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Reactions of Niobium(III) and Tantalum(III) Compounds with Acetylenes. 4. Polymerization of Internal Acetylenes

F. Albert Cotton[*1a] **and William T. Hall**[1a]

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Kevin J. Cann[1b] **and Frederick J. Karol**[1b]

Polyolefins Division, Union Carbide Corporation,
Bound Brook, New Jersey 08805. *Received August 25, 1980*

ABSTRACT: It has been found that the compounds $M_2Cl_6(SC_4H_8)_3$ (M = Nb, Ta) catalyze the polymerization of substituted acetylenes. With RCCH (R = C_6H_5, Et, *i*-Pr) only cyclotrimers (1,3,5 and 1,2,4 isomers in approximately equal amounts) were obtained. With RCCR′ monomers, high polymers were obtained. With R = CH_3, R′ = *sec*-C_4H_9 both catalysts gave exclusively polymer. With R = C_6H_5, R′ = CH_3 the Nb catalyst gave only polymer while the Ta catalyst gave a 2:1 ratio of polymer to cyclotrimer. With R = R′ = C_2H_5 the Nb catalyst gave a 10:1 ratio of polymer to cyclotrimer, while the Ta catalyst gave only trimer.

Introduction

In several previous papers in this series[2-4] certain reactions of acetylenes with the niobium(III) and tantalum(III) compounds $M_2Cl_6(SC_4H_8)_3$, **1a** and **1b**, respectively, have been reported, namely, those leading to the formation of mono-[2] or binuclear[3,4] complexes. The characterization of these complexes by X-ray crystallography has been described.

With some acetylenes, compounds **1a** and **1b** catalyze polymerization instead of forming complexes. In this paper we describe our studies of these polymerization reactions and partial characterization of the products. The reactants used were internal acetylenes, RC≡CR′, or terminal acetylenes, RC≡CH, and the products are either cyclotrimers (substituted benzenes), linear polymers, or a mixture of both.

Experimental Section

General Remarks. All reactions were run under dry nitrogen, and the toluene solvent was distilled from sodium/benzophenone ketyl. The alkynes were vacuum distilled from 4-Å molecular sieves just prior to use. The catalysts, $Nb_2Cl_6(THT)_3$ (**1a**) and $Ta_2Cl_6(THT)_3$ (**1b**), were synthesized according to literature methods.[5-7]

Reaction of 3-Hexyne with the Ta Catalyst. Compound **1b** (100 mg, 0.12 mmol) was dissolved in 10 mL of toluene, and a few drops of 3-hexyne was syringed into the solution. After several minutes the solution became lighter in color; a total of 1 mL (59.4 mmol) of 3-hexyne was then added dropwise. Care was required to be sure that the solution did not become too hot, since the reaction is rapid and exothermic. When all the alkyne had been added and the mixture had cooled, the reaction was quenched with 95% ethanol. This decomposes the catalyst to insoluble $Ta_2O_5 \cdot xH_2O$. All the solvent was then allowed to evaporate, and the organic portion of the residue was extracted with acetone. The acetone-soluble portion was recrystallized and identified as hexaethylbenzene (IR and NMR spectra, mp 129 °C). Almost all the 3-hexyne could be accounted for as cyclotrimerized product, showing the reaction to be catalytic.

Reaction of 3-Hexyne with the Nb Catalyst. The alkyne (3 mL, 178 mmol) was syringed into a solution of **1a** (50 mg, 0.077 mmol) in 6 mL of toluene. The solution was heated to 80 °C for 2 h, during which time the solution became very viscous. The flask was allowed to cool to room temperature and methanol was added to precipitate a white polymer which was isolated and dried (~70% yield based on initial alkyne). Only a small amount of hexaethylbenzene was recovered (≈7% of initial alkyne).

Polymerization occurred also at room temperature but required longer reaction times (ca. 6 h).

Reaction of 1-Phenylprop-1-yne with the Ta Catalyst. The alkyne (3 mL, 241 mmol) was syringed into a solution of **1b** (100 mg, 0.12 mmol) in 10 mL of toluene. On standing for 3 h the mixture became quite viscous, and white needles, identified as 1,3,5-trimethyl-2,4,6-triphenylbenzene (IR, NMR, mass spectra), were found suspended in the mixture. Addition of ethanol precipitated a white polymer which was washed with several more portions of ethanol. The poly(phenylpropyne) was found to be contaminated with trimer, and separation was accomplished by dissolving the polymer in dichloromethane and adding a small amount of ethanol. This precipitated the polymer, leaving the trimer in the supernatant liquid, which was decanted. Approximately 35% of the phenylpropyne was recovered as polymer, and about 18% as cylotrimer.

