Kinetics and Mechanism in the Electrophilic Addition of Triphenylaluminum to Para-Substituted Diphenylacetylenes[1]

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Abstract: The kinetics of the carbalumination of para-substituted diphenylacetylenes by triphenylaluminum were studied in mesitylene solution in the temperature range of 110–140°. Para substituents on the acetylene having Lewis basic character, such as $(CH_3)_2N$, CH_3O, and CH_3S, led to rate data not readily analyzable in terms of integrated rate expressions. However, a rate analysis was achieved for diphenylacetylene itself, as well as for its *p*-chloro and *p*-methyl derivatives. The carbalumination reaction was found to obey three-halves-order kinetics in the concentration range of 6–26 m*M*, first order in the acetylene and one-half order in the triphenylaluminum. The *p*-chloro group retarded modestly, and the *p*-methyl enhanced definitely the reactivity of the diphenylacetylene system to carbalumination. These relative rates are taken together with the strong retarding influence of donor molecules on the rate and with our previous study on isomer distribution in arriving at a reaction mechanism. In our view monomeric, tricoordinate triphenylaluminum attacks the acetylene electrophilically in the rate-determining step.

Since the addition of organoaluminum compounds to unsaturated hydrocarbons is of increasing significance in modern organic synthesis,[3] it is curious that so little research on the kinetic laws of carbalumination has been reported in the scientific literature. The rate of absorption (at a constant pressure of 1 atm) of ethylene at 110°, as well as of acetylene at 25°, by triethylaluminum in decalin was found to be proportional to the square root of the concentration of triethylaluminum. This behavior held over a 100-fold range of concentration. Triisobutylaluminum, on the other hand, absorbed acetylene at a rate directly proportional to the concentration of the aluminum alkyl. Because the ethyl- and isobutylaluminum alkyls were dimeric and monomeric, respectively, under these reaction conditions, the monomeric aluminum alkyl was considered to be the reactive species.[4] In another study the rate of formation of products and the rate of disappearance of ethylene in the reaction of this olefin with triethylaluminum led to the conclusion that the reaction was first order in ethylene and first order in triethylaluminum.[5] Finally, a kinetic study of the reaction of 1-hexene with triethylaluminum found that the reaction was close to first order in each reagent, but calculations of Arrhenius parameters led to the further conclusion that some of the reaction proceeded through dimeric triethylaluminum.[6]

In view of these discordant, and rather limited, kinetic results, the present study sought to determine the overall kinetics for the carbalumination of alkynes. The addition of triphenylaluminum to certain diphenylacetylenes seemed to be a most advantageous case to examine, both for theoretical and practical reasons. In the first place, the previous report in this series describes the stereochemistry and isomer distribution in the carbalumination of para-substituted diphenylacetylenes by this aluminum aryl. The tentative conclusion of electrophilic attack by the aluminum aryl on the acetylenic linkage was based upon a Hammett σ value correlation with the logarithm of the ratio of orientation isomers.[1] This regioselectivity in isomer distribution could be considered to reflect an intramolecular competition between the two modes of cis carbalumination. Now overall rate data would be desirable to compare with these intramolecular relative rates.

Secondly, triphenylaluminum does not suffer from certain side reactions to which aluminum alkyls are prone. The formation of R_2AlH by the thermal elimination of olefin from most aluminum alkyls permits hydralumination to compete with carbalumination,[7] and the resulting adducts from unsaturated hydrocarbon and aluminum alkyls can themselves compete with the starting aluminum alkyl for further hydrocarbon insertions into the carbon–aluminum bond.[8] Triphenylaluminum's inability to form benzyne thermally and its tendency to undergo only monoinsertion of alkyne make it an ideal aluminum aryl reagent for a kinetic study.

Finally, both the aluminum aryl and the diphenylacetylenes could be recrystallized to a high and reliable degree of purity, and their reaction rates measured conveniently in the vicinity of 120° in mesitylene solution.

Results

Rate data on the parent diphenylacetylene and on each of the para-substituted derivatives considered in the isomer distribution study[1] were sought. However, only the data from diphenylacetylene (runs 1–5, Table I), *p*-chlorodiphenylacetylene (typical run, run 6), and *p*-methyldiphenylacetylene (typical run, run 7) could be readily fitted to any empirical rate expression. An example of the kinetic runs for which such a fit

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(1) Part XVII of the series "Organometallic Compounds of Group III" devoted to carbometallation and hydrometallation. XVI: J. J. Eisch and C. K. Hordis, *J. Amer. Chem. Soc.*, **93**, 2974 (1971).

(2) National Aeronautics and Space Administration Trainee, 1963–1966.

(3) G. Bruno, "The Use of Aluminum Alkyl in Organic Synthesis," Ethyl Corporation, Baton Rouge, La., 1970, pp 75 with 473 references.

(4) K. Ziegler and H. Hoberg, *Chem. Ber.*, **93**, 2938 (1960).

(5) G. Natta, P. Pino, and M. Farina, *Ric. Sci., Suppl.*, **No. 25**, 120 (1954); as reported in ref 6.

(6) P. E. M. Allen, J. P. Allison, J. R. Majer, and J. C. Robb, *Trans. Faraday Soc.*, **59**, 2080 (1963).

