Russian Chemical Bulletin, International Edition, Vol. 52, No. 9, pp. 2083—2085, September, 2003 2083

Study of the initial stages of alkoxo synthesis involving Ti(OBu)$_4$ and cyclophosphites

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The reactivities of cyclophosphite precursors in alkoxo syntheses involving titanium(IV) tetra(*n*-butoxide) were studied by ^{31}P NMR and IR spectroscopy. 2-Diethylamido-4-methyl-1,3,2-dioxaphosphinane and 4-ethyl-2,6,7-trioxaphosphabicyclo[2.2.2]octane in benzene are inert toward Ti(OBu)$_4$. Gelation is accompanied by hydrolysis 2-diethylamido-4-methyl-1,3,2-dioxaphosphinane to give the corresponding hydrophosphoryl compound, while 4-ethyl-2,6,7-trioxaphosphabicyclo[2.2.2]octane remains intact during gelation.

Key words: cyclophosphites, alkoxo synthesis, ^{31}P NMR spectroscopy, IR spectroscopy.

Earlier, we found that the use of bicyclophosphite, namely, 4-ethyl-2,6,7-trioxaphosphabicyclo[2.2.2]octane (etriol phosphite)[1] (**1**), or amidocyclophosphite, namely, 2-diethylamido-4-methyl-1,3,2-dioxaphosphinane[2] (**2**), and titanium(IV) tetra(*n*-butoxide) as precursors in alkoxo synthesis affords, by high-temperature gel treatment, single-phase phosphorus-containing titanate oxides with highly ordered crystalline and porous structure.[3—5] Phosphorus titanate oxides obtained from monodentate phosphites are catalytically active and very highly selective in oxyethylation of ethylene glycol because of molecular sieve effect in homogeneous pores.[6]

In this work, reactions of organophosphorus precursors with Ti(OBu)$_4$ in aqueous organic solvents were studied by ^{31}P NMR and IR spectroscopy.

Experimental

Alkoxo synthesis was carried out in several steps. The initial solutions were prepared as follows. An equimolar amount of acetylacetone (acacH) was added to 1.5 *M* Ti(OBu)$_4$ in anhydrous benzene. The solution was magnetically stirred for 30 min, and then 0.5 *M* bicyclophosphite **1** (solution **1a**) or amidocyclophosphite **2** (solution **2a**) in benzene were added under argon.

Benzene solution of Ti(OBu)$_4$ + acacH + Benzene solution of cyclophosphite **1a**, **2a** ⟶ Initial solution **1b**, **2b**

The resulting solutions **1b** and **2b** were stirred for 30 min, and then 80% EtOH was added in such an amount that contains the stoichiometric water amount with respect to titanium alkoxide (gels **1c** and **2c** from phosphites **1** and **2**, respectively).

Solution of **1b** or **2b** + aqueous 80% EtOH ⟶ Gel **1c** or **2c**

For comparison, 0.5 *M* phosphites **1** and **2** were mixed with Ti(OBu)$_4$ in benzene (without acetylacetone) to give solutions **1d** and **2d**.

Benzene solution of Ti(OBu)$_4$ + Benzene solution of cyclophosphite **1a** or **2a** ⟶ Initial solution **1d** or **2d**

Gels **1e** and **2e** were prepared by addition of aqueous ethanol to solutions **1d** and **2d**.

Benzene solution of Ti(OBu)$_4$ and cyclophosphite **1d** or **2d** + aqueous 80% EtOH ⟶ Gel **1e** or **2e**

^{31}P NMR spectra were recorded at 30 °C on a Bruker WP-80 instrument (32.4 MHz) with 85% H_3PO_4 as the external standard. IR spectra were recorded on a Specord 75IR instrument (KBr).

Chelation with acetylacetone was carried out to extend the induction period of gelation upon addition of aqueous ethanol.[7] It was preliminarily found that the induction period of gelation in a chelated sol is 1.5 months, while without prechelation it takes four minutes for colorless transparent homo-

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Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1973—1975, September, 2003.

geneous gels **1e** and **2e** to form throughout the bulk of the reaction mixture.