Reaction of 1-Phenylprop-1-yne with the Nb Catalyst. The alkyne (3 mL, 241 mmol) was syringed into a solution of **1a** (50 mg, 0.077 mmol) in 10 mL of toluene. The solution was heated to 80 °C for ~3 h, during which time a thick viscous mixture formed. After the flask had cooled, methanol was added to precipitate a white polymer which was isolated and dried (~72% yield based on initial alkyne). No trimer was detected. On

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addition of more monomer to a polymerization reaction that was >90% complete according to gas chromatographic analysis, additional polymerization (at 80 °C) took place. Polymerization at room temperature was extremely slow, requiring many days to produce a comparably viscous reaction mixture.

Reaction of 4-Methylhex-2-yne with the Ta Catalyst. The alkyne (2 mL, 140 mmol) was syringed into a solution of **1b** (100 mg, 0.12 mmol) in 10 mL of toluene. The solution became very viscous on standing overnight. Methanol was added to the solution, precipitating a white polymer which was isolated and dried. No trimer was observed, and the poly(4-methylhex-2-yne) accounted for 65% of the initial alkyne.

Reaction of 4-Methylhex-2-yne with the Nb Catalyst. The alkyne (3 mL, 241 mmol) was syringed into a solution of **1a** (50 mg, 0.077 mmol) in 10 mL of toluene. The solution was heated to 80 °C for 3 h, during which time a thick viscous mixture formed. The flask was allowed to cool to room temperature, and methanol was added to precipitate a white polymer (yield 75% based on initial alkyne). No trimer was detected. Polymer formation at room temperature was very slow (days).

Reactions of 1-Butyne, Phenylacetylene, and 3-Methylbut-1-yne with the Catalysts. The reactions of these primary alkynes with the Ta and Nb catalysts yielded, in all cases, only trimers. In a typical reaction, the alkyne was added to a toluene solution of **1a** or **1b**. The cyclotrimerization proceeded rapidly, in a very exothermic reaction; several milliliters of alkyne could be consumed by 100 mg of catalyst in minutes. The products were 1,3,5- and 1,2,4-trisubstituted benzenes formed in about a 1:1 ratio.

Nonreaction of Ethylene with the Nb Catalyst. With compound **1a** in hexane at 100 °C under a 13-atm pressure of ethylene, no polyethylene was detected. On addition of triethylaluminum (Al:Nb mole ratio of 2) under the same conditions low activity (ca. 8 g of polyethylene/h) was observed.

A limited quantity of phenylpropyne (15 mol/mol of **1a**) was added to the Nb catalyst in hexane, under 9 atm of C_2H_4 and 2 atm of H_2, to determine if a species formed only in the course of the polymerization of an acetylene might serve as a catalyst for polymerization of ethylene. After 30 min at 85 °C no polyethylene or polyacetylene was detected and the original purple color persisted, whereas in the acetylene polymerization reactions the purple color was lost and the reaction mixtures had a plum color as polymerization occurred. When essentially this same experiment was repeated with the addition of Et_3Al, no polymers or trimers were detected and unreacted phenylpropyne was recovered.

Characterization and Physical Properties of Poly(3-hexyne) and Poly(phenylpropyne)

The polymers derived from 3-hexyne and 1-phenylprop-1-yne using both the tantalum and niobium catalysts were selected for physical testing. The phenylpropyne polymer dissolved readily in the organic solvents toluene, benzene, CH_2Cl_2, and $CHCl_3$. Extremely dilute solutions (1%) were obtained with the other polymers because severe gelling took place with the poly(3-hexyne) (Nb catalyzed) and the poly(phenylpropyne) (Ta catalyzed).

Only the polymer produced from phenylpropyne (Nb catalyzed) was capable of casting a film suitable for physical testing using solvent evaporation techniques (CH_2Cl_2). Plaque formation via pressing or extrusion was not attempted because of the notorious behavior of polyacetylenes under heat. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) data will be discussed later.

