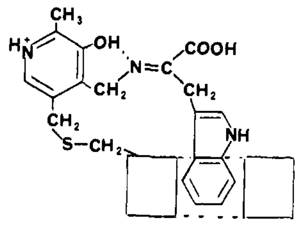

13

ination. This is illustrated in structure **13**, an intermediate in the reaction of **8** with **11** to form **12**. The binding should accelerate both the forward and the reverse reactions involving the aromatic substrates; so the product selectivity is lost with time because of rapid equilibration of keto acid with amino acid.

Because β-cyclodextrin is chiral, one might expect that the product amino acids could be optically active. Chiral induction has been seen with cyclodextrin reactions in the past,[16] but our dinitrophenyltryptophan has only 12% enantiomeric excess of the L isomer.[17] However, the dinitrophenylphenylalanine has a 52 ± 5% excess of the L enantiomer,[17] so this reaction shows significant optical induction.

Compound **8** shows selectivity and rate acceleration and is thus a good first generation artificial transaminase. Further improvements should result from better definition of geometry and the addition of other catalytic groups to facilitate the proton transfers involved in the overall reaction.[18]

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(2) Cf. Metzler, D. E.; Ikawa, M.; Snell, E. E. *J. Am. Chem. Soc.* **1954**, *76*, 648–652, and earlier papers.

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(7) ^{1}H NMR spectrum in accord with the assigned structure.

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(10) Calcd (found): C, 42.61 (42.36); H, 6.58 (6.69); N, 1.98 (1.70); S, 2.27 (1.81).

(11) This high concentration was used since these reactions show buffer catalysis.[1]

(12) The reaction is apparently quenched immediately, since the analyzed yield of DNP-amino acids was a function only of the reaction time before quenching. Qualitatively similar results, e.g., the rapid formation of tryptophan relative to alanine, were also obtained by direct thin layer chromatograph of the original reaction mixture and detection of the amino acids with ninhydrin.

(13) On Partisil PXS 10 with 40% v/v $CH_3CN–H_2O$ containing 2.5 mL of HOAc and 0.4 g of NaOAc/L.

(14) That is, the area of the amino acid peak in the LC of the product from reaction with **8** after 10 min corresponded to a conversion (1–5%, depending on pH and concentration) which was achieved only after 30 h with simple pyridoxamine (**5**).

(15) As judged from the areas of LC peaks after 1 h, when ~0.2–0.5% of alanine was formed with either **8** or **5**.

(16) Reference 3, Chapter VII.

(17) By isolation and comparison of the rotation of the pure compound with the rotation of an authentic sample. The rotation is opposite to that of our cyclodextrin catalyst.

(18) Support of this work by the National Institutes of Health is gratefully acknowledged.

(19) NIH Postdoctoral Fellow.

(20) Holder of the Liebig Postdoctoral Fellowship of the Fonds der Chemischen Industrie.

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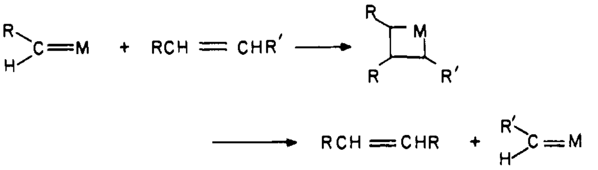
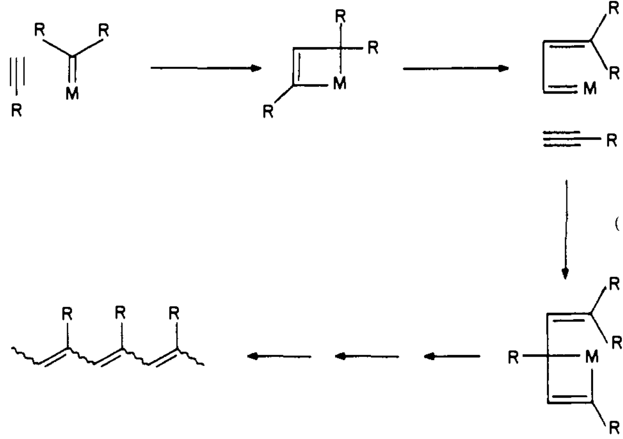
Initiation of Acetylene Polymerization by Metal Carbenes

Sir:

A corollary of the hypothesis that metal carbenes combine with olefins as in eq 1 to propagate the metal-catalyzed metatheses of olefins[1] is the hypothesis that they similarly combine with acetylenes as in eq 2[2] to propagate the metal-catalyzed polymerizations of acetylenes.[3,4] This suggests that isolable metal carbenes[8] can serve as initiators of acetylene polymerization, and we demonstrate here that they do.

