comes from the fact that it is based on chemistry.<sup>1,2</sup> A deeper knowledge of the chemical reactions involved in inorganic polymerization would allow better control of the ultrastructure processing of glasses and ceramics.<sup>3,4</sup> Many reports have been published during the last few years, describing the role of catalysts or chemical additives.<sup>5,6</sup> Many techniques have been used in order to get information on each step of the process.<sup>7</sup> Even quantum chemistry is now used to explain some of the observed mechanisms.<sup>8</sup>

However, there is a need for some theoretical models that could be used to predict, or at least to describe, the chemical reactions involved in the sol-gel process. Such models should be completely valid, all the way from the molecular precursor to the colloidal state and the solid network. It should also be based on simple ideas as well as being easy to handle, thus requiring no huge computer.

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It should at least be quantitative enough to be able to predict the chemical reactivity of the species involved in the process.

In this chapter, we shall describe a model based on the electronegativity concept introduced by L. Pauling as well as on the principle of electronegativity equalization suggested by R. T. Sanderson.<sup>9</sup> This model will allow calculation of a partial charge distribution from which the chemical reactivity can be predicted.

## 2. ELECTRONEGATIVITY EQUALIZATION AND PARTIAL CHARGE DISTRIBUTION

When two atoms combine, an electron transfer occurs that mainly depends on the electronegativity difference between the atoms. The atom, initially higher in electronegativity, attracts electrons. It must acquire partial negative charge and therefore decrease in its attraction for electrons. Thus, its electronegativity decreases. The other atom acquires partial positive charge and its electronegativity increases. Electron transfer should then stop when both electronegativities become equal. A principle of "electronegativity equalization" was stated by R. T. Sanderson<sup>9</sup> as follows: "When two or more atoms initially different in electronegativity combine, they adjust to the same intermediate electronegativity in the compound."

It has been shown that the electronegativity actually corresponds to the electronic chemical potential.<sup>10</sup> Therefore, the electronegativity equalization is simply the well-known thermodynamic principle of chemical potential equalization, which describes an equilibrium state.

The main consequence of this analysis is that the electronegativity of an atom should not be constant. It varies with the partial charge  $\delta_i$  of the atom. A relationship between the electronegativity,  $\chi_i$ , and  $\delta_i$  has to be discerned.

It is usually assumed that the electronegativity of an atom changes linearly with its charge<sup>12</sup>:

$$\chi_i = \chi_i^0 + \eta_i \delta_i \quad (1)$$

where  $\chi_i^0$  is the electronegativity of the neutral atom, and  $\eta_i$  corresponds to its hardness in the frame of Pearson's model.<sup>13</sup>

Following Sanderson, we propose<sup>11,14</sup>:

$$\eta_i = k\sqrt{\chi_i^0} \quad (2)$$

where  $k$  is a constant that depends on the electronegativity scale. In the case of Pauling electronegativities estimated according to the Allred-Rochow formula<sup>15,16</sup> we have shown that  $k = 1.36$ .<sup>14</sup>

Total charge conservation,  $Z = \sum p_i \delta_i$ , where  $p_i$  corresponds to the stoichiometry of the atom  $X_i$  in the compound, together with Eqs. (1) and (2), leads

to the two basic formulas of our model, giving the mean electronegativity:

$$\bar{\chi} = \frac{\sum_i p_i \sqrt{\chi_i^0} + 1.36z}{\sum_i p_i \sqrt{\chi_i^0}} \quad (3)$$

For a diatomic molecule AB, the mean electronegativity actually corresponds to the geometric mean of both electronegativities:

$$\bar{\chi}_{AB} = (\chi_A^0 \cdot \chi_B^0)^{1/2}$$

The partial charge distribution is given by

$$\delta_i = \frac{\bar{\chi} - \chi_i^0}{1.36\sqrt{\chi_i^0}} \quad (4)$$

Equation (4) can also be written as

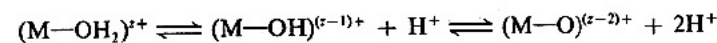
$$\delta_i = S_i(\bar{\chi} - \chi_i^0) \quad (5)$$

where  $S_i = 1/1.36\sqrt{\chi_i^0} = 1/\eta_i$  corresponds to the so-called softness of the atoms  $X_i$ .<sup>17</sup>