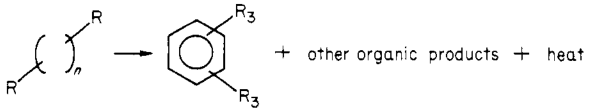
The physical properties of poly(phenylpropyne) (Nb catalyzed) were found to be very similar to those of polystyrene (Table I). The only notable feature of this polymer is the apparent high glass transition temperature (275 °C) as compared to that for polystyrene ($T_g \approx 100$ °C).

DSC data were collected in an attempt to determine if the apparent T_g was actually the melting point of the polymer. The results clearly showed no substantial endothermic absorptions over the range 50–500 °C. This indicates that the polyacetylenes are most likely amorphous and the observed T_g is not a simple melting point. Qualitative analysis of the poly(phenylpropyne) produced with the Nb-based catalyst via X-ray diffraction indicated little or no crystallinity. It is important to note that a change in the specific heat of the polymers was not observed at 275 °C by DSC. However, a T_g unaccompanied by a detectable (DSC) change in specific heat, although unusual, is not unprecedented.

Table I
Physical Testing Data of Poly(phenylpropyne) Polymerized by $Nb_2Cl_6(SC_4H_8)_3$

1% secant modulus, psi	337000
tensile strength, psi	6570
elongation at break, %	2.1
pendulum impact strength, (ft·lb)/in^3	9.5
T_g, °C	275

Beginning shortly above 300 °C, the DSC scans show an exotherm for all the polymers tested, indicative of thermal decomposition of polyacetylenes.[8] An exothermic decomposition would be expected as aromatic products are formed and a substantial energy gain occurs, as expressed in the following equation:



This interpretation is supported by TGA results which show that in the range where the exotherm appears in the DSC, a substantial weight loss occurs. Between 300 and 400 °C an approximately 50% weight reduction occurs, which would be expected as the much more volatile benzene derivatives are lost from the polymer.

Conclusions based on the DSC, TGA, and the physical testing data available at this time suggest that the polymer produced from phenylpropyne is amorphous with an exceptionally high T_g. However, it must be realized that thermal decomposition begins only 25 °C above the reported T_g and that the observed T_g might also be a result of polymer decomposition.

The infrared spectra and ^1H and ^{13}C NMR spectra of the poly(phenylpropyne) produced with the Nb-based catalyst agree with the spectra published for poly(phenylpropyne) produced with a tungsten halogen alkyltin coupled catalyst.[9] However, the infrared and proton NMR spectra cannot elucidate whether the polymer is indeed a polyene or ladder polymer. The ^{13}C NMR spectrum shows only one signal upfield (≈22 ppm) indicative of a polyene structure. For a ladder polymer, two signals would occur upfield due to the methyl group and the cyclobutane carbon atoms. However, the severe gelling problems found with these polymers indicate that a significant amount of cross-linking must be occurring in these polyenes.

The Raman spectrum of poly(3-hexyne) showed no band in the unsaturated C–H stretching region, as expected; it has a double-bond stretching frequency of 1615 cm^{-1}, which is consistent with some degree, but not a high degree, of conjugation. For poly(phenylpropyne) no information was obtained since the phenyl group accounts for all strong bands in the spectrum (3055, 1592, and 995 cm^{-1}).

A simple bromination in carbon tetrachloride showed rapid uptake of Br_2 by a gel of polyhexyne in CCl_4, while the poly(phenylpropyne)[2] produced by both catalysts only very slowly reacted with Br_2.

Gel permeation chromatographic (GPC) analysis of the poly(phenylpropynes) produced by each catalyst is vastly different (Figure 1). The poly(phenylpropyne) produced

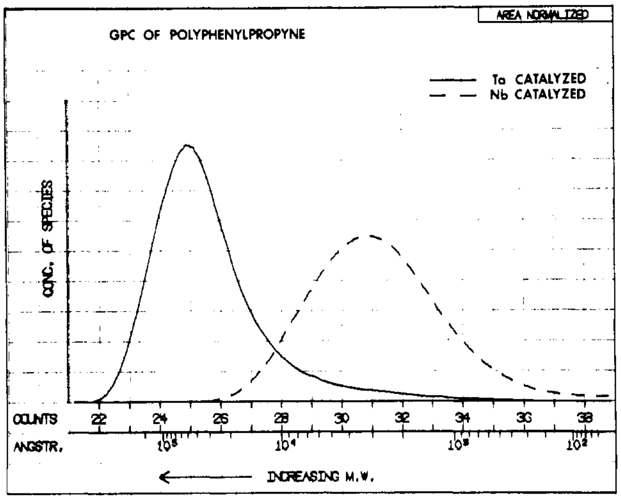


Figure 1. Polymer chain length distributions by gel permeation chromatography for poly(phenylpropynes).

