

# The Polymerization of Acetylenes by Nickel-Carbonyl-Phosphine Complexes.

## IV. Kinetics and Polymerization Mechanisms<sup>1</sup>

L. S. MERIWETHER, M. F. LETO, E. C. COLTHUP, AND G. W. KENNERLY

Central Research Division, American Cyanamid Company, Stamford, Connecticut

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The effects of variations in solvent, temperature and gas sweeping, acetylene-catalyst ratio, and catalyst structure are reported. A kinetic study has been made of the polymerization of 1-heptyne and phenylacetylene by  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$ , including effects of deuterium substitution and catalyst pretreatment. Possible structures for the "active" nickel catalyst are considered. Mechanisms are proposed for the linear and cyclic polymerization of monosubstituted acetylenes, which are consistent with the observed kinetic and deuterium isotope effects and product structures. A mechanism for the aromatization of disubstituted acetylenes is also suggested.

In previous papers<sup>2</sup> we have discussed the polymerization of various classes of acetylenes with nickel-carbonyl-phosphine catalysts and the structures of the aromatic and linear oligomers obtained. The effects on the course of the polymerization due to changes in solvent, temperature and gas sweeping, acetylene-catalyst ratio, and catalyst structure have now been examined. In this paper we also present the results of kinetic studies of these reactions, including pretreatment of catalyst and deuterium isotope effects, and conclusions regarding the reaction mechanisms.

### Results and Discussion

For most of the studies two representative acetylenes were used, 1-heptyne and ethyl propiolate. Ethyl propiolate polymerizes very rapidly to exclusively aromatic products; 1-heptyne reacts at a somewhat slower rate to a mixture of predominantly linear dimers and trimers. The same catalyst complex,  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ , was used in most of the experiments with the exception of the catalyst variation and pretreatment studies.

**Solvent.**—The trimerization of ethyl propiolate was attempted in sixteen different solvent systems. Most of the common organic solvents are satisfactory media for the reaction. Best yields were obtained in cyclohexane, methanol, benzene, acetonitrile, and ethanol. Ethyl acetate, toluene, nitromethane, dimethylformamide, and nitrobenzene gave moderate yields. No direct relationship between reaction rate and solvent polarity is evident. A simple anionic or cationic polymerization process does not seem to be indicated. The inhibiting effect of water is apparent by comparison of 100% reaction in pure methanol with only 29% in a 10% aqueous methanol solution. Other poor solvents included carbon tetrachloride, dioxane, methyl ethyl ketone, tetrahydrofuran, and glacial acetic acid. Failure of these latter solvents to support the reaction is probably due either to their

strong coordination properties or their tendency to destroy irreversibly the catalyst.

A similar solvent behavior was observed in the polymerization of 1-heptyne. Greater than 95% conversions were obtained in cyclohexane, benzene, acetonitrile, and methanol.

**Reaction Temperature and Gas Sweeping.**—These reactions are very sensitive to temperature and degree of agitation in the solution. No polymerization was observed in unstirred solutions of 1-heptyne and catalyst in cyclohexane or acetonitrile between 25 and 75°. However, if the solution was brought to the boiling point (about 81°) or if the solution at 75° was agitated, complete reaction occurred after a short induction period. These results were confirmed by similar experiments with the more reactive propiolate ester (see Table I).

The experiments with carbon monoxide sweeping (Table I) show that this gas has a strong inhibitory effect, since, in spite of the agitation of the solution, the per cent reaction is considerably lower than in the nitrogen or carbon dioxide-flushed reactions. These results suggest that the reversible dissociation of carbon monoxide from  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  is an essential step in the formation of the "active" catalyst. Agitation simply promotes the release of carbon monoxide gas from the carbon monoxide-supersaturated solutions.

TABLE I  
EFFECT OF TEMPERATURE AND GAS SWEEPING ON ETHYL PROPIOLATE TRIMERIZATION<sup>a</sup>

Initial temp., °C.	Gas passed through	Per cent reaction	
		After 3 min.	After 90 min.
80	None	75	99
80	CO	70	90
80	O <sub>2</sub>	0	0
65	N <sub>2</sub>	75	100
56	None	21	21
41	None	3	9
43	N <sub>2</sub>	49	92
42	CO <sub>2</sub>	80	89
43	CO	0	0
33	None	0	2
36	N <sub>2</sub>	1	18

<sup>a</sup> [ester] = 1.0 M;  $[\text{Ni}(\text{CO})_2(\text{PPh}_3)_2]$  = 0.005 M; cyclohexane solvent.

(1) Presented in part at the 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 11-16, 1960.

(2) (a) L. S. Meriwether, E. C. Colthup, G. W. Kennerly, and R. N. Reusch, *J. Org. Chem.*, **26**, 5155 (1961); (b) L. S. Meriwether, E. C. Colthup, and G. W. Kennerly, *ibid.*, **26**, 5163 (1961); (c) E. C. Colthup and L. S. Meriwether, *ibid.*, **26**, 5169 (1961).

Oxygen gas sweeping caused complete inhibition of the polymerization of both 1-heptyne and ethyl propiolate in refluxing solvents. The catalyst appeared to be irreversibly decomposed by this treatment.

**Acetylene-Catalyst Ratio.**—In attempting to evaluate the ultimate catalytic efficiency of  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  in polymerizing acetylenes, a series of experiments at monomer-catalyst ratios from 100:1 down to 10,000:1 were performed. It was found that the ability of  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  to support the polymerization of several monosubstituted acetylenes under these reaction conditions diminished significantly between the ratios of 1000:1 and 10,000:1.

**Catalyst Variation.**—In order to gain a better understanding of the role of the nickel-carbonyl-phosphine catalyst, extensive variations in the structure of the catalyst were made. Both the number of phosphine and CO ligands and the phosphine substituents were varied and chelated phosphine complexes were also tried. Reppe and Schweckendiek<sup>3</sup> have reported that the following nickel-carbonyl complexes are all effective catalysts for the trimerization of acetylene:  $\text{Ni}(\text{CO})_3(\text{PPh}_3)_3$ ,  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$ ,  $\text{Ni}(\text{CO})_3[\text{P}(\text{C}_7\text{H}_7)_3]$ ,  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_4\text{H}_9)_3]_2$ ,  $\text{Ni}(\text{CO})_3(\text{AsPh}_3)_3$ , and  $\text{Ni}(\text{CO})_3(\text{SbPh}_3)_3$ . However, comparative efficiencies of these catalysts were not reported. We have now compared the relative efficiencies of sixteen different nickel-carbonyl-phosphine complexes toward the polymerization of 1-heptyne in refluxing cyclohexane or acetonitrile. The results of this study are given in Table II.

TABLE II

ORDER OF ACTIVITY OF NICKEL-CARBONYL-PHOSPHINE CATALYSTS TOWARD 1-HEPTYNE POLYMERIZATION<sup>a</sup>

Catalyst	Induction period (min.)	Per cent reaction <sup>b</sup>	
		After 40 min.	After 90 min.
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_4\text{CN})_2]_2^c$	10	100	100
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_4\text{CN})_3]_2^c$	15	88	100
$\text{Ni}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	46	57	81
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_4\text{CN})_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_4\text{CN})_2]^c$	13	50	62
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$	34	46	96
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)]_2$	20	45	64
$\text{Ni}(\text{CO})_2[\text{PH}_2(\text{C}_2\text{H}_4\text{CN})]_2^c$	5	33	55
$\text{Ni}(\text{CO})_3\text{P}(\text{OC}_2\text{H}_5)_3$	20	32	39
$\text{Ni}(\text{CO})_2[\text{PH}_2(n\text{-C}_8\text{H}_{17})]_2^d$	10	30	51
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)]_2$	25	24	45
$\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_2\text{H}_5)_3]_2$	25	22	34
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2]$	25	18	23
$\text{Ni}(\text{CO})_2[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$	90	8	11
$\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_2\text{H}_5)_3]_2$	>200	<1	<1
$\text{Ni}(\text{CO})[\text{P}(\text{OC}_2\text{H}_5)_3]_3$	>200	<1	<1
$\text{Ni}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3 + \text{Ni}(\text{CO})_2(\text{P}(\text{C}_6\text{H}_5)_2\text{Cl})_2$	Decomposes at 80°		

<sup>a</sup> [1-heptyne] = 0.9 M, [catalyst] = 0.006 M, solvent—80% cyclohexane, 20% *n*-hexane (except where indicated), *T* = reflux (~81–82°). <sup>b</sup> Times recorded after polymerization began (at the end of the induction period). <sup>c</sup> Acetonitrile solvent. <sup>d</sup> Sample contained a small amount of  $\text{Ni}(\text{CO})_3\text{PH}_2(n\text{-C}_8\text{H}_{17})$ .

The length of the induction period prior to polymerization, the activity of the catalyst during polymerization and the total conversion of 1-heptyne varied greatly for the different catalysts. The induction period ranged from five to ninety minutes for the complexes that displayed any activity, but the length of this period, during which the "active" catalyst is presumably being formed, was in no way related to the relative catalytic activity as measured by conversions of 1-heptyne either during or at the end of the reaction.

