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THE MECHANISMS OF PHENYLACETYLENE POLYMERIZATION BY
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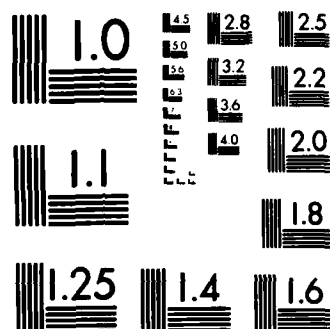
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The Mechanisms of Phenylacetylene Polymerization

by Molybdenum and Titanium Initiators

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Thomas J. Katz^{*} and Scott M. Hacker

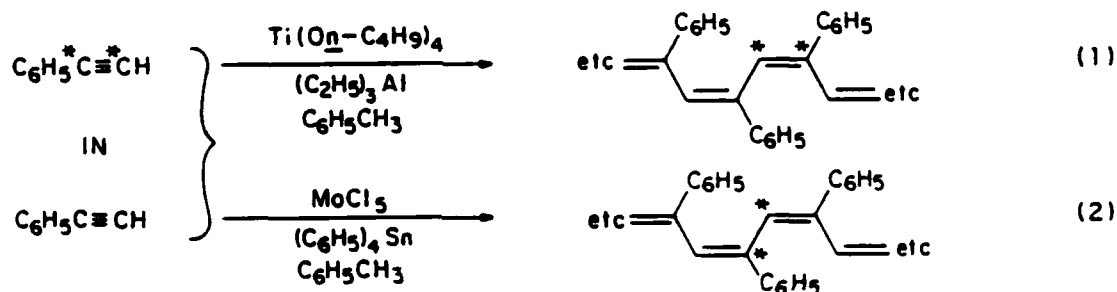
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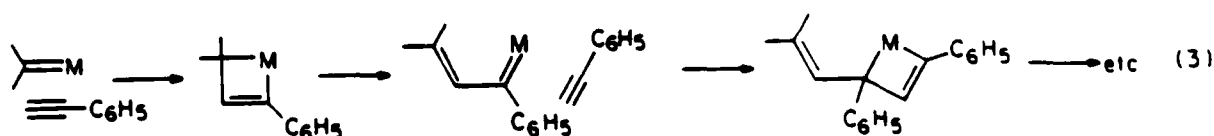
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Abstract. Polymerizing phenylacetylene, a few of whose molecules are doubly labeled by ^{13}C 's on the triple bond, gives poly(phenylacetylene) in which the labels are separated by a double bond when the initiator is titanium tetrabutoxide plus triethylaluminum and by a single bond when it is molybdenum pentachloride plus tetraphenyltin. This tallies with the idea that the acetylene polymerizations induced by derivatives of molybdenum are olefin metatheses, while those induced by derivatives of titanium are acetylene insertions. The locations of the ^{13}C nuclei were analyzed by nutation NMR spectroscopy.

We are reporting that while phenylacetylene, a few of whose molecules are doubly labeled by ^{13}C 's on the triple bond, is polymerized by some catalysts including titanium tetrabutoxide plus triethylaluminum to give poly(phenylacetylene) in which the labels are separated by a double bond (eq 1), when the initiator is molybdenum pentachloride plus tetraphenyltin, the labels are separated by a single bond (eq 2). This tallies with the idea that derivatives of molybdenum are effective initiators of both olefin



metatheses^{1,2} and acetylene polymerizations,^{3,4} not by coincidence, but because the acetylene polymerizations they induce are olefin metatheses (eq 3).^{5,6} In contrast, the titanium initiated acetylene polymerizations---both the one reported here and one reported earlier, in which titanium tetrabutoxide plus triethylaluminum polymerized unsubstituted acetylene⁷---seem to follow an insertion mechanism like that believed to apply to the titanium-catalyzed polymerization of ethylene.⁸



Whether the labeled carbons are separated in the polymers by single or by double bonds was analyzed by nutation NMR spectroscopy.^{7,9} Thus the spectra displayed in figure 1 exhibit Pake doublets, produced by the dipole-dipole interaction of adjacent ^{13}C nuclei, that are separated by 2196 Hz in a sample prepared with the titanium catalyst and by 1765 Hz in one prepared with the molybdenum catalyst. The best theoretical simulations, also displayed in the figure, correspond in the first sample to 91 % of the carbons being separated by 1.36 Å, and 9 % by 1.48 Å. In the second sample (made with the molybdenum catalyst), the analysis is optimized if 88 % of the carbons are separated by 1.48 Å and 12 % by 1.36 Å. The only parameters in the theoretical simulations are the two bond lengths, the fraction of the bonds having these lengths, and a natural width (75 Hz) for lines assumed to be Lorentzian.⁹ The accuracy of the nutation method and fitting procedure is demonstrated by the measured C-C length for acetic acid agreeing with X-ray diffraction measurements within 0.7 %, ⁹ by the C≡C length in phenylacetylene agreeing with microwave measurements within 1.8 %, ¹⁰ and by the single- and double-bond lengths analyzed above agreeing with those (averaging 1.47 ± 0.01 Å and 1.35 ± 0.01 Å) determined for a variety of polyenes.¹¹