(7) K. Ziegler, W.-R. Kroll, W. Larbig, and O.-W. Steudel, *Justus Liebigs Ann. Chem.*, **629**, 53 (1960).

(8) K. Ziegler, H.-G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll, and W.-R. Kroll, *ibid.*, **629**, 121 (1960).

Table I. Summary of Conditions, Kinetic Order, and Rate Constants for the Addition of Triphenylaluminum to Para-Substituted Diphenylacetylenes[a]

Kinetic run no.	Z	Concentration of reactants[b] $ZC_6H_4C{\equiv}CC_6H_5$	$(C_6H_5)_3Al$	Temp, °C[c]	$k_{3/2}$, l.$^{1/2}$ mol$^{-1/2}$ min^{-1} [d]	k_2, l. mol^{-1} min^{-1} [e]
1	H	0.0130	0.0131	120	0.123	2.97
2	H	0.0131	0.0132	120	0.131	3.18
3	H	0.00621	0.0132	120	0.121	2.92
4	H	0.0129	0.00657	120	0.104	2.67
5	H	0.0133	0.0133	110	0.055	1.52
6	Cl	0.0130	0.0131	120	0.109	2.63
7	CH_3	0.0133	0.0131	120	0.150	3.63
8	CH_3O	0.0138	0.0136	120	2560[f]	
9	H	0.0134	0.0132	120	0.113	2.73
10	H	0.0263	0.0263	120	0.132	3.05
11	H	0.0254	0.0256	140	0.485	8.9

[a] In mesitylene solution, where the data fit an integrated rate expression for an empirical, three-halves-order reaction. [b] The concentrations are expressed in normality, which equals the molar concentration for the acetylene but which is twice the molar concentration of triphenylaluminum, known to exist as dimer. [c] Temperature uncertainty of ±0.1°. [d] Graphically determined value according to eq 13. [e] Bimolecular rate constant calculated according to eq 6 with an estimate of $K_{eq} = 2.3 \times 10^{-3}$. [f] These results do not fit kinetic expressions for k_1, k_2, or k_3, and the experimental deviation for $k_{3/2}$ is abnormally large.

Table II. Typical Kinetic Data for the Addition of Triphenylaluminum to Diphenylacetylene in Mesitylene Solution at 120° [a]

Time, min	Concn[b] Diphenylacetylene $B - X$[c]	Triphenylethylene X[c]	$(1/\sqrt{B-X} - 1/\sqrt{B})$[c]	$k_{3/2}$, l.$^{1/2}$ mol$^{-1/2}$ min^{-1}
0	0.0130	0.000		
5	0.0126	0.00048	0.16	0.0906
20	0.0107	0.00175	0.91	0.129
30	0.00937	0.00260	1.56	0.147
50	0.00832	0.00416	2.18	0.123
70	0.00710	0.00503	3.11	0.126
90	0.00628	0.00543	3.86	0.121
100	0.00586	0.00613	4.32	0.122
120	0.00546	0.00667	4.78	0.113
183	0.00411	0.00828	7.24	0.112
				Av 0.124

[a] Kinetic no. 1 of Table I, where $k_{3/2}$ has been determined graphically by use of eq 13 and the plot in Figure 1. [b] Molarity in mesitylene. [c] *Cf.* eq 10–12.

of data was not achieved is run 8, the behavior of *p*-methoxydiphenylacetylene. Here the results could not be made to yield an empirical rate constant with expressions for k_1, $k_{3/2}$, k_2, or k_3, and the experimental deviation in the data for $k_{3/2}$ was abnormally large.

The majority of kinetic data were obtained from the reaction of diphenylacetylene with triphenylaluminum. A series of runs was made in which were varied the concentrations of reactants, together and separately, the temperature, and the para substituent. The reactions were followed by measuring the disappearance of the acetylene, as well as the appearance of the triarylethylene, in periodically removed hydrolyzed samples. Analytical data from the individual kinetic runs, taken up to *ca.* 70–90% consumption of the acetylene, were found to fit the expression for three-halves-order kinetics. The observed empirical rate constants were calculated by use of the appropriate, integrated forms (*cf.* Experimental Section) of differential eq 12, 14, and 17, and are given in Table I with other individuating details of the kinetic runs. As an example of the precision of a typical kinetic run, Table II gives the analytical data for run 1, the calculated values of the empirical $k_{3/2}$, and the bimolecular rate constant derived from it.

Over a range of concentration from 6 to 26 m*M* in mesitylene at 120° the carbalumination is empirically quite close to three-halves-order overall. For selected kinetic runs this conclusion was reached by three different methods of analyzing the data, the integral, differential, and fractional lifetime methods, which indicated the overall order was 1.5 1.5, and 1.6, respectively. For all kinetic runs, except run 8, this agreement with three-halves-order kinetics was shown by the linearity of the plot made according to the appropriate integrated forms of the rate equation (plot of run 1 in Figure 1). Moreover, data from runs in which the concentration of one reactant was changed while the other remained constant (runs 1 and 3; runs 1 and 4) were analyzed by the differential method. This showed that the reaction was first order in diphenylacetylene and close to half order (0.58) in triphenylaluminum.