The order of catalyst activity was arbitrarily determined at forty minutes after beginning of polymerization, since at this point more than one half of the ultimate conversion had been attained and the effects of tailing-off later in the reactions were negligible. Among the dicarbonyl-diphosphine complexes,  $\text{Ni}(\text{CO})_2(\text{PR}_3)_2$ , the activity varied with the substituent R in the following general way:  $\text{C}_2\text{H}_4\text{CN} > \text{C}_6\text{H}_5 > \text{H} > \text{OC}_2\text{H}_5 > n\text{-alkyl} \gg \text{OC}_6\text{H}_5 \sim \text{Cl}$ . No simple explanation of this order of activity has been found, but it is interesting to see what a large influence variations in the phosphine substituents have on the activity of these catalysts. This result strongly suggests that the phosphine ligands are not completely lost from the nickel in the catalyst activation process. An essential role for the phosphine is further shown by our inability to obtain either the expected aromatic or linear oligomers from the reaction of monosubstituted acetylenes with nickel tetracarbonyl. Variation of the number of phosphine ligands revealed that the nickel tricarbonyl-monophosphine gave slightly better conversions than the corresponding dicarbonylbisphosphine.

The monocarbonyltrisphosphine and tetrakisphosphine complexes were not catalysts for 1-heptyne polymerization, although several tetrakisphosphinenickel complexes have been found in this laboratory to cyclotrimerize and cyclotetramerize ethyl propiolate at 25°. The very great reactivity of ethyl propiolate is further emphasized by the nearly quantitative aromatization of this monomer at reflux temperatures in the presence of most of the complexes listed in Table II. Chelation generally had only a slight effect on catalyst activity. Variation of the phosphine substituents gave the same order as observed in the unchelated complexes,  $\text{C}_2\text{H}_4\text{CN} > \text{C}_2\text{H}_5$ .

In Table III are recorded the results of a brief investigation of the effect of varying the catalyst complex on the polymerization of phenylacetylene. Generally, better conversions were obtained than with 1-heptyne, *e.g.*, the triphenylphosphite complex gave a 45% yield versus marginal activity toward 1-heptyne. The product distribution from the phenylacetylene was also sensitive to catalyst structure, linear trimerization being favored by

(3) W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

(4) J. R. Leto and M. F. Leto, *J. Am. Chem. Soc.*, **83**, 2944 (1961).

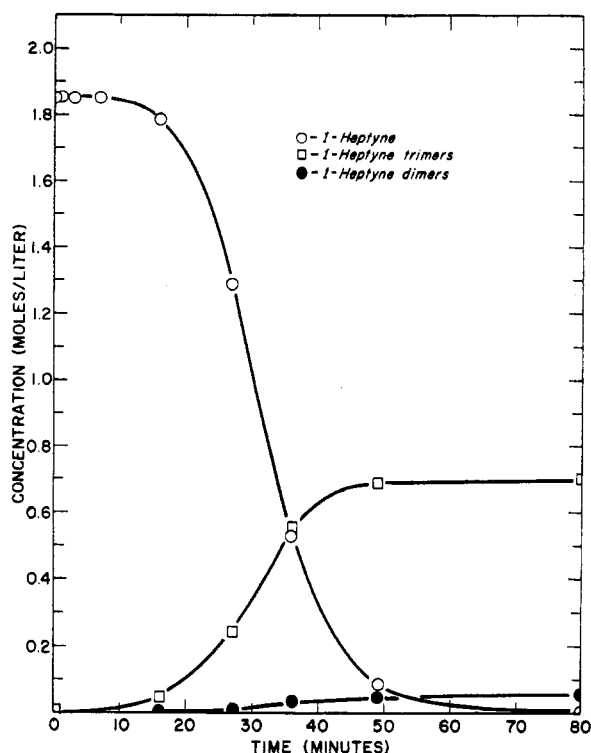


Fig. 1.—Concentration-time plot of the polymerization of 1-heptyne (1.85 *M*) with  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  (0.005 *M*) in refluxing cyclohexane.

TABLE III

EFFECT OF SOLVENT AND CATALYST VARIATION ON THE POLYMERIZATION OF PHENYLACETYLENE<sup>a</sup>

Catalyst	Solvent <sup>b</sup>	Per cent reaction	Per cent linear trimer	Per cent aromatic
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$	C	100	42	58
	A	100	59	41
$\text{Ni}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$	C	100	38	62
$\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_6\text{H}_5)_3]_2$	C	45	29	71
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_4\text{CN})_3]_2$	A	100	73	27
$\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_4\text{CN})_2\text{CH}_2\text{-CH}_2\text{P}(\text{C}_2\text{H}_4\text{CN})_2]$	A	35	70	30

<sup>a</sup> Catalyst concentration = 0.006 *M*,  $[\text{C}_6\text{H}_5\text{C}\equiv\text{CH}] = 0.9$  *M*, 60 ml. of solvent at reflux in carbon dioxide atmosphere. <sup>b</sup> C = cyclohexane, A = acetonitrile.

the cyanoethylphosphine complexes and aromatization by the triphenylphosphite complex.

In order to test whether the free phosphines alone could effect acetylene polymerization, cyclohexane solutions of 1-heptyne with  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(n\text{-C}_4\text{H}_9)_3$ ,  $\text{PH}(\text{C}_2\text{H}_4\text{CN})_2$ , and  $\text{PH}_2(n\text{-C}_8\text{H}_{17})$  were refluxed in an inert atmosphere for several hours. In no case was any disappearance of the 1-heptyne detected. Many of the free phosphines did react with ethyl propiolate, sometimes violently when the pure reactants were mixed. However, no propiolate polymers were isolated. The formation of adducts of acetylenic esters with other Lewis bases, such as pyridine and aniline, have been reported<sup>5</sup> and similar reactions may occur with phosphines.

The stability of most of these carbonyl-phosphine complexes in refluxing solvents under inert atmospheres is reasonably good for short periods. When  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  was refluxed under nitrogen for six hours in the two solvents, ethanol and benzene, about 60% and 30%, respectively, of the complex was recovered unchanged. Catalytic activity can be maintained for even longer periods in the presence of unreactive disubstituted acetylenes. When phenylacetylene was added to a benzene solution of  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$  and 2,5-dimethyl-3-hexyne-2,5-diol which had been refluxing with no apparent change for twenty-four hours, the solution turned dark brown and polymerization of the phenylacetylene occurred.

**Kinetic Studies.**—In an attempt to elucidate the mechanism of the linear polymerization, a kinetic study of the reaction of 1-heptyne with  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  in refluxing cyclohexane was undertaken. This monomer was chosen because of its convenient rate of polymerization and relatively low volatility at 80° and for the fact that the products of the reaction are almost exclusively linear dimers and trimers.<sup>2a</sup> The usual technique of analyzing quenched aliquots in the infrared at 2130  $\text{cm}^{-1}$  was used in following the disappearance of the monomer. An ultraviolet analytical method was developed for following the formation of total linear dimer and total linear trimer. This was based upon the observation that in cyclohexane solution the dimer product had maximum absorption at 227  $\mu\text{m}$  ( $\epsilon$  12,000) and the trimer product at 270  $\mu\text{m}$  ( $\epsilon$  11,900). Unfortunately, after correction for the absorption of dimer at 270  $\mu\text{m}$  ( $\epsilon$  1060) and of trimer at 227  $\mu\text{m}$  ( $\epsilon$  5830) and of catalyst species at these wave lengths, these results were subject to considerable error. The total final concentrations of dimer and trimer found were generally 115–130% of those calculated, based on 100% conversion of monomer. However, they were sufficiently accurate to establish certain gross effects.

A typical concentration-time plot of the reaction of 1-heptyne with  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  is shown in Fig. 1 in which the build-up of trimer and dimer products is seen to parallel the disappearance of the monomer. The relative rate of dimer and trimer formation is fairly constant throughout the reaction, showing no dependence on monomer concentration. In Fig. 2 are plotted the results of varying the initial 1-heptyne concentration at constant catalyst concentration. Six runs were made over a range of initial 1-heptyne concentration of 0.023 *M* to 2.5 *M* with  $4.7 \pm 0.5 \times 10^{-3}$  *M*  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  in refluxing cyclohexane. The results of the run with 0.23 *M* 1-heptyne are not plotted since only 10% of the monomer reacted. Duplicate runs with 1.85 *M* 1-heptyne were identi-

(5) R. M. Acheson and G. A. Taylor, *Proc. Chem. Soc.*, 186 (1959); F. Strauss and W. Voss, *Ber.*, **59**, 1681 (1926).

cal in all respects, showing the reproducibility of the experiments. At high 1-heptyne to catalyst ratios ( $> 250:1$ ) the disappearance of 1-heptyne, after the usual induction period, was independent of the acetylene concentration up to about 75–80% conversion. By plotting the data at lower monomer to catalyst ratios (40:1) as a first-order reaction, the disappearance of 1-heptyne was found to be proportional to the acetylene concentration over more than 60% reaction. The tailing off of all of the plots in the last 10–20% of reaction could be attributed either to reactions of even higher order in acetylene or to "active" catalyst decomposition. However, the latter seems less likely, since the linear polymer products have been found to stabilize the "active" catalyst (*vide infra*). Furthermore, subsequent additions of fresh monomer to the spent system are readily polymerized. A marked decline in catalyst activity occurs only after several such polymerization cycles.