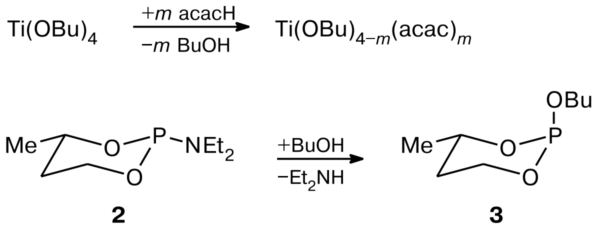
For this reason, spectra of solutions of **1b—d** and **2b—d** were recorded in sealed tubes every 48 h for two months. Solutions of **1a**,**e** and **2a**,**e** were prepared in NMR tubes under argon.

Results and Discussion

According to the ^{31}P NMR data, bicyclophosphite **1** is stable in the initial solutions until gels **1c**,**e** form. Spectral lines remain virtually constant throughout the experiment and coincide with a signal for bicyclophosphite in blank solution **1a** and in solutions **1b**,**d** (δ_P 92). Apparently, bicyclophosphite **1** is mainly converted into single-phase titanates at the later steps of high-temperature synthesis.[3—5]

Amidocyclophosphite **2** in a blank solution and in solutions **2a**,**d** is manifested by two ^{31}P signals at δ 145 and 137 (integral intensity ratio 95 : 5) for its two geometrical isomers.[8] Unlike bicyclophosphite **1**, amidocyclophosphite **2** reacts almost immediately upon the addition of acetylacetone to solution **2a**. The ^{31}P NMR spectrum of the resulting solution **2b** contains characteristic higher-field signals (δ_P 133, 128, 31 and 7); the ratio of the total intensity of these signals to the intensity of the signals for the starting amidocyclophosphite (δ_P 145 and 137) is 1 : 1. In hot solution **2b** (90 °C, 1 h), this ratio becomes 6 : 1. Amidophosphite **2** reacts with solution **2b** to give amidophosphite and acetylacetone derivatives[9] and a complete phosphite, namely, 2-butoxy-4-methyl-1,3,2-dioxaphosphinane **3** (Scheme 1). The complete phosphite (δ_P 133) forms as a result of alcoholysis of amidophosphite **2** [10] with butanol released in the reaction of $Ti(OBu)_4$ with acetylacetone[11].

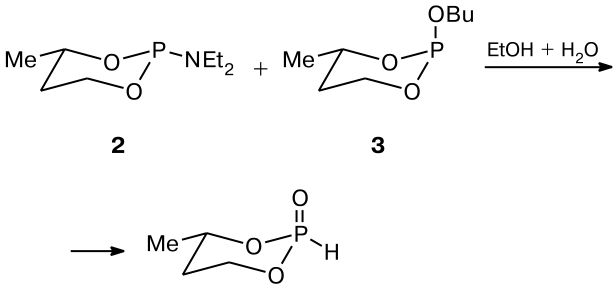
Scheme 1



The spectra of gels **2c**,**e** (*i.e.*, upon the addition of aqueous EtOH to solutions **2b**,**d**) show only signals characteristic of hydrolyzed amidocyclophosphite[10] (δ_P 3.8 and 2.4, $^1J_{P,H}$ = 610 and 617 Hz, respectively) (Scheme 2).

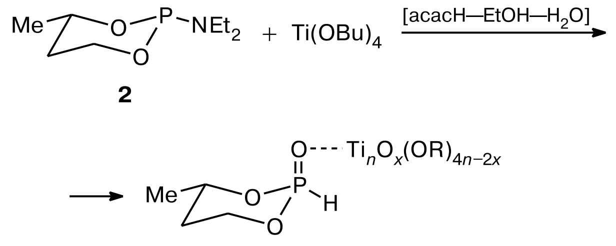
No products of a reaction of the hydrophosphoryl compound with titanium alkoxide were detected in solution. However, the IR spectrum of xerogel obtained by removal of the solvent from gel **2e** contains an absorption band ν(P—H) at 2420 cm^{-1}, while the characteristic absorption band of gel **2e** appears at 2485 cm^{-1}.

Scheme 2



Because $Ti(OBu)_4$ during gelation gives an oxoalkoxo system with the empirical formula $Ti_nO_x(OR)_{4n-2x}$,[12] its reaction with amidocyclophosphite can be represented by the following general scheme (Scheme 3).

Scheme 3



R = H, OBu

Hence, amidocyclophosphite is significantly more reactive than bicyclic etriol phosphite at the initial steps of alkoxo synthesis with the intermediacy of $Ti(OBu)_4$.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-33053) and the Presidium of the Russian Academy of Sciences (Grant "Nanoclusters and Supramolecular Compounds").

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Received December 15, 2002;
in revised form May 15, 2003