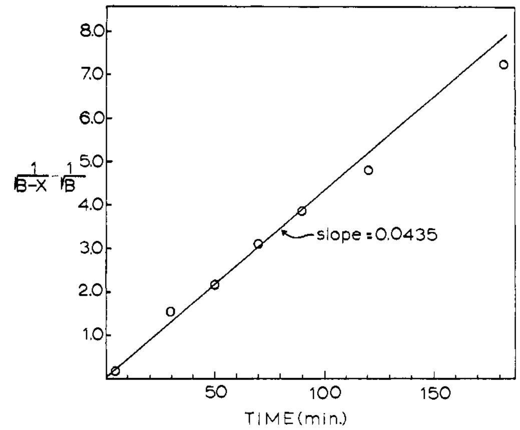

Figure 1. Plot of kinetic run no. 1 as a three-halves-order reaction: ordinate, value of $k_{3/2}t/2\sqrt{2}$ in eq 12; abscissa, time in minutes.

Since triphenylaluminum is known to be dimeric in these hydrocarbon solvents, literature data were used to estimate what the equilibrium constant for the dimer–monomer equilibrium would be at the reaction temperature. With anticipation of the assumptions to be made in the ensuing discussion of the reaction mechanism, this K_{eq} of 2.3 × 10^{-3} could be

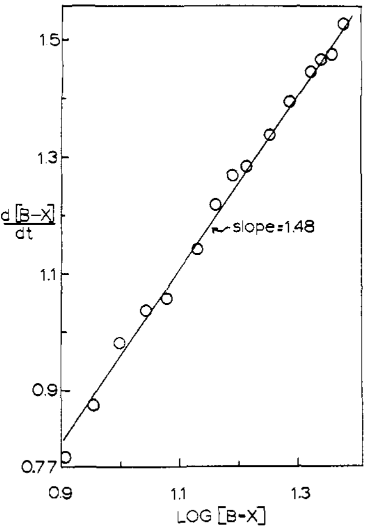

Figure 2. Plot of the logarithm of the rate of change of the diphenylacetylene concentration *vs.* the logarithm of the diphenylacetylene concentration for kinetic run no. 10.

used to calculate the bimolecular rate constants given in Table I. In terms of relative rates where the unsubstituted diphenylacetylene is given a rate of 1.0 (k_2 = 2.96 l. mol^{-1} min^{-1} (average, std dev ±6%)), the relative rate for *p*-methyldiphenylacetylene is 1.23 and that for the *p*-chlorodiphenylacetylene is 0.88. The clear increase in rate produced by the methyl group (*ca.* 25%), coupled with the smaller but probably real decrease in rate produced by the chloro group (*ca.* 10%), is ample evidence that in the rate-determining step the triphenylaluminum acts as an electrophile toward the acetylene.

No extensive range of temperatures was explored in estimating the Arrhenius activation energy by the equation, $\log k_2 = -E/RT +$ constant. From the plot of the rates of the triphenylaluminum–diphenylacetylene reaction at 110, 120, and 140°, however, a reasonably linear relationship was obtained, where E = 18.5 kcal/mol ± 1.0.

Finally, the inhibiting effect of a donor solvent on the carbalumination of an acetylene was seen in the failure of the addition of triphenylaluminum to *p*-methoxydiphenylacetylene at 180°, when the mesitylene solvent was replaced by cineole. This ether is known to form a very stable complex with the starting aluminum aryl.[9]

Discussion

The overall kinetics of three-halves order for the carbalumination reaction permit a number of reaction schemes to be eliminated for these experimental conditions. It should be noted that under these conditions, the triphenylaluminum exists almost entirely as the dimer. First of all, the rection of the triphenylaluminum dimer with the acetylene in the rate-determining step would require second-order kinetics. Secondly, if the rate-determining step were to be the formation of the triphenylaluminum monomer from the dimer, the rate would be first order in the aluminum compound and independent of the acetylene concentration. Thus, the most straightforward reaction scheme consistent with the results is that involving a rapid preequilibrium between dimeric triphenylaluminum and its monomer, followed by the rate-limiting reaction of triphenylaluminum monomer with the acetylene

$$\mathrm{D} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\mathrm{M} \tag{1}$$

$$\mathrm{M} + \mathrm{B} \xrightarrow{k_2} \mathrm{P} \tag{2}$$

D = initial molar concentration of triphenylaluminum as dimer, M = molar concentration of triphenylaluminum as monomer, B = initial molar concentration of the diphenylacetylene. The initial reaction rate is

$$\frac{dP}{dt} = -\frac{dB}{dt} = k_2MB \tag{3}$$

With the assumption that the equilibrium in eq 1 is relatively rapid, the concentration of monomer at equilibrium is available from the relations

$$K = \frac{k_1}{k_{-1}} = \frac{M^2}{D - M/2}$$

and

$$M = (K/4)(-1 + \sqrt{1 + 16D/K})$$

Thus, the rate law is

$$-\frac{dB}{dt} = \left(\frac{k_2K}{4}\right)(-1 + \sqrt{1 + 16D/K})(B) \tag{4}$$

As long as $16D/K \gg 1$, the rate will obey three-halves-order kinetics. Since K has been estimated to be 2.3×10^{-3} and D typically was 0.0065, this condition was met.