## 3. INORGANIC PRECURSORS

### 3.1. Charge-pH Diagram

When an inorganic salt is dissolved into water, the cation becomes solvated by the dipolar water molecules, giving rise to hydrated species  $M^{z+}(\text{OH}_2)_n$ , where  $z$  is the charge of the cation and  $n$  is its coordination number. An electron transfer actually occurs in the  $M-\text{OH}_2$  bonds, from the highest occupied  $3a_1$  molecular orbital of  $\text{H}_2\text{O}$  toward the empty orbitals of the cation. This draws away electrons from the  $\text{O}-\text{H}$  bonds and weakens them. Depending on this  $\sigma$  transfer, we may have the following equilibrium:



The nature of the species that can be found in an aqueous solution depends mainly on the oxidation state  $Z$  of the cation ( $\text{Mn}^{2+}(\text{H}_2\text{O})_6-\text{MnO}_4^-$ ) and the pH ( $\text{Cr}^{3+}(\text{H}_2\text{O})_6-\text{Cr}(\text{OH})_4^-$ ).<sup>18</sup> Therefore, the well-known "charge-pH" diagram gives pH intervals in which  $\text{H}_2\text{O}$ ,  $\text{OH}^-$ , or  $\text{O}^{2-}$  are common ligands to a central cation of oxidation state  $Z$ .<sup>19</sup> Such a diagram may be very useful for predicting the ionic species in aqueous solution. Moreover, the partial charge model will give quantitative information.

## 3.2. Ionic Species

## 3.2.1. Cationic Species

When dissolved in water, a cation is strongly hydrated by water molecules, giving rise to  $(M(OH)_n)^{z+}$  species. Because of the  $\sigma$  transfer, O-H bonds can be broken, and water molecules are ionized according to



The coordinated water molecules then behave as a stronger acid than do solvent water molecules, and the pH of the aqueous solution decreases. This deprotonation process will go on as long as  $\delta(OH)$  remains positive, because negatively charged OH groups would attract  $H^+$  and prevent deprotonation. The reaction will then stop when  $\delta(OH) = 0$ , giving rise to stable ionic species,  $[M(OH)_p(OH_2)_{n-p}]^{(z-p)+}$ . The corresponding value of  $p$  can be estimated with the partial charge model.

Charge conservation leads to

$$p = \frac{z - n\delta(H_2O) - \delta(M)}{1 - \delta(H_2O)}, \quad \text{when } \delta(OH) = 0$$

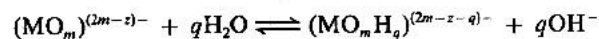
The mean electronegativity is given by  $\bar{\chi} = \bar{\chi}(OH) = 2.71$ . The partial charges  $\delta(H_2O)$  and  $\delta(M)$  can be calculated from Eq. (4), leading to

$$p = 1.45z - 0.45n - \frac{1.07(2.71 - \chi^o(M))}{\sqrt{\chi^o(M)}}$$

The quantity  $p$  can be easily determined if we know the oxidation state,  $Z$ , of the cation, its coordination number,  $n$ , and its electronegativity,  $\chi^o(M)$ . Some results are reported in Table 1. They give the cationic species that can be found in a dilute solution at very low pH. For instance, V(V) will give  $VO_2^+$  ions, Ti(IV) will give  $TiO^{2+}$  ions, and Fe(II) will give  $Fe^{2+}$  ions.

## 3.2.2. Anionic Species

Let us consider now a high-valence cation ( $z > 4$ ) giving rise to nonprotonated anionic species  $(MO_m)^{(2m-z)-}$ . These negatively charged species will be able to attract protons from the surrounding water molecules:



Protonation will go on as long as  $\delta(H) < 0$ . The reaction stops when  $\delta(H) = 0$ .

TABLE 1. Cationic and Anionic Species That Can Be Found in Dilute Acid or Basic Aqueous Solutions