Attempts to vary significantly the initial catalyst concentration at constant 1-heptyne concentration were unsuccessful since polymerization of this monomer could not be initiated below  $2 \times 10^{-3} M$  catalyst and the upper limit of solubility of  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  in cyclohexane is about  $6 \times 10^{-3} M$ . Catalyst activity dropped off sharply above a 1-heptyne to catalyst ratio of 1000:1 and below a ratio of about 10:1. These effects are probably associated with the catalyst activation process rather than the polymerization reaction. Studies of the catalyst activation process<sup>6</sup> indicate that only part of the original dicarbonyl-diphosphine complex is converted into "active" catalyst. Unfortunately, no method of following the concentration of "active" catalyst during the polymerization has been found.

One possible mechanism for the linear polymerization reaction is a stepwise process whereby two monomers combine to form dimer, dimer reacts with monomer to form trimer, trimer reacts with monomer to form tetramer, etc. The product results for several runs at different initial monomer concentrations were analyzed to determine whether the dimer was peaking up earlier in the run and then leveling off as the trimer reached its maximum. Although the data for the dimer is very poor, there is no evidence for peaking. The relative rates of dimer and trimer formation appear to be constant throughout the reaction. In a further test of the stepwise mechanism, the final trimer/dimer product ratios were compared in reactions of 1-heptyne alone (1.85  $M$ ) and of 1-heptyne (0.90  $M$ ) mixed with preformed heptyne dimer (0.45  $M$ ). If the dimer did not take part in the reaction, a final trimer/dimer ratio of less than 1 would be expected. The final trimer/dimer ratio for the run with added dimer was 0.7, compared with a ratio for the run with 1-heptyne alone of

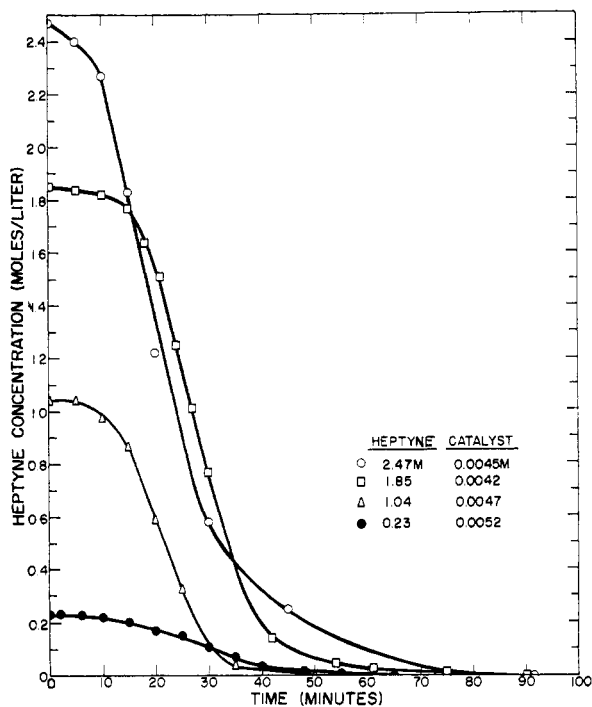
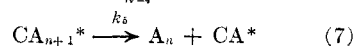
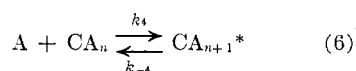
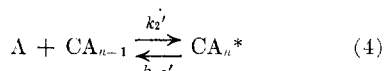
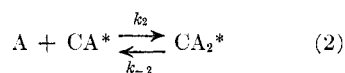
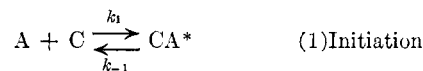


Fig. 2.—Effect of varying the initial monomer concentration on the polymerization of 1-heptyne with  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  in refluxing cyclohexane.

13.5. Therefore, the dimer was essentially inert to the reaction. This rules out a stepwise process in which trimer is formed by reaction of monomer with free dimer or complexed dimer in equilibrium with free dimer.

The above results are consistent with the following reaction scheme (where A = 1-heptyne; C, CA, CA<sub>2</sub>... CA<sub>n+1</sub> represent catalytic complex intermediates; A<sub>n</sub> = product; and \* refers to those complexes in reversible equilibrium with free monomer), when it is assumed that  $k_1, k_{-1}$ ,



$k_2, k_{-2}, k_2', k_{-2'}, k_4, k_{-4} > > k_3, k_3' > k_5$  and that at high acetylene concentrations essentially all of the "active" catalyst is in the form of CA\*, CA<sub>2</sub>... CA<sub>n</sub> and CA<sub>2</sub>\*... CA<sub>n+1</sub>\*. The steady-state assumption is then valid for the latter species over most

(6) To be reported in Part V.

of the reaction. Ultimately, the reaction would be expected to undergo a transition from zero to first and higher order kinetics as A became exhausted and equilibria of equations 1, 2, 4, and 6 no longer lay 100% to the right.

**Deuterium Isotope Studies.**—Since the formation of linear acetylene polymers requires the transfer of at least one hydrogen atom per product molecule formed, it was hoped that the use of deuterated acetylenes would help to elucidate the reaction mechanism. If the rate-determining step involved a hydrogen atom transfer, deuterium substitution would be expected to depress the reaction rate.<sup>7</sup>

A competitive experiment was carried out in which equimolar quantities of 1-heptyne and 1-heptyne-1-*d* were treated with Ni(CO)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub>. The disappearance of the hydrogen and deuterium compounds was followed by infrared analysis of quenched aliquots at 3300 cm.<sup>-1</sup> (≡C—H stretch) and 2585 cm.<sup>-1</sup> (≡C—D stretch), respectively. The deuterated 1-heptyne reacted at a significantly slower rate than 1-heptyne itself. The ratio of D to H compound remaining increased from the initial 1.00 to 2.50 after 97% conversion (Table IV). A kinetic

TABLE IV  
ISOTOPE EFFECT IN POLYMERIZATION OF 50%  
1-HEPTYNE-1-*d* WITH 1-HEPTYNE

Time (min.)	Per cent reaction	$\frac{X}{X_0}$	$V$ (found)	$V$ (calcd.)
0	0	1.000	1.00	1.00
20	13	0.894	1.01	1.03
25	27	.750	1.05	1.07
30	46	.582	1.16	1.15
35	59	.462	1.27	1.23
40	72	.380	1.37	1.28
45	83	.198	1.52	1.52
50	88	.140	1.85	1.66
60	95	.071	2.36	2.00
70	97	.040	2.50	2.36

and mathematical analysis of these data, assuming that (1) only trimer product was formed, (2) only one hydrogen transfer occurred in the slow step, and (3) the position of the reversible equilibria was unaffected by deuterium substitution, resulted in the following rate equation,

$$2 \ln(V + 1) + \frac{3K}{1 - K} \ln V - 1.38629 = \ln X$$

where  $X$  = concentration of H compound,  $Y$  = concentration of D compound,  $V = Y/X$ ,  $k_H$  and  $k_D$  = rate constants for the reaction of the H and D compounds, respectively, and  $K = k_H/k_D$ . A least squares fit of the experimental data to solutions of the above equation gave a value of  $K = 2.56 \pm 0.46$ , which is comparable to results observed in organic reactions in which a carbon-hydrogen bond cleavage is the rate-controlling step.<sup>7</sup>

(7) K. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

In order to determine whether the nickel complex catalyzed hydrogen-deuterium exchange between the monomers, equimolar concentrations of 1-heptyne-1-*d* and 1-pentyne were treated with Ni(CO)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> in refluxing cyclohexane. Several aliquots were taken during the run, each separated into 1-pentyne and 1-heptyne fractions, and each fraction was analyzed in infrared at 3300 and 2585 cm.<sup>-1</sup>. The results show (Table V) that after the induction period rapid deuterium exchange occurred. The fact that *only* the "active" catalyst promotes deuterium exchange lends support to the conclusion that it is a different species from the original carbonyl-phosphine complex. No deuterium exchange occurred in a control experiment omitting the nickel complex.

TABLE V  
DEUTERIUM EXCHANGE BETWEEN 1-HEPTYNE-1-*d* AND  
1-PENTYNE<sup>a</sup>

Time (min.)	Per cent D in 1-heptyne	Per cent D in 1-pentyne	Per cent polymerization
0	83	0	0
20	83	0	1
42	77	12.4	22
67	72	17.5	38

<sup>a</sup> 0.5 M 83% C<sub>8</sub>H<sub>11</sub>C≡CD, 0.5 M C<sub>4</sub>H<sub>7</sub>C≡CH, 0.006 M Ni(CO)<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> in refluxing cyclohexane.

**Aromatization.**—Attempts to obtain kinetic data on the cyclic trimerization of monosubstituted acetylenes have been unsuccessful. This has been principally due to the very high rates of polymerization and the exothermic nature of these reactions. The trimerization of ethyl propiolate with all active nickel-carbonyl-phosphine catalysts was too fast to measure even at lower temperatures, being essentially complete in less than three minutes. Propargyl alcohol was found to aromatize at a somewhat slower rate, but a satisfactory common solvent for the monomer, catalyst, and products could not be found. Similar problems were encountered with other monomers which polymerized exclusively to aromatic products.