In order to estimate k_2, one can make use of the empirical rate equation

$$-\frac{dB}{dt} = kD^{1/2}B \tag{5}$$

and equate the right side with eq 4

$$\left(\frac{k_2K}{4}\right)(-1 + \sqrt{1 + 16D/K}) = kD^{1/2}$$

$$k_2 = \frac{kD^{1/2}}{(K/4)(-1 + \sqrt{1 + 16D/K})} \tag{6}$$

The initial bimolecular rate constants in Table I were calculated by substitutions in this equation. Alternatively, k_2 was estimated by means of instantaneous rates of reaction. For runs involving initial concentrations of reactants of equal normality ($D = B/2$), eq 4 can be used. After the reaction has progressed and X acetylene has reacted, the instantaneous rate becomes

$$-\frac{d(B - X)}{dt} = \left(\frac{k_2K}{4}\right)(-1 + \sqrt{1 + 8(B - X)/K})(B - X) \tag{7}$$

The instantaneous rate of reaction is the slope of the acetylene *vs.* time curve for any given concentration of acetylene remaining, $B - X$. These data were obtained from runs 9 and 10 in the course of determining the reaction order by the differential method (Figure 2). The agreement between values of k_2 obtained *via* eq 6 and 7 was excellent.

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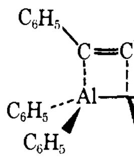
[9] J. J. Eisch and W. C. Kaska, unpublished studies.

The observed values of the k (empirical $k_{3/2}$) are a function of k_2 and K (eq 6) and k_2 naturally also depends upon the estimate made of K from published data (eq 4). As to the internal consistency of the values of k_2, runs 1, 2, and 9 should be compared, since the reaction conditions were nearly identical (2.97, 3.18, and 2.73, respectively). For these the k_2 (average) = 2.92 l. mol^{-1} min^{-1} (std dev ± 0.18). As to the absolute reliability of k_2, the widest range of estimates for K must be considered, $1.6\text{–}3.1 \times 10^{-3}$. The value of k_2 for run 1 could range between 2.57 and 3.47 l. mol^{-1} min^{-1}.

The nature of the rate-determining step, eq 2, now deserves further attention. The known cis stereochemistry of the reaction would stem from the approach of the triphenylaluminum monomer to one face of the acetylene π cloud; the nature of the interaction in the transition state would depend upon the relative progress in bond making. For four-center transition states three limiting cases can be conceived: (a) perfectly concerted attack, where essentially both the new C–C and the new C–Al bonds have the same progress, **1**; (b) nucleophilic attack, where the phenyl group migrating from the $(C_6H_5)_3Al$ unit is more closely bound than the incipient C–Al bond, thus bestowing negative charge on the acetylenic system, **2**; and (c) electrophilic attack, where the trivalent aluminum center initiates attack, leading to a positively polarized acetylenic substrate, **3**.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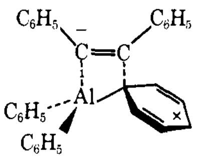
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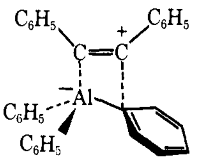
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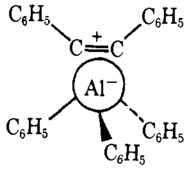
From the overall relative rates of p-chlorodiphenylacetylene (0.88), diphenylacetylene (1.00), and p-methyldiphenylacetylene (1.23), we can conclude that electron availability in the acetylene causes a moderate, but definite, rate enhancement. Furthermore, a donor reaction medium, such as the ether, cineole, inhibits the carbalumination altogether (eq 8). Since the observed reaction order already points to the monomeric triphenylaluminum as the reactive species, the effect of cineole supports the conclusion that only tricoordinate triphenylaluminum **5** can play the role of the reactive carbaluminating reagent, not **6**. Thus, both the relative rates of para-substituted diphenylacetylenes and the effect of donor solvents lead to the conclusion that the carbalumination of alkynes proceeds by an electrophilic mechanism through a transition state similar to **3**. If model **2** were operative, then the rate for p-chlorodiphenylacetylene should be larger than that of the other two acetylenes. If model I were involved, then the observed electronic effects on intramolecular relative rates (structure **8**[1]) would be difficult to understand.

$$\underset{\mathbf{4}}{[(C_6H_5)_3Al]_2} \rightleftharpoons \underset{\mathbf{5}}{2(C_6H_5)_3Al} \xrightarrow{C_{10}H_{18}O} \underset{\mathbf{6}}{2(C_6H_5)_3Al\cdot OC_{10}H_{18}} \quad (8)$$

The effect of donor solvents now makes understandable our inability to obtain satisfactory, relatively simple kinetic expressions for the rates of para-substituted diphenylacetylenes bearing donor groups ($(CH_3)_2N$, CH_3O, CH_3S). Clearly, at the reaction temperature the availability of monomer **5** was suppressed by an equilibrium with the **5**·donor.