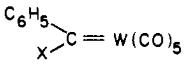


(1)

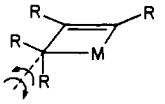


(2)

Tables I-III summarize the data. They show that (phenylmethoxycarbene)pentacarbonyltungsten (**1a**)[9] and (diphenylcarbene)pentacarbonyltungsten (**1b**),[10] metal carbenes that previously initiated metatheses of a few olefins,[11] also effect the polymerizations of a variety of acetylenes.


$$\overset{C_6H_5}{\underset{X}{\searrow\!\!\nearrow}}C{=}W(CO)_5$$

1a : X = OCH_3
b : X = C_6H_5



2

The polymerizations are slow, but they do work well. Thus compared with previous preparations, the yield of poly(*tert*-butylacetylene) is 3-12 times the best recorded[12,13] and of poly(2-butyne) 10 times the only one recorded,[16] the purity of polypropyne as indicated by IR and NMR spectra is much greater,[17] and the formation of soluble polymers containing 2-butyne or 4-octyne units is, with possibly one exception,[18] unique. (In fact, polymers of disubstituted acetylenes are very rare,[19] and, except for those of phenyl-1-propyne[6i,7a,b,20] and possibly 2-butyne,[18] none had previously been obtained in soluble form.[16a,21]) The structural purity of each polymer[22] is also high as evidenced by the ^{1}H and ^{13}C NMR spectra (displayed for the homopolymers in the supplementary material) and the IR spectra.[23,24]

A comparable ability to initiate acetylene polymerizations is not displayed by $(C_6H_5)_3PW(CO)_5$;[28] after 7 days at 50 °C with 50 equiv of phenylacetylene it gives no polymer. Mesitylene-$W(CO)_3$ is also said to be a bad initiator.[7b] However, cycloocta-1,5-diene-tungsten tetracarbonyl[29] in a similar experiment (the molar ratio was 100) gives a 30% yield, which could be accounted for if, as noted above for **1a** and **1b** and previously for WCl_6 + $(C_6H_5)_4Sn$[30] and $Re(CO)_5Cl$,[6i] the

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Table I. Polymerizations of Terminal Acetylenes, RC≡CH, Induced by Metal Carbenes **1a** and **1b**[a]

R	initiator	time, h	yield,[b] %	[η],[c] dL/g	"$\overline{M}_w$"[d] × 10^{-3}	"$\overline{M}_n$"[d] × 10^{-3}
C_6H_5	**1b**	46	49		17.0	9.0
C_6H_5	**1a**[e]	18	55	0.06	24.5	10.4
n-C_4H_9	**1b**	19	60	0.4	78.0	25.0
n-C_4H_9	**1a**	22	45	0.09	15.0	9.0
CH_3	**1b**	22	75	0.13	12.5	5.2
CH_3	**1a**	45	44		12.7	6.3
t-C_4H_9	**1b**	15	15			
t-C_4H_9	**1a**[e]	20	28[f]	1.1[g]	570.0	260.0

[a] Except where noted, no solvent, 40 °C. The molar ratio of acetylene and initiator was 50 for R = C_6H_5 and *n*-C_4H_9 and 100 for R = CH_3 and *t*-C_4H_9. [b] The yields recorded are those of materials isolated after the products had twice been dissolved in CH_2Cl_2, twice precipitated with CH_3OH, and then dried under vacuum, except that poly(*tert*-butylacetylene), which does not dissolve well in CH_2Cl_2, was dissolved in hot $CHCl_3$, precipitated with CH_3OH, and then dried. [c] Viscosities in toluene at 30 °C. [d] Molecular weights according to gel permeation chromatographic (GPC) analysis of solutions in tetrahydrofuran on Waters Associates' microstyragel columns. The weights are those of polystyrenes that should have GPC's like those observed. For polyphenylacetylene molecular weights according to GPC analysis (in an unspecified solvent) were found to be *f* times the true molecular weights, where, approximately, $1 < f < 2$ (see ref 2). In another study (the solvent was toluene), *f* was found to be greater (Biyani, B.; et al. *J. Macromol. Sci., Part A* **1975,** *9*, 327). Small discrepencies in the data are unresolved (Nguyen, H. X.; et al. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1977,** *18*, 200). [e] 60 °C. [f] With four times as much initiator and 2.5 times as much time, the yield rises to 66%. [g] In heptane at 30 °C.