It was then decided that even more valuable mechanistic clues might be obtained from the study of a monomer which formed a mixture of aromatic and linear products. Phenylacetylene was chosen, since it had been previously found<sup>2a</sup> to react cleanly to give an isolated product consisting of roughly 30% aromatic and 70% linear trimers at a rate comparable to that for the reaction of 1-heptyne to linear polymers. A concentration-time plot for the reaction was determined in the usual way by following the disappearance of monomer at 2130 cm.<sup>-1</sup> and the formation of 1,2,4-triphenylbenzene at 840 cm.<sup>-1</sup> and the triphenylbutadienylacetylene at 975 cm.<sup>-1</sup>. The results are shown in Fig. 3. The reaction followed the usual sigmoid curve with a twenty-minute induction period. Surprisingly, the relative rates of

formation of aromatic and linear products were nearly constant, perhaps signifying a common catalytic agent.

It is of particular interest to determine the effect of deuterium substitution on the rate of the aromatization reaction, since the cyclic products can be formed either *via* hydrogen transfer mechanisms or by routes involving no carbon-hydrogen bond cleavage. Unfortunately, a rigorous solution to this problem has not been found, because of the very high reaction rates of the aromatizing monomers. Several experiments were performed on partially deuterated phenylacetylene with  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  in cyclohexane in order to ascertain the size of the isotope effect in a reaction leading to roughly equal amounts of aromatic and linear products. Phenylacetylene containing 87%  $\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$  polymerized at a slower rate than the undeuterated monomer. In the polymerization of phenylacetylene containing initially 64%  $\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$  the unreacted monomer contained 65.5, 70, and 72%  $\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$  after 41, 70, and 88% reaction, respectively. An initially 80% deuterated monomer showed an enrichment to 86%  $\text{C}_6\text{H}_5\text{C}\equiv\text{CD}$  after 77% reaction. For comparison, data on the polymerization of 53% 1-heptyne-1-*d* in 1-heptyne under the same conditions indicated 58.5 and 62%  $\text{C}_6\text{H}_{11}\text{C}\equiv\text{CD}$  in the monomer remaining after 72 and 83% reaction, respectively. The relative enrichments of the two monomers are very similar (6 vs. 5.5% at about 71% reaction and 9 vs. 8% at about 85% reaction for the phenylacetylene and 1-heptyne, respectively) even though more than one third of the polymer product from the phenylacetylene was cyclic trimer. Although not conclusive, the above results suggest the existence of a common step involving a hydrogen transfer in both the linear and cyclic polymerizations of phenylacetylene.

**Catalyst Pretreatment.**—During the course of this work it was inadvertently discovered that the polymerization of reactive acetylenes could be enhanced by pretreating the nickel-carbonyl-phosphine complex solution at reflux with an unreactive disubstituted acetylene. As a solution of nickel complex and disubstituted acetylene was refluxed for an hour with inert gas sweeping, the solution gradually developed an intense yellow color and carbon monoxide gas was evolved. This yellow solution appeared to be stable for long periods in the absence of oxygen. However, when exposed to air the solution was instantly decolorized. The yellow color was found to be due to a species with a very intense absorption band at 290  $\text{m}\mu$ . When a reactive acetylene was added to this yellow solution between 25 and 40°, rapid polymerization of this monomer occurred to the usual products. The unreactive acetylene was recovered unchanged from the reaction.

In Table VI are shown some of the experiments

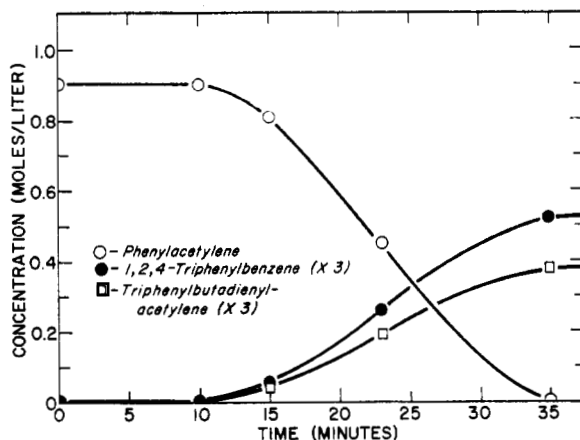


Fig. 3.—Concentration-time plot of the trimerization of phenylacetylene (0.9 *M*) with  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  (0.006 *M*) in refluxing cyclohexane.

that were done to extend the scope of this pretreatment to different catalysts and acetylenes. The phenomenon was found to be quite general for different pretreating acetylenes, different catalysts, including chelated complexes, and different reactive acetylene monomers. The effectiveness of the disubstituted acetylenes in catalyst pretreatment decreased in the order:  $\text{C}_6\text{H}_5\text{—C}\equiv\text{C—C}_6\text{H}_5$   $\sim$  linear  $(n\text{-C}_3\text{H}_7\text{C}\equiv\text{CH})_3$   $>$   $\text{C}_2\text{H}_5\text{—C}\equiv\text{C—C}_2\text{H}_5$   $>$   $(\text{CH}_3)_2\text{C}(\text{OH})\text{—C}\equiv\text{C—C}(\text{OH})(\text{CH}_3)_2$   $>$   $(\text{CH}_3)_2\text{C}(\text{OH})\text{—C}\equiv\text{C—C}\equiv\text{C—C}(\text{OH})(\text{CH}_3)_2$   $>$   $\text{HOCH}_2\text{—C}\equiv\text{C—CH}_2\text{OH}$ . Molar ratios of pretreating acetylene to catalyst even as low as 2:1 were found to be effective. However, pretreatment at temperatures below reflux was not effective in activating the catalyst. The reaction with linear 1-pentyne trimer demonstrates that the linear polymer products, which are disubstituted acetylenes, are also capable of activating and stabilizing the catalyst. This explains the observation mentioned above that spent linear polymerization reaction mixtures would repeatedly polymerize fresh additions of monomer. That this does not apply to the aromatic products is seen from the experiment with 2-butyne-1,4-diol (Table VI). This disubstituted acetylene polymerized quantitatively to hexamethylbenzene.<sup>2a</sup> Ethyl propiolate, added subsequently at 25°, failed to react. Hence, aromatic compounds do not stabilize the "active" catalyst and aromatization of acetylenes cannot be revived after the monomer has once disappeared.

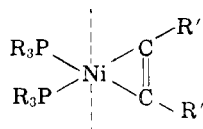
Attempts to isolate these yellow complexes have been unsuccessful so far due to their great oxygen sensitivity, instability in the solid state, and the very low concentrations attainable in solution. The similarity of their ultraviolet spectra to those of a series of bisphosphine-platinum-acetylene complexes recently prepared by Chatt, Rowe, and Williams<sup>8</sup> suggests that they may be the analogous,

(8) J. Chatt, G. A. Rowe, and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

TABLE VI  
 CATALYST PRETREATMENT EXPERIMENTS

Catalyst <sup>a</sup>	Pretreating acetylene <sup>b</sup>	Solvent <sup>c</sup>	Temp., °C.	Color <sup>d</sup>	Reactive acetylene added <sup>e</sup>	Temp. at addition, °C.	Per cent reaction
1	$C_6H_5-C\equiv C-C_6H_5$	C	81	Y	E	25	100
1	$C_2H_5-C\equiv C-C_2H_5$	C	81	Y	E	25	100
1	$\begin{array}{c} CH_3 \qquad \qquad CH_3 \\   \qquad \qquad \qquad   \\ CH_3-C-C\equiv C-C-CH_3 \\   \qquad \qquad \qquad   \\ OH \qquad \qquad \qquad OH \end{array}$	B	80	Y	E	25	75
1	linear ( $n-C_3H_7-C\equiv CH$ ) <sub>3</sub>	C	81	B	E	25	100
1	$HOCH_2-C\equiv C-CH_2OH$	B	80	DB	E	25	0
2	$C_6H_5-C\equiv C-C_6H_5$	A	82	Y	H	25	70
2 <sup>f</sup>	$C_6H_5-C\equiv C-C_6H_5$ <sup>g</sup>	A	82	Y	E	25	100
2	$\begin{array}{c} CH_3 \\   \\ (CH_3-C-C\equiv C-)_2 \\   \\ OH \end{array}$	A	82	B	E	25	20
2	$C_2H_5-C\equiv C-C_2H_5$	A	82	LY	E	25	0
3	$C_6H_5-C\equiv C-C_6H_5$	A	82	Y	E	25	100
3	$C_6H_5-C\equiv C-C_6H_5$	A	82	Y	H	40	30
3	$C_6H_5-C\equiv C-C_2H_5$	A	82	LY	E	25	0
2	$C_6H_5-C\equiv C-C_6H_5$	A	40	LY	E	25	0
2	$C_6H_5-C\equiv C-C_6H_5$	A	40	LY	H	40	0
2	$C_6H_5-C\equiv C-C_6H_5$	A	25	C	E	25	0

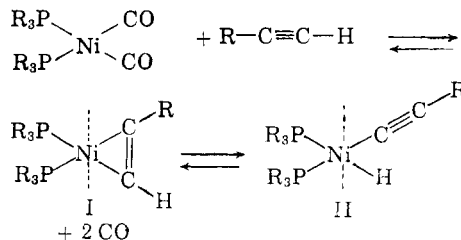
<sup>a</sup> Catalyst concentration = 0.006 M; 1 =  $Ni(CO)_2[P(C_6H_5)_3]_2$ ; 2 =  $Ni(CO)_2[P(CH_2CH_2CN)_3]_2$ ; 3 =  $Ni(CO)_2[P(CH_2CH_2CN)_2CH_2CH_2P(CH_2CH_2CN)_2]$ . <sup>b</sup> Concentration = 0.6 M. <sup>c</sup> C = cyclohexane; B = benzene; A = acetonitrile. <sup>d</sup> Color of solution after 2-hr. pretreatment with  $CO_2$  sweeping; Y = yellow; B = brown; DB = dark brown; LY = light yellow; C = colorless. <sup>e</sup> Acetylene concentration = 0.6 M; E = ethyl propiolate; H = 1-heptyne. <sup>f</sup> 0.015 M. <sup>g</sup> 0.030 M.



less stable nickel complexes of the structure given above.