One last point on the nature of the electrophilic transition state **5** concerns the possible role of a π complex. Because of the covalent radius of aluminum (1.26 Å) one could envisage that a π complex **7** could be formed, where the aluminum would be centrally coordinated at the acetylenic linkage, encompassing both carbon centers (C≡C, 1.20 Å). Such a complex might be a weak interaction formed on the way to transition state **3** (eq 9, $k_1 \gg k_2$) or it might be an approximation for the transition state of carbalumination. In the latter case its decomposition with phenyl migration from aluminum to carbon would be relatively fast ($k_2 \gg k_1$). Although very stable complexes similar to **7** are well known with transition metals (*e.g.*, $C_6H_5C{\equiv}CC_6H_5$ with $Pt[(C_6H_5)_3P]_2$[10]), decisive evidence for their existence with organoaluminum compounds is lacking.[11] However, even if they do occur in such reaction systems, it does not seem likely that their formation would be rate determining (eq 9). In their structure, **7**, the phenyl group to be added still would be held quite far from its ultimate bonding site on the acetylenic carbon.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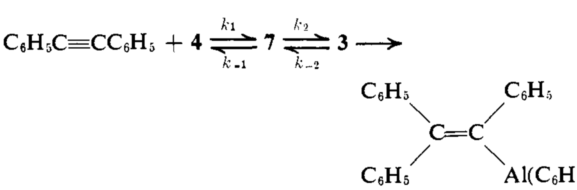
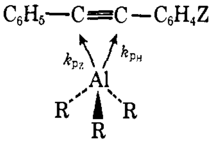


(9)

Moreover, the proportion of the two cis isomers (attack of aluminum at either of two acetylenic carbons in **8**) reported in our previous study[1] is an intramolecular measure of relative rates that can be compared with the intermolecular relative rates found here. Although the temperatures used in the two studies (180 *vs.* 120°) could not conveniently be made the same, the following gross comparison could be made. The partial rate $k_{p\text{-H}}$ for one carbon of diphenylacetylene was taken as $0.5 \cdot k_2$, 1.46 l. mol^{-1} min^{-1}. This $k_{p\text{-H}}$ was subtracted from the overall rates (k_2) of the p-chloro and the p-methyl



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[10] J. O. Glanville, J. M. Stewart, and S. O. Grim, *J. Organometal. Chem.*, 7, P9 (1967).

[11] G. Hata (*Chem. Commun.*, 7 (1968)) has suggested an intramolecular π complex interaction to explain the shifts in the infrared and nmr spectra of alkenyl(dialkyl)aluminum systems and their etherates. Additional data on the 5-heptenylaluminum member (a case where such a proposed interaction would be especially favorable) and on other alternative explanations are needed, however, before such a theory becomes convincing.

derivatives, respectively, to yield $k_{p\text{-Cl}}$ and $k_{p\text{-CH}_3}$, the partial rates for the attack at the acetylenic carbon β to the para substituent in **8**. Adjusted to 180° by use of the Arrhenius equation and the estimated activation energy of 18.5 kcal/mol, these rates become 33.9 ($k_{p\text{-H}}'$), 50.4 ($k_{p\text{-CH}_3}'$), and 27.2 ($k_{p\text{-Cl}}'$). The ratios $k_{p\text{-CH}_3}/k_{p\text{-H}}'$ and $k_{p\text{-Cl}}'/k_{p\text{-H}}'$ are thus 1.5 and 0.8, respectively. The corresponding ratios derived from analyzed ratios of products[1] are 1.3 and 0.7. In view of the various uncertainties in the comparison, the agreement is acceptably good. We conclude, therefore, that the same electronic factors determine both the overall rate and the proportion of products. The transition state shown in **3**, where the rate- and product-determining step involves electrophilic attack by tricoordinate aluminum, is the most satisfactory mechanistic model. Finally, the discussion given previously[1] concerning the magnitude and composite nature of $\Delta\rho$ for the intramolecular competition (*cf.* **8**) can thus be applied to the overall kinetics of carbalumination as well. This assumes, of course, the absence of interfering donor sites (Z = $(CH_3)_2N$, CH_3O, and CH_3S in **8**) in the hydrocarbon substrate.

Experimental Section

General Experimental Technique. The purification of the nitrogen used as an inert atmosphere, the reagents for carbalumination, and the reaction solvents have been described in a previous article. In the present kinetic studies more elaborate precautions were observed to exclude moisture, oxygen, and other impurities. After each kinetic run the reaction vessel and the cold finger condenser were washed with the following sequence of solvents: benzene, acetone, water, concentrated hydrochloric acid, water, benzene, and acetone. Before each run the apparatus was dried for at least 5 hr at 200° and then allowed to cool to be stored under an atmosphere of pure nitrogen. The 1.00-ml hypodermic syringes used for sampling during a kinetic run were dried for at least 1 hr at 110° and then flushed three times with pure nitrogen.

The mesitylene for the kinetic studies (J. T. Baker, bp 164–166°) was heated at reflux over sodium metal under nitrogen and then distilled directly into a storage vessel, after a large forerun had purged out the distillation apparatus. The mesitylene storage vessel was opened only in the well-purged, nitrogen-filled inert atmosphere chamber.

Cineole was dried by the method recommended for di-*n*-butyl ether.[12] After a negative test for peroxide with starch–iodide paper had been obtained, the cineole was dried over anhydrous calcium sulfate and then distilled through a helices-filled fractionation column under nitrogen, bp 175–177°. This solvent was stored and handled under nitrogen.