$M^{z+}$	$\chi^o$	$n$	$p$	Theoretical Formula	Experimental Formula	$m$	$q$	Theoretical Formula	Experimental Formula
$V^{5+}$	1.59	6	3.6	$[V(OH)_4(OH_2)_2]^+$	$[VO_2(OH_2)_4]^+$	4	1.1	$[VO_2(OH)]^{2-}$	$[VO_2(OH)]^{2-}$
$Si^{4+}$	1.74	4	3.3	$Si(OH)_4$	$Si(OH)_4$	4	2.0	$[SiO_2(OH)_2]^{2-}$	$[SiO_2(OH)_2]^{2-}$
$Ti^{4+}$	1.32	6	1.9	$[Ti(OH)_2(OH_2)_4]^{2+}$	$[TiO(OH)_2]^{2+}$	6	5.2	$[Ti(OH)_6]^{-}$	—
$Zr^{4+}$	1.29	8	0.9	$[Zr(OH)(OH_2)_7]^+$	$[Zr(OH)(OH_2)_7]^+$	5	3.8	$[ZrO(OH)_4]^{2-}$	$[Zr(OH)_4]^{-}$
$B^{3+}$	2.02	3	2.5	$B(OH)_3$	$B(OH)_3$	4	2.8	$[BO_2(OH)_2]^{2-}$	$B(OH)_4^{-}$
$Al^{3+}$	1.47	6	0.5	$[Al(OH)(OH_2)_5]^+$	$[Al(OH)(OH_2)_5]^+$	4	3.2	$[AlO(OH)_3]^{2-}$	$Al(OH)_4^{-}$
$Fe^{3+}$	1.72	6	0.8	$[Fe(OH)(OH_2)_5]^+$	$[Fe(OH)(OH_2)_5]^+$	4	3.0	$[FeO(OH)_3]^{2-}$	$Fe(OH)_4^{-}$
$Fe^{2+}$	1.72	6	<0	$[Fe(OH)_6]^{2+}$	$[Fe(OH)_6]^{2+}$	4	4.0	$[Fe(OH)_4]^{2-}$	$Fe(OH)_4^{-}$

The partial-charge model gives

$$q = 2m - z + m\delta(O) + \delta(M)$$

with mean electronegativity

$$\bar{\chi} = \chi^{\circ}(H) = 2.1$$

Thus, one obtains

$$q = 1.45m - z + \frac{0.74(2.1 - \chi^{\circ}(M))}{\sqrt{\chi^{\circ}(M)}}$$

Results of our calculations are reported in Table 1. They give the anionic species that can be found in dilute aqueous solutions at high pH. V(V), for instance, will give  $VO_3(OH)^{2-}$  species, Si(IV) will give  $SiO_2(OH)_2^{2-}$ , and Fe(II) will give  $Fe(OH)_4^{2-}$ .

### 3.2.3. Condensed Species

Precipitation in an aqueous solution occurs, at room temperature, at a pH corresponding to the point of zero charge. Around this pH, electrostatic repulsions do not prevent collisions anymore, and highly condensed species (gels or precipitates) can be obtained.

Condensation of cationic species  $[M(OH)_p(OH_2)_{n-p}]^{(z-p)+}$  occurs when the pH is increased by adding  $OH^-$  ions. Precipitation should be observed at the point of zero charge when  $p = z$ .

Condensation of anionic species,  $(MO_nH_q)^{(2n-z-q)-}$ , can be obtained by decreasing the pH. Precipitation may occur at the point of zero charge corresponding to  $q = 2n - z$ .

In both cases, the rough formula of the precursor for condensation corresponds to the neutral species  $(MO_nH_{2n-z})^0$ .

Condensation occurs through olation or oxolation. In both cases, the condensation process starts with the nucleophilic addition of a negative OH group onto a positive metal ion. No condensation is observed when  $\delta(OH) > 0$ . We can therefore calculate a critical value corresponding to  $\delta(OH) = 0$ . The partial-charge model leads to

$$\delta(M) + n\delta(O) + (2n - z)\delta(H) = 0$$

given

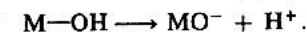
$$\bar{\chi} = \bar{\chi}(OH) = 2.71$$

then

$$\sqrt{\chi_A^{\circ}} = 0.21(n - z) + [2.71 + 0.04(z - n)^2]^{1/2}$$

We then have two possibilities:

1.  $\chi_M^{\circ} > \chi_A^{\circ}$ ,  $\delta(OH) > 0$ . In this case, no condensation will be observed. The proton within the OH bond has a very high positive charge. A spontaneous ionization occurs in water and the species behave like an acid:



2.  $\chi_M^{\circ} < \chi_A^{\circ}$ ,  $\delta(OH) < 0$ . Condensation is now possible. Highly condensed species (gels or precipitates) will be obtained at a pH close to the point of zero charge. Less condensed species, known as *polyanions*, will be obtained above this point.