Table II
Summary of Catalytic Reactions of Alkynes with $Ta_2Cl_6(SC_4H_8)_3$ and $Nb_2Cl_6(SC_4H_8)_3$

	$Ta_2Cl_6(SC_4H_8)_3$	$Nb_2Cl_6(SC_4H_8)_3$
3-hexyne	trimer	polymer (70%) trimer (7%)
1-phenylprop-1-yne	polymer (35%) trimer (18%)	polymer
4-methylhex-2-yne	polymer	polymer
phenylacetylene	trimer	trimer
1-butyne	trimer	trimer
3-methylbut-1-yne	trimer	trimer

by the Nb-based catalyst shows maxima at approximately 3000 Å, while different formed polymers whose maxima were about 30 000 Å. This suggests a tenfold increase in the molecular weight of the Ta-catalyzed polymer. Although both polymers have a substantial number of low molecular weight species, the Ta-catalyzed polymer appears to possess a narrower molecular weight distribution. Only minimal changes in the polymer size for either catalyst were achieved when the initial monomer concentration was varied from 40 to 70%. Approximate molecular weights have been calculated by comparison of the polymer size of the repeating unit. On the basis of the assumption that the polymer is a polyene (concluded from ^{13}C NMR), the molecular weight of the highest concentration of polyene species is approximately 1×10^5 for the Nb-catalyzed material and 2×10^6 for the Ta-catalyzed polymer.

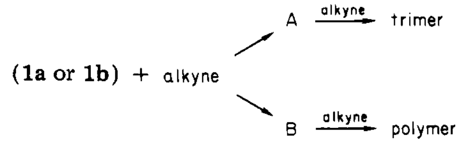
GPC analysis of the poly(3-hexyne) produced by the Nb-based catalyst showed an unusual bimodal distribution. About 80% of the polymer had a mean molecular weight of 1×10^5 with the remainder centered around 1.4×10^6. Significant cross-linking is the simplest explanation for the much higher molecular weight polymers observed in both the polyhexyne and poly(phenylpropyne) (Ta catalyzed) systems. This would explain the gel formations found upon addition of solvents to these polymers.

Discussion

The catalytic systems we have discovered and studied are of interest for two reasons. For one thing, catalysts for the polymerization of internal alkynes are uncommon,[10] although there are many known for primary alkynes and there are many catalysts that will cyclotrimerize alkynes. Secondly, the group 5 elements have not, in general, found much employment as homogeneous catalysts, although it has been reported that $NbCl_5$ and $TaCl_5$ catalyze the trimerization of acetylene.[11]

The catalytic reactions of alkynes with **1a** and **1b** are summarized in Table II. The internal acetylenes give two types of product—trimer and polymer. The primary acetylenes gave, in all cases, only trimer.

The important step in these reactions seems to be the initial interaction of the alkyne with the niobium or tantalum compound to produce a reactive intermediate that then goes on to catalyze the production of trimer or polymer. This is illustrated in eq 1, where the alkyne

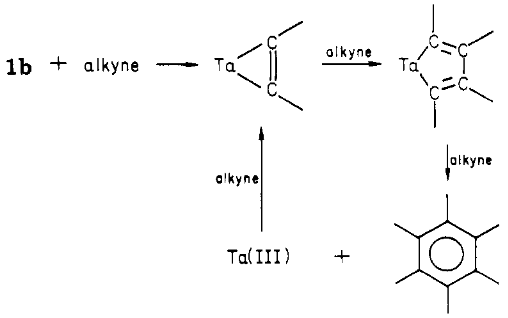


(1)

reacts with **1a** or **1b** to form the cyclotrimerization intermediate, A, or the polymer intermediate, B. We postulate that A and B cannot interconvert and that they are quite different in nature. If this were not true, the thermodynamic preference for cyclotrimerization would cause mostly trimer formation with, at best, only low molecular weight polymer. Once an A species is formed it then gives only trimer, and likewise a B species, once formed, gives only polymer.