A dual-columned vapor-phase chromatograph, F & M Model 720, with thermal conductivity detectors, was used for all analyses of the kinetic runs. The columns measuring 24 × 0.25 in. were packed with 10% methylphenylsilicone polymer (supplied through the kindness of Dr. Donald R. Weyenberg, Dow-Corning Corp., Midland, Mich.) spread on 100–120 mesh Gas Chrom Z, which had been acid washed and siliconized. The helium flow rate was 60 ml/min, injection port temperature, 425–450°, detector temperature, 340°. The column temperature was programmed to rise from about 100 to 310° at a rate of 15°/min.

Reagents. The final purification of these reagents was conducted under an atmosphere of pure nitrogen. Previously purified triphenylaluminum (15.2 g) was dissolved by warming in 200 ml of dry, degassed toluene and the hot solution filtered through a sintered glass frit. The resulting filtrate was collected in one flask of a two-flask apparatus whose flasks were interconnected by a ground-glass joint. Such an apparatus could be used for recrystallization by heating the solution of the aluminum aryl in flask A and by collecting the volatilized toluene in cooled flask B. Upon chilling the remaining solution in flask A the triphenylaluminum crystallized. The mother liquor in flask A could easily be decanted off the crystals by tilting flask A and letting the liquid flow into flask B. Fresh solvent for washing the crystals in flask A or repeating the recrystallization was furnished by heating the contents of flask B and by cooling flask A. In this manner the triphenylaluminum was recrystallized four times and the crystals washed with fresh solvent and then dried under reduced pressure. After being dried for 1 hr at room temperature and for 16 hr at 99° *in vacuo*, the product was 9.5 g of small, colorless needles, mp 241–243°, corrected (sintered 238°) (lit.[13] mp 241–243°).

The acetylenes, diphenylacetylene, *p*-chlorodiphenylacetylene, *p*-methyldiphenylacetylene, and *p*-methoxydiphenylacetylene, were prepared and purified in the manner previously described. Repeated recrystallizations and drying in an Abderhalden pistol (heated with refluxing acetone and charged with phosphorus pentoxide) under reduced pressure were employed to obtain highly pure samples for the kinetic studies. The purity of the samples was assayed, not only by their melting point sharpness and their ir and nmr spectral properties, but also by their ultraviolet data and vpc homogeneity. A 20-mg sample of each acetylene dissolved in benzene was injected into the vapor-phase chromatograph using a programmed column temperature which rose at least 70° above the temperature at which the compound was eluted. Maximum amplification was used on each side of the peak. In each case the acetylene peak area comprised more than 99.99% of the peak areas other than that of solvent.

Kinetic Investigation. A. Preparation for a Kinetic Run. All kinetic studies were conducted in a 100-ml round-bottomed flask that had been modified in the following way: the one-neck joint was removed and an elongated neck (15 cm), surmounted by a standard-taper 19/38 joint, sealed on the flask. Halfway up this elongated neck a 1-mm tube bearing a three-way stopcock was sealed onto the neck, to provide for the nitrogen-line connection. Finally, a glass tube (8 mm in diameter and 30 mm in length) was sealed onto the body of the flask at an angle 30° with respect to the elongated neck. This glass tube was provided with a rubber serum cap, wired in place, so that samples could be removed or introduced by means of a hypodermic syringe. The elongated neck was provided by a 19/38 jointed, cold-finger condenser, which extended down the length of the tube (past the aperture for the nitrogen gas).

The reaction apparatus was loaded in the inert atmosphere chamber with a previously weighed amount of triphenylaluminum and a weighed quantity of mesitylene amounting to about 98% of that to be used. A gas-tight hypodermic syringe was filled in the chamber with a solution of a known quantity of the acetylene dissolved in 2% of the total amount of the mesitylene to be used.

The reaction vessel was removed from the inert atmosphere chamber and its solution degassed by evacuating twice for 2-min periods and then refilling with nitrogen. After degassing, the reaction vessel was placed in the oil-filled constant temperature bath equipped with a circulation pump and the vessel allowed to warm to the selected bath temperature. The hypodermic syringe containing the diarylacetylene solution was adjusted to the desired volume and weighed and then its contents injected through the serum cap into the triphenylaluminum solution. Reweighing of the syringe gave the weight of diarylacetylene solution delivered to the reaction vessel.

B. Performance of a Kinetic Run. At appropriate time intervals during a run, samples of about 0.25 ml were removed from the reaction solution with 1-ml hypodermic syringes. Thus, a nitrogen-filled syringe was brought to the serum cap, the nitrogen expelled from the syringe, the needle inserted through the serum cap, the sample withdrawn, and the contents of syringe immediately ejected into a nitrogen-filled test tube containing 1 ml of dilute hydrochloric acid. The sample tube was immediately stoppered and vigorously shaken to ensure complete hydrolysis. The hydrolyzed sample was neutralized with aqueous sodium hydroxide solution, and the separated organic layer washed with 2 ml of water. Thereupon the organic layer was analyzed for its content of mesitylene, diarylacetylene, and triarylethylene by vapor-phase chromatography

The specific gravity of mesitylene at the temperatures to be used was determined by standard techniques: 0.769 at 110°, 0.758 at 120°, and 0.739 at 140°. These values were used in all calculations of molarity.

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(12) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1956, p 165.

(13) This reagent, made according to the description in ref 1, was always used shortly after purification.