However,  $\delta(OH) < 0$  is not the only condition for condensation. Spontaneous basic ionization will also occur in water if  $\delta(OH)$  is close to  $-1$ :



Such an ionization process will be possible if  $\delta[M(OH)_{z-1}] = +1$ , giving rise to another critical point:

$$\delta(M) + (z - 1)\delta(OH) = +1$$

$$\bar{\chi} = \chi(H_2O) = 2.49$$

$$\sqrt{\chi_B^{\circ}} = -0.14(z + 4) + [2.49 + 0.02(z + 4)^2]^{1/2}$$

We again have two possibilities:

1.  $\chi_M^{\circ} < \chi_B^{\circ}$ . No condensation is observed. A spontaneous ionization occurs in water and the species behaves like a base:  $M-OH \longrightarrow M^+ + OH^-$ . This critical electronegativity is, however, very low; only alkaline cations behave that way.

TABLE 2. The Three Classes of Elements That, Depending on Their Electronegativity Can Give Rise to Basic Aquo-ions, Acid Oxy-ions or Condensed Species

z	Aquo-ions	$\chi_B^{\circ}$	Condensed Species	$\chi_A^{\circ}(n)$	Oxy-ions
1	Li, Na, K	1.04	Ag, Cu, Au	3.50(2)	—
2	—	0.96	Hg, Cd, Co, Cu, Ni, Zn	2.71(2)	—
3	—	0.89	B, Cr, Fe, Al	2.10(2)	—
4	—	0.83	Si, Ge, Sn, Ti, Zr	2.71(4)	S
5	—	0.77	Sb, V, Nb, Ta	2.10(4)	N, Cl, P, As
6	—	0.72	Cr, Mo, W	1.63(4)	S, Se
				2.71(6)	
7	—	0.68	—	1.28(4)	Cl, Mn
				2.10(6)	

2.  $\chi_M^o > \chi_B^o$ . Condensation is now possible. Highly condensed species (gels or precipitates) will be obtained at a pH close to the point of zero charge. Less condensed species, known as *polycations*, will be obtained below this point. Results of our analysis are gathered in Table 2. They show that the elements of the periodic table can be divided into three classes:

*Class I:*  $\chi_M^o > \chi_A^o$ . No condensation is observed. Aqueous species give oxy-ions, which behave like acids.

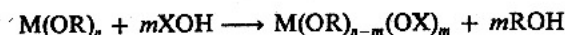
*Class II:*  $\chi_M^o < \chi_B^o$ . No condensation is observed. Aqueous species give aquo-ions, which behave like bases.

*Class III:*  $\chi_A^o < \chi_M^o < \chi_B^o$ . These cations can lead to highly condensed species and therefore could give rise to gel formation or precipitation.

#### 4. METAL-ORGANIC PRECURSORS

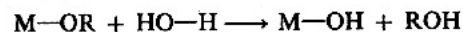
##### 4.1. Chemical Reactivity of Alkoxides $M(OR)_n$

Alkoxides  $M(OR)_n$  react with X-OH species according to:



Depending on the chemical nature of X, this reaction corresponds to:

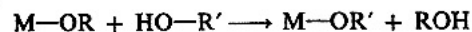
1. Hydrolysis of an alkoxide (X = H):



2. A condensation reaction (X = M):

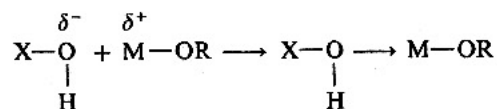


3. The chemical modification of the alkoxide (X = R'):



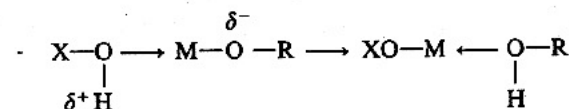
In all cases, the chemical reaction could be described according to a three-step process as follows:

1. The nucleophilic addition of a negatively charged OH group onto a positively charged metal atom M:



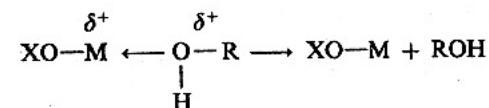
This step requires  $\delta(OH) < 0$  and  $\delta(M) > 0$ .

2. A prototropic reorganization, within the transition state, of a positively charged proton from the entering ligand (XOH) toward a negatively charged oxygen of an adjacent OR group:



This step requires  $\delta(OR) < \delta(H)$ .

3. The departure of the protonated (ROH) species:



Such an ROH can only be removed if it is positively charged, that is,  $\delta(ROH) > 0$ .

The whole process therefore depends on the partial charge distribution. It requires three successive conditions:

$$\delta(M) > 0, \quad \delta(OR) < \delta(H), \quad \delta(ROH) > 0$$

If one of these conditions is not fulfilled, the corresponding step becomes a limiting step for the overall reaction.