The nutation experiments were carried out as described previously.^{7,9} The ^{13}C magnetization (at 15 MHz) was generated by an ^1H - ^{13}C cross polarization sequence using a 40 kHz Hartmann-Hahn match,¹² and proton broadening was then removed during data acquisition by a strong (2.5 mT) 60 MHz decoupling field. The nutation excitation sequence was the same for both samples: an 8 μsec carbon transmitter pulse (3.6 mT rotating component), followed by a 9.9 μsec delay and a 7 μsec receiver window. The carbon carrier frequency was kept close to the center of the spectrum in the

laboratory frame. The temperature of the samples was 77 K.

The phenylacetylene (93 % $^{13}\text{C}_0$, 4 % $^{13}\text{C}_2$)¹³ was polymerized by combining it in toluene either at -20 °C for 3 h with MoCl_5 plus $(\text{C}_6\text{H}_5)_4\text{Sn}$ (1/100 equivalents each, previously incubated for 10 min at room temperature)^{14,15} or at 0 °C for 4.5 h with titanium tetrabutoxide and triethylaluminum (1/50 and 4/50 equivalents, previously incubated for 20 min at room temperature).¹⁶ The polymers were purified by repeatedly dissolving them in cold chloroform and precipitating them with methanol, and they were then dried at -35 °C for 12 h. The yields were 28 and 4 %, respectively, and the ^1H NMR spectra were characteristic of 97 % and 75 % "cis" (E) materials.^{17,18}

For the experiments to succeed with the catalysts containing molybdenum pentachloride, the poly(phenylacetylene) samples had to be prepared, purified, and maintained below 0 °C. When they were prepared at room temperature, the spectra exhibited prominent peaks characteristic of ^{13}C 's separated both by single and by double bonds, implying that the positions of the double bonds, which remain fixed in the cold samples, move on warming.^{7b,17,19} When WCl_6 was substituted for MoCl_5 ,¹⁴ it was impossible, even with samples prepared at -20 °C,²⁰ to distinguish whether equations 1 or 2 applied, for the intensities of the two kinds of peaks were similar.

When the Casey metal-carbene [pentacarbonyl(diphenylmethylene)-tungsten]^{6a,21} or the Fischer metal-carbyne [trans-bromotetracarbonyl-(phenylmethyldiyne)tungsten]^{18,22} was used as the initiator, the experiments did distinguish the alternatives, but the results were unexpected and are at present unexplained. The composition of the polymers was essentially the same as when the titanium-containing mixture was the initiator.²³

However, that the titanium- and molybdenum-initiated reactions seemingly follow different paths agrees with the observation that compounds of

titanium, unlike those of molybdenum, are only marginally effective in bringing about olefin metatheses.²⁴ It might also account for another distinction, in selectivity, that the literature seems to reveal: that titanium-containing initiators are more effective than those containing molybdenum in polymerizing unsubstituted acetylene,²⁷ whereas the reverse is true for substituted acetylenes.^{5b,28}

Acknowledgements. We are grateful for the support of the U.S. Navy, Office of Naval Research, the National Science Foundation (CHE81-08998), and the American Cyanamid Company.

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(13) Analyzed by electron impact mass spectrometry: 92.8 % $^{13}\text{C}_0$, 3.2 % $^{13}\text{C}_1$, 4.0 % $^{13}\text{C}_2$ for the sample used for the experiment in equation 1 and 93.9 % $^{13}\text{C}_0$, 2.1 % $^{13}\text{C}_1$, and 4.0 % $^{13}\text{C}_2$ for the one in equation 2. The materials were prepared from $^{13}\text{CH}_3^{13}\text{CO}_2\text{Na}$ (90 atom % ^{13}C) according to the procedures described in (a) Murray, III, A.; Williams, D. L., Eds. "Organic Syntheses with Isotopes," Part I; Interscience Publishers, Inc.: New York, 1958; p. 662 and (b) Casanova, Jr., J.; Geisel, J. M.; Morris, R. N. Org. Prep. Proc. Int. 1969, 1, 81.

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(19) The scrambling was much less when the titanium initiator was used. A sample prepared (14% yield, 63 % E) at room temperature during 9 1/2 h (acetylene : Ti : Al = 140 : 1 : 4) had 13% of ¹³C's separated by single bonds.

(20) 47% yield after 2 h, 39 % E. The greater structural inhomogeneity of samples of poly(phenylacetylene) prepared with WCl₆ rather than MoCl₅ has been analyzed by Percec (see references 17d, e and 18).

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(23) In the polymer obtained in 33% yield (35% E) after 5 h in a vacuum at 30 °C with the carbene (acetylene : W = 53), 15 % of the ¹³C's were separated by single bonds. In the polymer obtained in 14% yield (74 % E) after 75 h at 0 °C with the carbyne (acetylene : W = 100), ca. 8 % of the

^{13}C 's were separated by single bonds. This last figure rose to only 13% in a similar sample prepared at ca. 25 °C.