For maximum accuracy in vpc analysis it was important that a substance in the solution to be analyzed come off the column at the same temperature and rate as that substance in the calibrating solution. Consequently, the constancy of the carrier gas flow and the starting column temperature were critical. Deviations encountered in earlier kinetic runs seemed to be magnified because of such variations

The vpc response for the substances to be analyzed was determined for each reaction by the use of known solutions of solvent, starting acetylene, and resulting triarylethylene. Mesitylene was used as the internal standard and response factors ($R_{A/M}$) were determined for the other two substances. $R_{A/M}$, which may be defined as the multiplier which changes the ratio of peak areas of two substances (M = mesitylene, A = substance) at equal attenuation into a ratio of weights of those substances, equals [(wt of A)/(wt of mesitylene)][(peak area of mesitylene)/(peak area of A)]·(attenuation factor).

C. Conditions for Individual Reactions in the Kinetic Studies. In the inert atmosphere chamber the reaction vessel was filled with 0.3491 g (1.35 mmol) of triphenylaluminum and 76.46 g of mesitylene. After being degassed and equilibrated at 120 ± 0.1, this solution was treated with 0.238 g (1.34 mmol) of diphenylacetylene in 1.51 g of mesitylene. At the reaction temperature the solution was 0.0131 *M* in triphenylaluminum and 0.0130 *M* in the acetylene. The analytical data for this typical run (no. 1), the empirical three-halves-order rate constant, and the bimolecular rate constant derived from it (*cf. infra*) are presented in Table II.

The reaction conditions for all the kinetic studies are given in Table I. Analytical data from these individual kinetic runs, taken up to *ca.* 70–90% consumption of the acetylene, were similarly expressible in terms of empirical three-halves order (Table I), except for the run with *p*-methoxydiphenylacetylene. Inability to fit the kinetic behavior of this acetylene and others bearing strongly donating substituents into simple kinetic expressions is considered in the Discussion.

D. Treatment of Kinetic Data. The molarities in the solution aliquots of both starting acetylene and the triarylethylene resulting from hydrolysis were determined by use of vpc and the following equation

$$\text{molarity in A} = R_{A/M}\frac{(\text{peak area of A})(d_{20^\circ}{}^{t}\text{ mesitylene})}{(\text{peak area of mesitylene})(\text{mol wt of A})(\text{solute corr})}$$

where solute corr = small correction factor needed to allow for the volume of the reagents (R'_3Al and RC≡CR) dissolved in the mesitylene.

The general differential equation for a reaction which is first order in substance B (the acetylene) and one-half order in dimeric substance A (the triphenylaluminum) and in which one molecule of B reacts with one unit of dimer A to give one molecule of X is

$$\frac{dx}{dt} = k(B - X)(A - X/2)^{1/2} \tag{10}$$

Integration for the case where $(A - B/2) = 0$ yields, in steps

$$\frac{dx}{dt} = \frac{k(B - X)^{3/2}}{\sqrt{2}}$$

or

$$\sqrt{2}(B - X)^{-3/2}dx = kdt \tag{11}$$

The latter equation can be integrated by formula[14] to give

$$\frac{2\sqrt{2}}{(B - X)} = kt + C$$

Since at $t = 0$, $X = 0$, then

$$kt = 2\sqrt{2}\left(\frac{1}{\sqrt{B - X}} - \frac{1}{\sqrt{B}}\right) \tag{12}$$

A plot of $1/\sqrt{B - X} - 1/\sqrt{B}$ *vs.* t should give a straight line for data obeying this rate law. The graphical value of k would thus be

$$k_{\text{graphic}} = 2\sqrt{2}\ (\text{slope}) \tag{13}$$

Most of the kinetic runs were conducted at 1:1 equivalences of the reagents (Table I) and hence their three-halves-order rate constants could be evaluated with eq 12.

For the case where $(A - B/2) > 0$

$$\frac{dX}{(B - X)(A - X/2)^{1/2}} = kdt$$

and the integrated rate equation becomes[15]

$$kt = \frac{1}{\sqrt{A - B/2}}\left[\log\frac{\sqrt{A - X/2} + \sqrt{A - B/2}}{\sqrt{A - X/2} - \sqrt{A - B/2}} - \log\frac{\sqrt{A} + \sqrt{A - B/2}}{\sqrt{A} - \sqrt{A - B/2}}\right] \tag{14}$$

If the reaction obeyed the stated conditions, then a plot of the bracketed quantity in eq 14 *vs.* t should give a straight line. The graphical value of k will thus be

$$k_{\text{graphic}} = \frac{1}{\sqrt{A - B/2}}(\text{slope}) \tag{15}$$

Finally, for the case $A - B/2 < 0$

$$\frac{dx}{(B - X)(A - X/2)^{1/2}} = kdt \tag{16}$$

and the integrated rate equation becomes[16]

$$kt = \frac{2}{\sqrt{B/2 - A}}\left[\tan^{-1}\frac{-\sqrt{A - X/2}}{\sqrt{B/2 - A}} - \tan^{-1}\frac{-\sqrt{A}}{\sqrt{B/2 - A}}\right] \tag{17}$$

If the reaction meets the stated conditions, a plot of the bracketed quantity above *vs.* t should give a straight line. The graphical value of k would be

$$k_{\text{graphic}} = \frac{2}{\sqrt{B/2 - A}}(\text{slope}) \tag{18}$$

Values of the rate constants, k, for three-halves-order kinetics were calculated from the appropriate equation (eq 12, 14, and 17), according to the value of $A - B/2$. The values, k_{graphic}, were derived from the corresponding eq 13, 15, and 18. Only three figures were significant in the experimental data; additional figures were used only for computation. In the computation of the average value of k, the value at 5 min was never used. All rate calculations were based on the concentration of the unreacted starting acetylene. The concentration of product was also determined, however, and is given in Tables I and II.