### Reaction Mechanisms

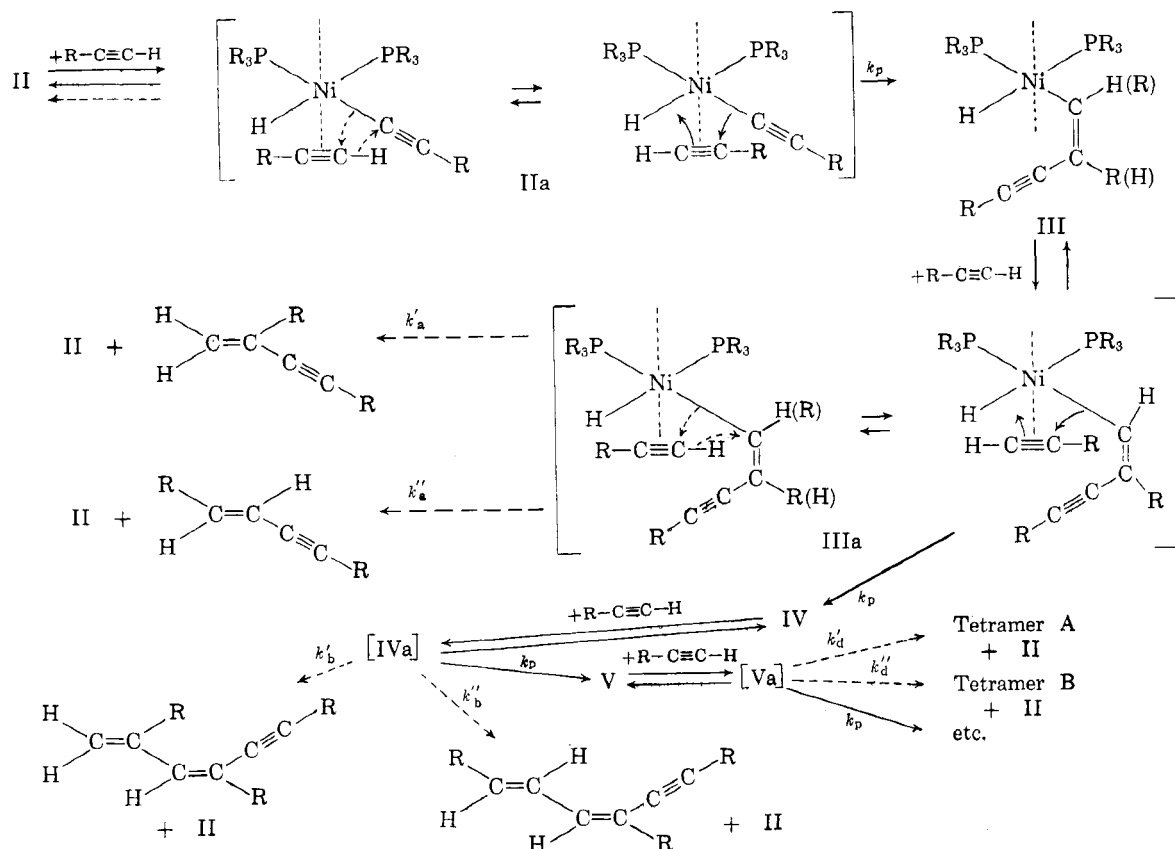
**“Active” Catalyst.**—It has been established<sup>6</sup> that the “active” polymerization catalyst is a nickel-phosphine-acetylene complex which is formed by the reaction of a nickel-carbonyl-phosphine complex with an acetylene. Furthermore, it (1) retains its original phosphine ligands; (2) has lost all of its CO ligands and thus has two of its original four coordination positions available for bonding to the acetylene; (3) is in a reversible equilibrium with the acetylene monomer and the original nickel-carbonyl-phosphine complex; (4) has a high “turn over” number and hence retains its original structure and activity after each reaction sequence; and (5) catalyzes the exchange of acetylenic hydrogens between different mono-substituted acetylenes. The “active” catalyst may actually consist of several nickel-phosphine-acetylene complexes in equilibrium with one another. Complex I is probably initially formed but is readily converted to II; the latter is proposed as the “active” catalyst for both the linear and cyclic polymerization of acetylene itself and of mono-



substituted acetylenes. Both I and II are planar complexes of formally nickel(II), which have a vacant  $p_z$  orbital available to  $\pi$ -bond with a second acetylene molecule.

**Linear Polymerization.**—It has previously been suggested<sup>2b</sup> that the linear products are formed by a Ziegler-Natta type process in which the central monomer units are introduced intact and stereospecifically and only one hydrogen atom transfer occurs per product molecule formed. This is consistent with the number of products obtained and the deuteration results. A more detailed mechanism for these reactions is outlined, p. 3937.

II is assumed to react rapidly and reversibly with a second molecule of acetylene to give IIa, involving  $\pi$ -complex formation between the triple bond and the nickel  $p_z$  orbital such that the  $z$ -axis goes through the center of the  $C\equiv C$  bond and the acetylene molecule lies roughly parallel to the plane of the complex. The symmetry of the  $p_z$  orbital about the  $z$ -axis permits many possible orientations of the linear acetylene molecule relative to the phosphine hydride (x) and phosphine-



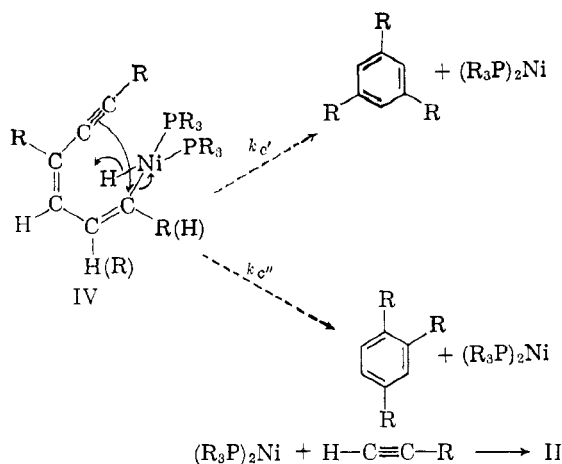
acetylide ( $\gamma$ ) axes. For this reason, it is entirely possible that the four reactions indicated [cis insertion of the new monomer between the nickel and acetylide carbon atoms such that (a) the R-group is adjacent to the triple bond or (b) to the nickel atom, (c) hydrogen exchange between the  $\pi$ -complexed acetylene and the acetylide group, and (d) dissociation of the  $\pi$ -complex] may proceed from different conformations of the  $\pi$ -complex. The two nickel-vinylacetylene complexes (III), resulting from insertion, can then reversibly form  $\pi$ -complexes (IIIa) with another acetylene. Four reactions are again possible for IIIa: (e) hydrogen transfer from the acetylene to the 2,4-disubstituted vinylacetylene group to form the vinylidene dimer isomer and II, (f) hydrogen transfer from the acetylene to the 1,4-disubstituted vinylacetylene group to form the *trans* dimer isomer and II, and *cis* insertion of the acetylene molecule between the nickel and vinyl carbon atoms of the 2,4-disubstituted vinylacetylene complexes *only* such that the R-group is adjacent (g) to the central double bond or (h) to the nickel atom. Insertion of the new acetylene into the 1,4-disubstituted vinylacetylene complexes appears to be inhibited in favor of reaction (f) by steric repulsions from the R-group in the 1-position. Reactions (e) and (f) above (labeled  $k'_a$  and  $k''_a$ ) are irreversible since exchange does not occur between acetylenic and ethylenic hydrogens. The nickel-butadienylacetylene complex (IV) and its  $\pi$ -complex with a

new monomer molecule (IVa) react in like fashion to produce the two linear trimer isomers and II or the nickel tetramer complex (V). This sequence is repeated for each higher homolog.

The slow rate-determining steps in the reaction sequence are the termination and catalyst recovery processes labeled  $k'_a$ ,  $k''_a$ ,  $k'_b$ ,  $k''_b$ , etc. These involve the transfer of a hydrogen and the cleavage and formation of new nickel-carbon bonds. These processes could alternatively be considered as  $\alpha$ -elimination reactions, with concerted loss of the hydride and hydrocarbon ligands from the nickel, followed by a rapid collapse of the  $\pi$ -complex to I or II, or also as  $\alpha$ -elimination reactions of the complexes III, IV, V, etc., to give product plus the ligand deficient species  $(\text{R}_3\text{P})_2\text{Ni}$ . However, it is felt that the latter compound must be quickly stabilized by combination with an acetylene molecule. Any of these mechanisms is consistent with the observed kinetics as long as the reversible equilibrations and the propagation steps, labeled  $k_p$ , are fast relative to the termination processes.