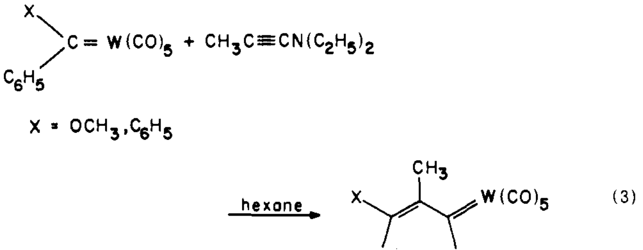
Table II. Polymerizations of Internal Acetylenes, RC≡CR, Induced by **1a** or **1b**[a]

			yield of polymer, %	
RC≡CR	initiator	time, h	soluble in $CHCl_3$[b]	insoluble
2-butyne	**1a**	113	4[c]	25
4-octyne	**1b**	92	small	much
cyclooctyne	**1a**	48	0	50[d]

[a] No solvent, 50 °C, except for 4-octyne where the temperature was 40 °C. The molar ratio of acetylene and initiator was 100 for **1a** and 50 for **1b.** [b] Precipitated by CH_3OH and dried under vacuum. [c] "$\overline{M}_w$" = 24 000, "$\overline{M}_n$" = 5800. In another experiment the yield was 14%. [d] Insoluble in $C_6H_5CH_3$ or C_6H_5Cl at reflux.

power of initiators to induce acetylene polymerizations parallels their ability to induce olefin matatheses.[31]

For some of these initiators the basis for this parallel is not understood because it is not known how they form the propagating metal carbenes, but, since **1a** and **1b** combine with special acetylenes as illustrated in eq 3,[32] the observation that



(3)

these same metal carbenes also initiate acetylene polymerizations provides the link necessary to implicate eq 2 as a polymerization mechanism.

Other evidence will have to be sought to support the hypothesis. However, the experiment with cyclooctyne (Table II) shows that migration of a triple bond to the end of a chain is not required to initiate reaction, a conclusion also suggested by an experiment with 2-butyne of 99.95% purity from which the recovered monomer was found to be essentially unchanged (GLC analysis and $AgNO_3$ test).

The stereochemical differences between different polyacetylenes[2,6f,27,33] might also be accounted for by eq 2 and controlled by the rotational motions on structure **2**.

Acknowledgment. We are grateful to the National Science Foundation for support under Grant CHE 77-22726.

Table III. Copolymerization of PhC≡CH and RC≡CR Induced by **1a** at 50 °C[a]

R	[RC≡CR]/ [PhC≡CH] reacted	time, h	yield of soluble polymer, %[b]	[RC≡CR]/ [PhC≡CH] in polymer[c]
n-C_3H_7	4	18	82,[d] 35[e,f]	0.5
CH_3	19	300	34[g]	~7

[a] **1a** (1 mol %) with 2-butyne and 2 mol % with 4-octyne. [b] Precipitated by CH_3OH. [c] ^1H NMR analysis. [d] Based on $C_6H_5C≡CH$. [e] Based on 4-octyne. [f] Soluble in CH_2Cl_2, $CDCl_3$. GPC analysis (see footnote *d*, Table I): "$\overline{M}_w$" = 160 000, "$\overline{M}_n$" = 50 000. [g] Soluble in hot $CHCl_3$.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of polypropyne (^1H NMR only), poly(*tert*-butylacetylene), poly(1-hexyne), and poly(2-butene) (7 pages). Ordering information is given on any current masthead page.

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(23) The ^{13}C NMR spectrum of polypropyne in $CDCl_3$ consists of broad resonances at 134 (–CH═) and 20 ppm (CH_3).

(24) The IR spectrum of poly(1-hexyne)[25] and the ^{13}C NMR,[20] ^{1}H NMR, and IR spectra[26] of polyphenylacetylene match those published. The IR spectrum of polypropyne resembles those in the literature[17] except that peaks attributable to oxidation are missing. The IR spectrum of the insoluble poly(2-butyne) in KBr exhibits peaks at 2970 (s), 2920 (s), 2850 (m), 2710 (vw), 1440 (m), 1365 (m), 1095 (m), 1040 (sh), and 1030 cm^{-1} (m). The soluble polymer exhibits the same spectrum, but with two weak unexplained absorptions added at 1260 and 800 cm^{-1}.