(24) Titanium catalysts do not metathesize common olefins appreciably.¹ Titanium tetrachloride plus triethylaluminum (or related materials) metathesizes strained olefins,²⁵ and the Tebbe reagent exchanges isotopically labeled terminal methylenes.²⁶

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Figure Caption

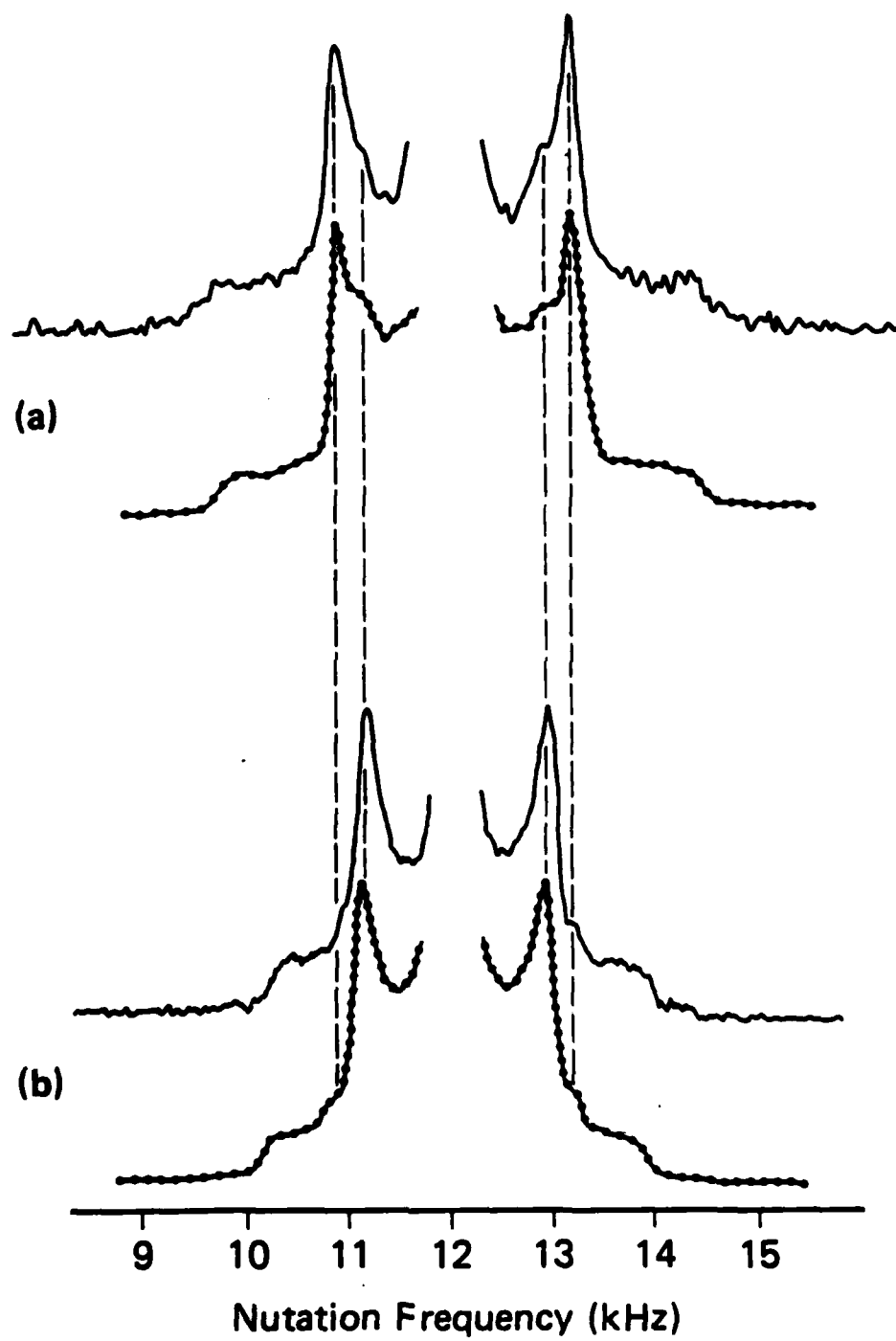
Figure 1. ^{13}C NMR nutation spectra of poly(phenylacetylene) at 77 K.

(a) Sample prepared according to equation 1. The cross polarization time was 0.5 ms and the recycle time 1s. The number of scans was 144000.

(b) Sample prepared according to equation 2. The cross polarization time was 1.0 ms and the recycle time 0.5 s. The number of scans was 115200. The dotted curves are simulated spectra, calculated as described in the text.

The center peaks, due to isolated ^{13}C nuclei, have been cropped for clarity.

The inner and outer pairs of dashed lines mark, respectively, the peaks of curves arising from ^{13}C 's separated by single and double bonds.



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