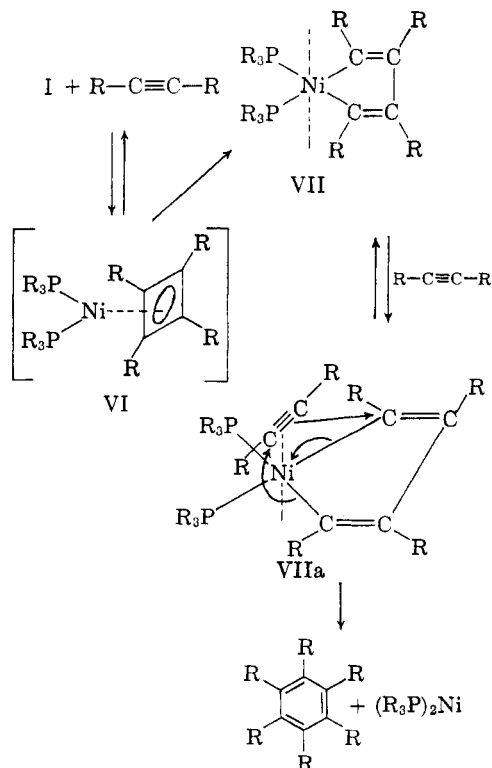
**Aromatic Polymerization.**—The mechanism for aromatization of acetylene or monosubstituted acetylenes is readily incorporated into the above scheme for linear polymerization by assuming that there is a favored conformation of IV or IVa in which the 1 and 6 carbon atoms of the butadienylacetylenyl group can approach bonding distance. A concerted hydrogen transfer and ring closure would give the following aromatic product.



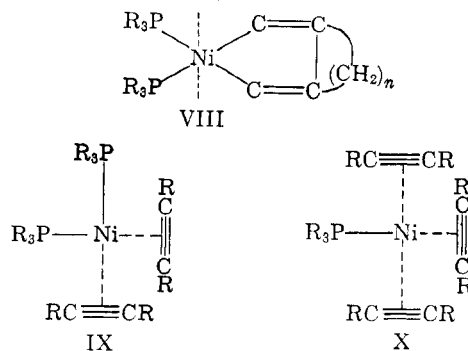


The general tendency of the 1,2,4-trisubstituted benzene to predominate over the symmetrical 1,3,5-isomer<sup>2a</sup> can now be explained by the stabilities and relative proportions of the two structures of complex IV. The occurrence of both cyclic and linear products together and other similarities between the two reactions, including an apparent deuterium isotope effect in both, are accounted for by the common intermediates in these mechanisms.

The formation of hexasubstituted benzenes from disubstituted acetylenes, observed with a few monomers in the nickel-carbonyl-phosphine reactions<sup>2a</sup> and more generally using bisacrylonitrile-nickel-phosphine catalysts,<sup>9</sup> may be best explained by a mechanism similar to those above in which complex I reacts with a second acetylene molecule,



perhaps by way of a bisphosphine-nickel-cyclobutadiene (VI), to form the planar complex VII in which the nickel and two acetylene groups have formed a five-membered ring. As in the case of II, VII has a vacant  $p$ , orbital for coordination of a third acetylene molecule. The resulting  $\pi$ -complex VIIa can then collapse to the aromatic ring and  $(R_3P)_2Ni$ . Synthesis of the condensed aromatic products from unconjugated terminal diacetylenes<sup>2a</sup> may occur *via* a similar route through the intermediate complex VIII. Of course, it is also possible that some (or even all, in some cases)



of the aromatic product from acetylene and mono-substituted acetylenes may be formed by this process. The very high yields of 1,2,4-trisubstituted benzene products (statistically, a 3:1 ratio of 1,2,4- to 1,3,5-isomer would be expected) can still be explained by the lower steric requirements of the substituents in the  $\beta$ -positions of the postulated 1-nickelocyclopenta-2,4-diene ring of VII.

Mechanisms for the aromatization reactions involving only  $\pi$ -complexes of formally zerovalent nickel with acetylenes or cyclobutadiene, such as VI, IX, or X, suffer from several serious shortcomings. First, they do not predict the high proportion of 1,2,4-trisubstituted benzene isomers in the products, since steric effects should strongly favor the symmetrical 1,3,5-isomers. Secondly, in the case of VI and IX, they do not provide a means of activating the third acetylene monomer by coordination to the metal. Finally, the ability of the species  $R_3P-Ni$  to survive more than one cyclization sequence seems doubtful.

### Experimental

**Materials.**—The sources of the undeuterated acetylenes have been reported previously.<sup>2a</sup> All solvents were reagent or "spectro" grade. The sweeping gases were Matheson prepurified nitrogen, bone dry carbon dioxide, and c.p. carbon monoxide.

1-Heptyne-1-*d* was prepared in 90% isotopic purity by hydrolysis of the Grignard reagent of 1-heptyne with 99.5% deuterium oxide.<sup>10</sup> Phenylacetylene-1-*d* of 87% isotopic purity was prepared in analogous manner from the Grignard reagent of phenylacetylene. Monomers of lower

(9) G. N. Schrauzer, *Ber.*, **94**, 1403 (1961).

(10) R. Romanet and B. Wojtkowiak, *Bull. soc. chim.*, **27**, 1500 (1960).

deuterium content were prepared by dilution with the undeuterated compound.

The following nickel-carbonyl-phosphine complexes were prepared as reported previously<sup>11</sup>:  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ,  $\text{Ni}(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_5\text{CN})_2]_2$ ,  $(\text{Ni}(\text{CO})_2[\text{P}(\text{n-C}_4\text{H}_9)_3])_2$ ,  $\text{Ni}(\text{CO})_2\text{P}(\text{OC}_2\text{H}_5)_3$ ,  $\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_2\text{H}_5)_2]_2$ ,  $\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_2\text{H}_5)_3]_2$ ,  $\text{Ni}(\text{CO})_2[\text{P}(\text{OC}_2\text{H}_5)_2]_2$ ,  $\text{Ni}(\text{CO})_2\text{P}(\text{OC}_2\text{H}_5)_3$ , and  $\text{Ni}(\text{CO})_2(\text{PCl}_2)_2$ .

**Dicarbonylbis[bis(2-cyanoethyl)phosphine]nickel**,  $\text{Ni}(\text{CO})_2[\text{PH}(\text{C}_2\text{H}_4\text{CN})_2]_2$ .—Nickel carbonyl (3.3 g., 0.019 mole) in 50 ml. of methanol was added dropwise to a solution of 5.4 g. (0.039 mole) of  $\text{PH}(\text{C}_2\text{H}_4\text{CN})_2$ <sup>12</sup> in 100 ml. of methanol under nitrogen. Vigorous evolution of carbon monoxide ensued. After 30 min. the mixture was heated to reflux and held there for an additional 30 min. The methanol was removed leaving a yellow air sensitive undistillable oil whose infrared spectrum contained metal carbonyl bands at 1950 and 2000  $\text{cm}^{-1}$  (mineral oil mull).

*Anal.* Calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}_4\text{P}_2\text{Ni}$ : N, 14.18. Found: N, 14.30.

**Dicarbonylbis(2-cyanoethylphosphine)nickel**,  $\text{Ni}(\text{CO})_2[\text{PH}_2(\text{C}_2\text{H}_4\text{CN})_2]_2$ , was prepared in the same manner from 1.7 g. (0.02 mole) of  $\text{PH}_2\text{C}_2\text{H}_4\text{CN}$ <sup>12</sup> and 1.7 g. (0.01 mole) of nickel carbonyl in methanol. The complex was an extremely air sensitive cherry red liquid having infrared metal carbonyl bands at 1950 and 2000  $\text{cm}^{-1}$  (mineral oil mull).

*Anal.* Calcd. for  $\text{C}_8\text{H}_{12}\text{O}_2\text{N}_2\text{P}_2\text{Ni}$ : N, 9.72; P, 21.52. Found: N, 10.48; P, 20.95.

**Dicarbonylbis(*n*-octylphosphine)nickel**,  $\text{Ni}(\text{CO})_2[\text{PH}_2(\text{n-C}_8\text{H}_{17})_2]_2$ .—A solution of 1.7 g. (0.01 mole) of nickel carbonyl in 25 ml. of ether was added dropwise to 2.9 g. (0.02 mole) of  $\text{PH}_2(\text{n-C}_8\text{H}_{17})_2$ <sup>13</sup> in 25 ml. of ether under nitrogen. After the initial evolution of carbon monoxide had subsided, the solution was refluxed for 15 min. and the solvent was quickly removed on a rotating evaporator. A bright yellow liquid (5 g.) remained whose infrared spectrum [bands at 1960, 2000, and 2060 ( $w$ )  $\text{cm}^{-1}$ ] indicated the presence of a small impurity of the tricarbonyl complex,  $\text{Ni}(\text{CO})_3\text{PH}_2(\text{n-C}_8\text{H}_{17})_2$ . It was not purified further.