The partial-charge model leads to an estimate of the charge distribution among the different compounds and transition states. It should therefore be possible to predict how chemical reactions occur. We shall illustrate this with some examples based on  $Si(OR)_4$  and  $Ti(OR)_4$  precursors.

According to our model, the softness of a  $C_nO_mH_p$  group, G, will be given by

$$S(G) = \frac{n\sqrt{\chi_C^o} + m\sqrt{\chi_O^o} + p\sqrt{\chi_H^o}}{1.36}$$

The mean electronegativity of this group is

$$\bar{\chi}(G) = \frac{(n\sqrt{\chi_C^o} + m\sqrt{\chi_O^o} + p\sqrt{\chi_H^o})/S(G)}{1.36}$$

The partial charge can then be computed:

$$\delta(G) = S(G)[\bar{\chi} - \bar{\chi}(G)]$$

All our calculations are based on the following electronegativities:<sup>15</sup>

$$\chi_C^o = 2.5, \quad \chi_O^o = 3.5, \quad \chi_H^o = 2.1, \quad \chi_{Si}^o = 1.74, \quad \text{and} \quad \chi_{Ti}^o = 1.32$$

4.2. Hydrolysis of Ti(OR)<sub>4</sub> and Si(OR)<sub>4</sub>

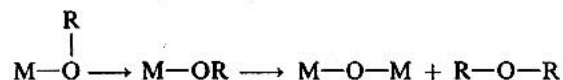
The first step of the hydrolysis of alkoxides is a nucleophilic addition on the metal atom. It will therefore depend mainly on the positive partial charge of this atom. The higher it is, the easier hydrolysis will be.

Table 3 gives the mean electronegativity of some typical alkoxides, together with the hydrolysis rate of Si(OR)<sub>4</sub>, as measured by Aelion and Akerman.<sup>20</sup> An analysis of these results indicates:

1. The positive charge  $\delta(M)$  decreases when the number of carbon atoms in the alkyl chain increases. The sensitivity toward hydrolysis should then decrease, in agreement with experimental observations. This is especially valid for the first terms of the series (R = Me, Et, Pr).
2. The positive charge of titanium is always almost twice that of silicon. Therefore, the hydrolysis rate of Ti(OR)<sub>4</sub> should always be much larger than that of the corresponding Si(OR)<sub>4</sub>.

4.3. Condensation of Ti(OR)<sub>4</sub> and Si(OR)<sub>4</sub>

Table 3 also shows that the negative charge on OR groups is larger in Ti(OR)<sub>4</sub> than in Si(OR)<sub>4</sub>. These groups will then have a greater tendency to coordinate to a positive Ti atom. Polymerization may then occur through the formation of OR bridges. As a matter of fact, according to the literature, silicon alkoxides are always monomers, whereas primary titanium alkoxides such as Ti(OBu)<sub>4</sub> give oligomers.<sup>21</sup> A more detailed analysis shows that a condensation process with the elimination of an ether molecule is not possible.



Step 1 would require the transfer of a negatively charged carbon atom onto a negatively charged oxygen atom. However,  $\delta(\text{R}_2\text{O}) > 0$  in the transition state; therefore an ether molecule could be removed through pyrolysis.<sup>20</sup>

TABLE 3. Charge Distribution in Ti(OR)<sub>4</sub> and Si(OR)<sub>4</sub> Alkoxides

R	Ti(OR) <sub>4</sub>			Si(OR) <sub>4</sub>			$k \times 10^2 M^{-1} \text{sec}^{-1} [\text{H}^+]^{-1}$
	$\bar{\chi}$	$\delta(\text{OR})$	$\delta(\text{Ti})$	$\bar{\chi}$	$\delta(\text{OR})$	(Si)	
Me	2.34	-0.16	+0.65	2.37	-0.09	+0.36	—
Et	2.30	-0.16	+0.63	2.32	-0.08	+0.32	5.1
Pr	2.28	-0.15	+0.61	2.29	-0.08	+0.31	—
Bu	2.27	-0.15	+0.61	2.28	-0.08	+0.30	1.9
Am	2.26	-0.15	+0.60	2.27	-0.07	+0.30	—
Hx	2.26	-0.15	+0.60	2.26	-0.07	+0.29	0.83

TABLE 4. Charge Distribution in the Transition State Corresponding to a Condensation Reaction Between Two Hydrolyzed Alkoxide Molecules, M(OR)<sub>3</sub>(OH)