With internal acetylenes the formation of a particular intermediate species seems to depend on the steric features of the alkyne, and these effects differ slightly with the metal. Thus 3-hexyne with **1b** gives only trimer while the slightly more bulky 4-methylhex-2-yne gives only polymer; but 3-hexyne with **1a** gives almost entirely polymer. Since there is no polymer formation with any of the primary alkynes, it may be that the acetylenic hydrogen allows some completely different reaction pathway which is not available to the internal alkynes.

The tantallocyclopropene complexes we have characterized,[2,4] where the acetylene added Ta^{III}, may provide a model for the A-type trimer intermediate. A possible mechanism for cyclotrimerization is shown in eq 2, where

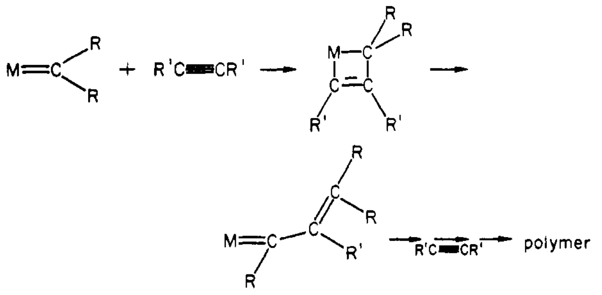


(2)

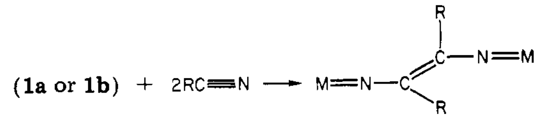
a metallocyclopropene is the first step in the catalytic cycle. Similar mechanisms have been proposed for other catalysts.[12]

The similarity of metathesis catalysts to acetylene polymerization catalysts has lead some researchers[13] to propose a metal–carbene mechanism for the propagation of the polymerization, eq 3. Support for this mechanism has come from Katz and Lee,[10] who have demonstrated that isolable metal carbenes can serve as initiators of acetylene polymerization. This suggests that the polymer intermediate B in our reaction may also involve a metal–carbene species.

One way in which a Ta–carbene species could be generated, although this is only speculative, is by two molecules of alkyne reacting with **1a** or **1b** in the same way as alkyl cyanides,[14] eq 4 and 5. Once the carbene species is



(3)



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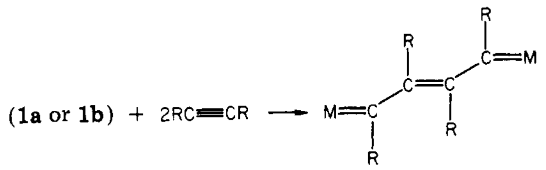
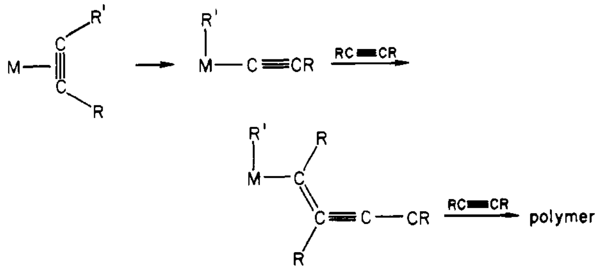


(5)

formed, polymerization could proceed as in eq 3.

Although we find a carbene mechanism the most appealing for our alkyne polymerizations, other mechanisms have been considered. A commonly proposed mechanism involves a metal acetylide, as shown in eq 6.[15] This



(6)

mechanism should be most favorable when R′ = H but seems very unlikely for R = alkyl. Since we obtained polymerization only for internal alkynes and not for primary alkynes, the acetylide intermediate can probably be ruled out for our catalysts.

A mechanism which incorporates successive 2 + 2 cycloadditions of alkyne to form (initially) a ladder polymer[16] (a polymer backbone of fused cyclobutane rings) has also been discussed. This ladder polymer is presumed to be converted to linear polyene later in the reaction by the same catalyst. This type of mechanism seems unlikely in our system.

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