**Dicarbonylbis(diphenylethylphosphine)nickel**,  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_2(\text{C}_2\text{H}_5)_2]_2$ .—A solution of 2.9 g. (0.017 mole) of nickel carbonyl in 25 ml. of ether was added dropwise under nitrogen to a refluxing solution of 7.5 g. (0.035 mole) of  $\text{P}(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5$  in 50 ml. of ether. Heating was continued for 15 min. after addition of the carbonyl was completed. The cooled solution was evaporated down to about one fourth its original volume. The pale yellow crystals which had formed were filtered, washed with a small amount of ether, and dried. Yield was 2.6 g., m.p. 165–168° dec., infrared bands at 1940 and 2000  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{28}\text{H}_{30}\text{O}_2\text{P}_2\text{Ni}$ : C, 68.17; H, 5.57; P, 11.41. Found: C, 67.49; H, 5.63; P, 11.42.

**Dicarbonylbis(phenyldiethylphosphine)nickel**,  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2]_2$ , was prepared by the reaction of 3.3 g. (0.02 mole) of  $\text{P}(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5)_2$  with 1.7 g. (0.01 mole) of nickel carbonyl in refluxing ether. A pale yellow liquid was isolated (4.0 g.) which solidified on standing to yellow crystals, m.p. 44–48°. The compound had infrared carbonyl bands at 1933 and 2000  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{22}\text{H}_{26}\text{O}_2\text{P}_2\text{Ni}$ : C, 63.65; H, 7.28. Found: C, 63.59; H, 7.34.

**Dicarbonyl-P,P,P',P'-[tetrakis(2-cyanoethyl)ethylenediphosphine]nickel**,  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_4\text{CN})_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_4\text{CN})_2]_2$ .—A solution of 2.4 g. (0.014 mole) of nickel carbonyl in 25 ml. of methanol was added dropwise to a warm (40°) solution of 4.4 g. (0.014 mole) of  $\text{P}(\text{C}_2\text{H}_4\text{CN})_2\text{CH}_2\text{CH}_2\text{P}$

$(\text{C}_2\text{H}_4\text{CN})_2$ <sup>14</sup> in 125 ml. of methanol. Carbon monoxide was evolved briskly. The mixture was refluxed for 30 min. after carbonyl addition was complete and allowed to cool to 25°. Fine, cream-colored crystals were formed which were filtered off, washed with ether, and dried. Yield of complex was 3.5 g., m.p. 132–133° dec., infrared carbonyl bands at 1950 and 2000  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{20}\text{O}_2\text{N}_4\text{P}_2\text{Ni}$ : C, 45.64; H, 4.79. Found: C, 45.22; H, 4.93.

The <sup>31</sup>P n.m.r. spectrum of this complex in acetonitrile solution had two resonance peaks, a strong peak at –44.2 p.p.m. and a weak one at –20.8 p.p.m. (relative to 85% phosphoric acid), revealing the presence of two different phosphine complexes. An analysis of these spectra is reported elsewhere<sup>15</sup> in which the more negative resonance is assigned to the monomeric five-membered ring chelate structure and the less negative resonance to a dimeric complex,  $\text{Ni}_2(\text{CO})_4[\text{P}(\text{C}_2\text{H}_4\text{CN})_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_4\text{CN})_2]_2$ , in which the two nickel atoms are joined by two diphosphine bridges forming a ten-membered ring.

When the above preparation was repeated, except that the nickel carbonyl solution was added all at once to the warm phosphine solution, a white crystalline product, m.p. 138° dec., was obtained having infrared carbonyl bands at 1950 and 2000  $\text{cm}^{-1}$  and a single <sup>31</sup>P resonance at –44.9 p.p.m. This pure monomeric complex was used in the 1-heptyne polymerization study.

**Dicarbonyl-P,P,P',P'-(tetraethylethylenediphosphine)nickel**,  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$ .—The pure monomeric complex was prepared by the method of Chatt and Hart<sup>16</sup> from 4.6 g. (0.027 mole) of nickel carbonyl and 5.0 g. (0.024 mole) of P,P,P',P'-tetraethylethylenediphosphine<sup>17</sup> in refluxing methanol. The product (3.5 g.) was a colorless oil at room temperature having infrared carbonyl bands at 1930 and 1992  $\text{cm}^{-1}$ . The <sup>31</sup>P n.m.r. spectrum contained one peak at –41.2 p.p.m.

When this reaction was run in refluxing ether instead of methanol a mixture of three complexes was obtained which was not further separated. However, infrared and n.m.r. analysis of this mixture<sup>15</sup> identified the components as the mononuclear  $\text{Ni}(\text{CO})_2[\text{P}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$  and two binuclear species,  $\text{Ni}_2(\text{CO})_4[\text{P}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2]_2$ <sup>16</sup> and a tricarbonyl  $\text{Ni}(\text{CO})_3[\text{P}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_2\text{H}_5)_2]\text{Ni}(\text{CO})_3$ . The tricarbonyl was unstable at room temperature, apparently disproportionating to the mononuclear dicarbonyl and nickel carbonyl.

**Solvent Variation Studies.**—In all experiments, 1.9 g. of the acetylene (ethyl propiolate of 1-heptyne) was added under nitrogen to 15 ml. of the solvent contained in a 50-ml. three-necked flask, provided with a thermometer, reflux condenser, and a self-sealing vaccine cap for taking aliquots. An initial 0.5-ml. aliquot was taken. The solid  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  catalyst (50 mg.) was then added and the solution was heated rapidly to reflux with an oil bath, or brought to 75–80° if the solvent boiled above 100°. After 5 min. at reflux a second aliquot was taken. A final aliquot was taken after 6 hr. at which time the reaction was terminated. The aliquots (which were stored at 0°) were analyzed in the infrared for disappearance of the triple bond stretching band, whose position varied in the different solvents from 2120 to 2139  $\text{cm}^{-1}$ . The concentration of acetylene was found to be proportional to the optical density after correcting for the solvent absorption at that frequency. The per cent reaction could then be calculated assuming no reaction in the initial aliquot. The acetylenes were stable in the pure refluxing solvents.

**Temperature Variation and Gas Sweeping Studies.**—For the experiments with 1-heptyne a 100-ml. four-necked

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flask was used, provided with a reflux condenser, thermometer, vaccine cap, and gas inlet tube reaching to the bottom of the flask. A solution of 9.6 g. of 1-heptyne and 0.16 g. of  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  in 50 ml. of solvent was heated to the desired temperature with an oil bath. Agitation was induced by bubbling gas through the solution, stirring with a magnetic stirrer or refluxing. The per cent reaction of the 1-heptyne was determined by infrared analysis of aliquots taken before and after the reaction as described above.

In the experiments with ethyl propiolate, the ester (2.7 g.) and  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  (0.10 g.) were each placed in separate 50-ml. flasks containing 15 ml. of solvent, which were provided with a reflux condenser and a gas inlet tube reaching to the bottom of the flask (for the gas sweeping experiments only) and a vaccine cap (one flask only). The two flasks were brought to equilibrium in an oil bath at the desired temperature and, when a gas was used, concurrently flushed for 30 min. with the gas at a flow rate of 20 cc./min. The solutions were then mixed in the flask containing the vaccine cap and this flask was maintained at the reaction temperature for the balance of the experiment, gas flow being continued at the above rate. The disappearance of the acetylene was determined by infrared analysis of aliquots.

**Variation of Acetylene-Catalyst Ratio**—In this series of experiments, the  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  catalyst in 60 ml. of cyclohexane was placed in a four-necked 100-ml. flask fitted with a reflux condenser, thermometer, gas inlet tube, and self-sealing vaccine cap. The system was deoxygenated by passing a slow stream of pure carbon dioxide through the solution at reflux for 20 min. The solution was then cooled to the desired temperature and the ethyl propiolate was injected into the solution with a hypodermic syringe. The disappearance of the acetylene was again determined by infrared analysis of aliquots taken during the reaction.

**Catalyst Variation Studies**.—These reactions were run in a four-necked 100-ml. flask fitted with thermometer, self-sealing vaccine cap, gas inlet tube, and a water condenser topped by a Dry Ice-acetone condenser. The system was flushed with carbon dioxide gas and a weighed sample (0.36 mmole) of the nickel complex was introduced into the flask. The appropriate solvent (53 ml.), previously deoxygenated with carbon dioxide, was injected into the flask, the carbon dioxide flow rate then being adjusted to 250 cc./min. Acetonitrile was used as solvent when complexes containing a 2-cyanoethyl-substituted phosphine were used. For all other complexes the solvent was cyclohexane containing 20% *n*-hexane to prevent deposition of the cyclohexane on the Dry Ice-acetone condenser. The solvent-catalyst mixture was brought to reflux with an oil bath. The reaction was started by injecting into the flask 7 ml. (0.054 mole) of 1-heptyne which had also been deoxygenated with carbon dioxide. Small aliquots were withdrawn periodically, chilled to 0°, and subsequently analyzed by infrared for the disappearance of the triple bond band of the acetylenic monomer at about 2130  $\text{cm}^{-1}$ . The end of the induction period was arbitrarily set at the point at which 2% of the 1-heptyne had disappeared. The results of several duplicate experiments checked to within 5%.