Formula	$\bar{\chi}$	$\delta(\text{OH})$	$\delta(\text{H})$	$\delta(\text{PrOH})$	$\delta(\text{H}_2\text{O})$	$\delta(\text{M})$
Ti <sub>2</sub> (OPr) <sub>6</sub> (OH) <sub>2</sub>	2.29	-0.38	+0.10	+0.02	-0.28	+0.62
Si <sub>2</sub> (OPr) <sub>6</sub> (OH) <sub>2</sub>	2.31	-0.36	+0.11	+0.12	-0.25	+0.32

Let us consider hydrolyzed species such as M(OR)<sub>3</sub>(OH). Two condensation processes may occur:

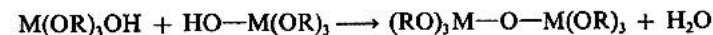
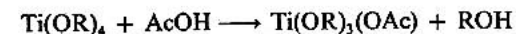


Table 4 gives the charge distribution calculated in the transition states M<sub>2</sub>(OR)<sub>6</sub>(OH)<sub>2</sub> for M = Si, Ti and R = Pr = C<sub>3</sub>H<sub>7</sub>. In both cases, charge conditions required for steps 1 and 2 [respectively  $\delta(\text{OH}) < 0$ ,  $\delta(\text{M}) > 0$ , and  $\delta(\text{H}) > 0$ ] are fulfilled. Step 3, however, requires the elimination of a positively charged molecule. Table 4 shows that, in both cases, the ROH molecule is positively charged, while the water molecule is negatively charged. Therefore condensation of hydrolyzed alkoxides will proceed via the elimination of alcohol molecules rather than water molecules.

4.4. Chemical Modification of Ti(OR)<sub>4</sub>

Acetic acid reacts with titanium alkoxides, giving rise to a new molecular precursor<sup>22</sup>:



As previously described, the first step of such a reaction is a nucleophilic addition. The charge conditions,  $\delta(\text{OH}) < 0$  and  $\delta(\text{Ti}) > 0$ , are fulfilled and the addition is possible. Then the question arises, which molecule will be released during the third step, (AcOH) or (ROH)? The charge distribution calculated for the two transition states leads to:

$$\text{Ti}(\text{OPr})_4(\text{AcOH}): \quad \bar{\chi} = 2.31, \quad \delta(\text{AcOH}) = -0.7$$

$$\text{Ti}(\text{OPr})_3(\text{OAc})(\text{PrOH}): \quad \bar{\chi} = 2.31, \quad \delta(\text{PrOH}) = +0.1$$

The positive alcohol molecule will then be removed, while the negative acetate group will remain bonded to titanium, in agreement with experimental observations.<sup>22</sup>

The question now arises as to whether the partial-charge model could provide

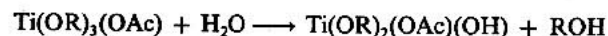
any information on the hydrolysis reaction of this new species. Referring to our mechanism, hydrolysis begins via a nucleophilic addition:



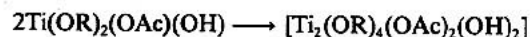
Proton transfer occurs within this transition state, and the more positively charged molecule will be removed during the third step. Calculations performed on  $\text{Ti}(\text{OPr})_3(\text{OAc})(\text{OH}_2)$  give

$$\bar{\chi} = 2.33, \delta(\text{PrOH}) = +0.2, \delta(\text{AcOH}) = -0.6$$

showing that OR groups are first removed in agreement with our own observations<sup>22</sup>:



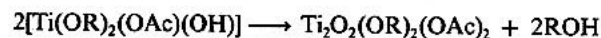
Condensation of this monohydrolyzed species leads to the following transition state:



Calculations performed with  $\text{R} = \text{Pr}$  lead to:

$$\bar{\chi} = 2.34, \delta(\text{PrOH}) = +0.3, \delta(\text{AcOH}) = -0.6$$

showing that alcohol will be removed rather than acetic acid:



Some acetate groups may then remain in the gel and even in the xerogel. They will be removed upon pyrolysis only, in agreement with our observations.<sup>22</sup>

## 5. CONCLUSIONS

We have tried to show that the partial-charge model could provide a useful guide for a better understanding of the chemical reactions involved in the sol-gel process. It requires easy calculations and can be applied to both inorganic and metal-organic precursors. However, we have to bear in mind that such a model is based on very simple ideas. Therefore, it should be applied carefully, without losing the chemical significance of the mathematical parameters. One of the most severe limitations is that the partial-charge model does not take into account the structure of the compound and cannot, therefore, discern the difference between two isomers.

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