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Theoretical Calculations of the Aqueous Medium Effects on the Basicities of Primary Amines[1]

Sir:

The success of ab initio molecular orbital theory in treating substituent effects on gas-phase acidities and basicities[2] (i.e., energy changes for isodesmic proton transfer reactions) suggests its applicability in treating appropriate aqueous medium effects. For neutral acids and bases, aqueous medium effects on proton-transfer equilibrium have recently been shown to be highly specific, ranging from ~0 to 35 p*K*.[3,4] Evidence has been presented which indicates that the principal cause of the aqueous medium effects on the basicities of nitrogen and oxygen bases is the selective stabilization imparted by formation of complexes between water and the ammonium or the oxonium ions.[4] These complexes involve hydrogen bonding of at least one water molecule at each protonic "active site" of the ion. For example, consider the following equilibria:

$$(CH_3)_2OH^+{}_{(g)} + (CH_3)_2S_{(g)} \rightleftharpoons (CH_3)_2SH^+{}_{(g)} + (CH_3)_2O_{(g)} \quad (1)$$

$$\Delta G°_{(g)} = -8.0\ \text{kcal/mol}^5$$

$$(CH_3)_2OH^+{}_{(aq)} + (CH_3)_2S_{(aq)} \rightleftharpoons (CH_3)_2SH^+{}_{(aq)} + (CH_3)_2O_{(aq)} \quad (2)$$

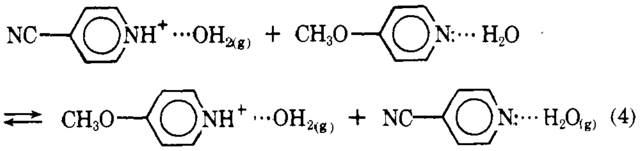
$$\Delta G°_{(aq)} = +62\ \text{kcal/mol}^3$$

The free-energy changes for these two reactions correspond to an aqueous medium effect which increases (and reverses) the apparent basicity of $(CH_3)_2O$ relative to $(CH_3)_2S$ by 10.3 p*K* units. This result is reproduced approximately by the difference in gas-phase binding energies of a single water molecules attached to $(CH_3)_2OH^+$ relative to $(CH_3)_2SH^+$ [6] (i.e., $\Delta G°$ for the hypothetical "model" reaction

$$(CH_3)_2OH^+ \cdots OH_{2(g)} + (CH_3)_2S_{(g)} \rightleftharpoons (CH_3)_2SH^+ \cdots OH_{2(g)} + (CH_3)_2O_{(g)} \quad (3)$$

$$\Delta G° \simeq +4.\ \text{kcal/mol}$$

agrees approximately with that for reaction 2 and accounts for most of the reversed basicity difference observed between the gas and aqueous phases). A few related equilibria involving single molecule attachment have been scrutinized both experimentally and by means of ab initio molecular orbital theory. In general the theoretical calculations have been moderately successful in reproducing the experimentally observed free energies (e.g., eq 4).



$$\Delta G°_{(4)} = -13.7\ \text{kcal/mol}^{7,8}$$

$$\Delta E°_{(4)(\text{STO-3G})} = -14.6\ \text{kcal/mol}^7$$

We report here the successful application of ab initio molecular orbital theory at the STO-3G level[9] to the calculation of the known medium effects of water (up to 8.5 p*K* units) on the basicities of primary amines.[3] The results are summarized in Table I. Typical are the results for two categories of substituent effects. The first equilibrium

$$CF_3CH_2NH_3^+{}_{(g)} + CH_3CH_2NH_{2(g)} \rightleftharpoons CH_3CH_2NH_3^+{}_{(g)} + CF_3CH_2NH_{2(g)} \quad (5)$$

$$\Delta G°_{(5)} = -14.6\ \text{kcal/mol}^{10}$$

has been the subject of a recent analysis[11] which indicates that the two ions, $CF_3CH_2NH_3^+$ and $CH_3CH_2NH_3^+$, are stabilized to a comparable degree by charge induced dipole interactions; destabilization of the $CF_3CH_2NH_3^+$ ion by the inductive-field effect (unfavorable internal charge-dipole interaction) therefore accounts for most of the observed $\Delta G°$ value. It has generally been argued that charge dispersal to the solvent effectively increases the distance between the centroids of charge and substituent dipole moment. It was further suggested that the extent of this charge dispersal is sufficient to reduce the destabilization of $CF_3CH_2NH_3^+{}_{(aq)}$ by a factor of ~2, thus accounting for the observed free energy for the aqueous phase proton transfer equilibrium[3]

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