A similar procedure was used in the experiments with phenylacetylene, except that the aliquots were analyzed in the infrared for formation of 1,2,4-triphenylbenzene at 840  $\text{cm}^{-1}$  and the triphenylbutadienylacetylene at 975  $\text{cm}^{-1}$  as well as for monomer disappearance at 2130  $\text{cm}^{-1}$ .

**Stability of  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$** .—Solid  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  (1.0 g.) was added to 100 ml. of refluxing benzene under a nitrogen atmosphere. The complex dissolved immediately with no gas evolution to give a yellow solution. Refluxing was continued for 6 hr., during which time a small amount of a flocculent precipitate formed. The cooled solution was filtered from 0.11 g. of a light gray solid (probably mostly nickel metal and nickel oxides) and the benzene was removed from the filtrate under vacuum. The residue was extracted

thoroughly with ether, leaving behind 0.28 g. (28%) of the original nickel complex, m.p. 209–212° dec. The ether solution contained 0.4 g. of triphenylphosphine.

When this experiment was repeated in ethanol, 0.61 g. (61%) of the complex was recovered.

A solution of 14.2 g. (0.1 mole) of 2,5-dimethyl-3-hexyne-2,5-diol and 0.5 g. (0.008 mole) of  $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$  in 100 ml. of benzene was refluxed under nitrogen for 22 hr. No color change or exotherm was observed. At this point 5 ml. (4.7 g., 0.046 mole) of phenylacetylene was added. The solution immediately turned dark brown. After refluxing for 2 hr. longer, the solution was cooled, filtered, and the solvent removed. No phenylacetylene was recovered in the distillation. Recrystallization of the residue from cyclohexane yielded 10.5 g. of unchanged diol. A mixture of phenylacetylene trimers<sup>2a</sup> (1.5 g.) was recovered from the cyclohexane mother liquors by concentration and addition of petroleum ether.

**Procedure for 1-Heptyne Rate Studies**.—Into a 100-cc. three-necked, round-bottom flask, fitted with an efficient reflux condenser, a gas inlet tube reaching to the bottom of the flask, and a vaccine cap, were placed the calculated amount of 1-heptyne and 50 ml. of "spectro" grade cyclohexane. The mixture was brought to reflux with a very slow stream of prepurified nitrogen passing through the solution. A weighed amount of  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  was then added in a glass weighing boat. The catalyst dissolved immediately. At selected intervals during the next 2 hr. 1-ml. aliquots were removed through the vaccine cap with a hypodermic syringe and quenched by cooling to 0°. These aliquots were analyzed in the infrared for disappearance of 1-heptyne at 2130  $\text{cm}^{-1}$  and in the ultraviolet for the appearance of the dimer at 227  $\text{m}\mu$  and the trimer at 270  $\text{m}\mu$ . These infrared and ultraviolet data, after correction for background and cross absorption, respectively, were converted into concentration units and are shown in Fig. 1 and 2.

**Deuteration Studies**.—The above procedure was used in the polymerization studies with deuterated 1-heptyne and phenylacetylene, except that the quenched aliquots were analyzed only by infrared at 3300  $\text{cm}^{-1}$  ( $\equiv\text{C}-\text{H}$  stretch) and 2585  $\text{cm}^{-1}$  ( $\equiv\text{C}-\text{D}$  stretch) in the case of 1-heptyne and at 3320 and 2590  $\text{cm}^{-1}$  with phenylacetylene. The concentration of each species was obtained by reference to empirical plots of concentration *vs.* corrected optical density. The initial concentration of total monomer was 1.0 *M* and of catalyst was 0.006 *M*.

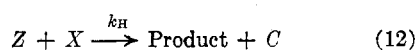
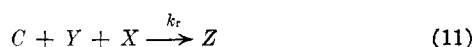
Attempts to analyze the reaction products for deuterium content by infrared and mass spectrometry were unsuccessful because of the complex nature of the mixtures obtained.

**Reaction between 1-Heptyne-1-*d* and 1-Pentyne**.—A solution of 7.80 g. of 83% deuterated 1-heptyne and 5.45 g. of 1-pentyne in 142 ml. of "spectro" grade cyclohexane was brought to reflux under nitrogen and 0.614 g. of solid  $\text{Ni}(\text{CO})_2(\text{Ph}_3\text{P})_2$  was added. A 10-ml. aliquot was taken at once and three other 50-ml. aliquots were taken at intervals of 20, 42 and 67 min. after catalyst addition. The chilled aliquots were each analyzed in infrared at 3300, 2585, and 2130  $\text{cm}^{-1}$ . Each of the three 50-ml. aliquots were then carefully fractionated to yield fractions of pure 1-pentyne (b.p. 40°) and 1-heptyne (b.p. 100°). The amount of deuterated and undeuterated monomer in these fractions was then determined by infrared analysis at 2585 and 3300  $\text{cm}^{-1}$ , respectively. The exchange results are recorded in Table V.

**Procedure in Pretreatment Studies**.—An apparatus similar to that used in the 1-heptyne rate studies was used. A slow stream of pure carbon dioxide gas was passed through the reaction solution during the whole experiment. The calculated amounts of catalyst and disubstituted acetylene were dissolved in 50 ml. of solvent and the solution was brought to the pretreatment temperature and held there for 2 hr. Ultraviolet spectra were obtained of aliquots taken at this point and maintained in an inert atmosphere. The solution was then brought to the lower temperature and the

reactive acetylene (at the same temperature) was injected through the vaccine cap with a hypodermic syringe. Disappearance of the added acetylene was determined by infrared analysis of the C≡C stretching band in the solution after an additional 2-hr. period. The disubstituted acetylene was recovered from the reaction mixture along with the usual polymer products from the added acetylene, when formed.

**Mathematical Analysis of Deuterium Isotope Effect in the Trimerization of 1-Heptyne.**—The reactions considered in the polymerization process were



where

- $X$  = a measure of hydrogen compound concentration
- $Y$  = a measure of deuterium compound concentration
- $Z$  = a measure of intermediate concentration
- $C$  = a measure of "active" catalyst concentration
- $k_H, k_D$  = rate constants for the rate-determining step involving reaction with an undeuterated and deuterated molecule, respectively
- $k_r$  = rate constant for the formation of intermediate  $Z$

The assumption was made that the product formed was exclusively trimer and that only one hydrogen atom was transferred in the rate-determining step. These reactions then led to the differential equations

$$-\frac{dX}{dt} = k_H ZX + k_r C(2X^2 + 2XY) \quad (14)$$

$$-\frac{dY}{dt} = k_D ZY + k_r C(2XY + 2Y^2) \quad (15)$$

$$-\frac{dZ}{dt} = k_H ZX + k_D ZY - k_r C(X^2 + 2XY + Y^2) \quad (16)$$

At steady state  $dZ/dt = 0$ . Solution of equation 16 and the subsequent substitutions  $V = Y/X$  and  $K = k_H/k_D$  into the ratio of equations 14 and 15 resulted in expression 17 in  $V, X$ , and  $K$ ,

$$2 \ln(V + 1) + \frac{3K}{1 - K} \ln V + \ln S = \ln X \quad (17)$$

where  $S$  = a constant of integration. With the initial condition ( $t = 0$ ) that  $V = X = 1$ , the final theoretical relationship was

$$2 \ln(V + 1) + \frac{3K}{1 - K} \ln V - 1.38629 = \ln X \quad (18)$$

In Table IV are shown the values of  $V$  predicted from the model chosen. The experimental data were first fitted to equation 17 by least squares to obtain estimates of  $K$  and  $S$ . The resulting estimate of  $S$  was found to be not significantly different from the theoretical value. Therefore, the data were refitted to equation 18 for which the best value of  $K$  was 2.56 with a 95% confidence interval of  $\pm 0.46$ .

Infrared analyses were performed on a Perkin-Elmer Model 21 infrared spectrophotometer with sodium chloride optics. Ultraviolet spectra were determined on a Cary Model 14 ultraviolet spectrophotometer.

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## Some Reactions of Monoolefins with Iron Carbonyls

T. A. MANUEL

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

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The treatment of monoolefins with iron carbonyls leads to isomerization. The effects of olefin structure and solvent upon the reaction are discussed, and a mechanism for the reaction is suggested.

Recent interest in reactions of iron carbonyl and its derivatives with nonconjugated diolefins<sup>1,2</sup> prompts us to report some of our data regarding reactions of iron carbonyls with monoolefins. It has been shown that the iron carbonyl hydrides are active catalysts for hydrogenation and isomerization of olefins,<sup>3,4</sup> as are the cobalt carbonyl hydrides,<sup>5,6</sup>

and it was noted that treatment of 1-octene with iron pentacarbonyl gave a mixture of internal isomers.<sup>7</sup> We have investigated the geometrical and positional isomerization occurring when monoolefins of various structures are heated with iron carbonyls.

Terminal olefins are rapidly converted to mixtures of internal isomers when heated with iron carbonyls.

Table I compares the experimental values for isomer distribution of hexenes after heating with 0.5 mole % triiron dodecacarbonyl with the thermodynamic equilibrium values calculated by stand-

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