Order of the Carbalumination Reaction. A. General Comments. The overall order of this reaction was determined by the method of integration, the differential method, and the method of fractional lifetimes. The differential method was then applied to determine the order of the reaction with respect to each component. These quantitative studies lead to the conclusion that the reaction of triphenylaluminum with these diarylacetylenes (*p*-CH_3O, *p*-H, *p*-Cl) is of three-halves-order overall, first order in the acetylene and one-half order in triphenylaluminum. This conclusion is meant to hold for mesitylene solutions of the concentrations studied.

This quantitative conclusion was borne out qualitatively by plotting the increase of triphenylethylene *vs.* time for kinetic runs 9 ($(C_6H_5)_3Al$–RC≡CR = 1:1), 4 (0.5:1.0), and 3 (1.0:0.5). At a given time the concentration of the ethylene was in order, run 9 > run 4 > run 3. This shows that rate is more dependent upon the acetylene concentration than upon that of the aluminum aryl.

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[14] C. D. Hodgman, Ed., "C.R.C. Standard Mathematical Tables," 12th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 284, eq 24.

[15] Reference 14, p 287, eq 56, first form.

[16] Reference 15, second form.

B. Method of Integration. A rate constant was calculated for kinetic runs 9 and 10, not only using the equation for three-halves-order kinetics (eq 12), but also for first-order ($kt = \log [B/(B - X)]$ and for second-order ($kt = 2X/B(B - X)$) kinetics. In these equations, B = initial concentrations of reactants. The downward drift in the rate constant when calculated for first-order kinetics (run 10, k = 0.01553–0.01049; k_{av} = 0.01289; std dev 130), its upward drift when determined for second-order kinetics (k = 1.316–1.618; k_{av} = 1.402; std dev 126), and its relatively random variation when determined for three-halves-order kinetics (k_{av} = 0.133; std dev 37) indicate that the reaction is closer to three-halves order than to either first or second. The coefficients of variation (100 std dev/k_{av}) for the rate constants so calculated for runs 9 and 10 were (run, cv, %) for reaction order: run 9, 8.4 (1st), 12.4 (2nd), 2.4 ($^3/_2$); run 10, 10.1 (1st), 8.9 (2nd), 2.8 ($^3/_2$).

C. Differential Method.[17] The differential equation for the present reaction of 1:1 stoichiometry and for runs 9 and 10, where A, B, and X are the normal concentrations of the aluminum aryl, the acetylene, and the product ethylene, respectively, is

$$\frac{-\mathrm{d}(B - X)}{\mathrm{d}t} = k(B - X)^b(A - X)^a \qquad (19)$$

Since $A = B$, $-\mathrm{d}(B - X)/\mathrm{d}t = k(B - X)^n$, where $n = a + b$ = overall reaction order. Taking logarithms and rearranging, one obtains

$$\log\left(\frac{-\mathrm{d}(B - X)}{\mathrm{d}t}\right) = n \log (B - X) + \log k \qquad (20)$$

From a plot of $\log (-\mathrm{d}(B - X)/\mathrm{d}t)$ *vs.* $\log (B - X)$ a straight line should be obtained whose slope is n, the overall reaction order.

This procedure was carried out for kinetic runs 9 and 10 in the following steps: (a) a plot of the acetylene concentration *vs.* time was made and a smooth curve drawn through the points; (b) at a number of points on the curve a small, plane mirror was placed perpendicular to the paper and a line normal to the curve was drawn (the alignment of the mirror was adjusted until the curve and its reflection in the mirror appeared as an unbroken line); (c) the slope of the curve, $-\mathrm{d}(B - X)/\mathrm{d}t$, at each point (whose corresponding acetylene concentration was noted) was obtained by taking the reciprocal of the slope of the normal; and (d) a plot was made of the logarithm of the slope against the logarithm of the acetylene concentration for each point (plot of run 10 shown in Figure 2). A straight line drawn through the plots showed random scatter, rather than drift, through 70% of the reaction. The order of the reaction according to this method is 1.48 for run 10 and 1.52 for run 9.

D. Method of Fractional Lifetimes.[18] For a reaction which obeys eq 19 and where $A = B$, this method due to Ostwald may be applied to two kinetic runs made at sufficiently different concentrations. This treatment was applied to the data from kinetic runs 10 and 9, and runs 10 and 2. The first comparison gave n_{av} = 1.75, the second comparison n_{av} = 1.42, and an overall n_{av} = 1.58.

E. Order of Reaction in Each Reactant by the Differential Method. For a reaction which obeys eq 19, if two runs are made in which the concentration of only one component varies, then the order of the reaction in that component is given by

$$n_b = \frac{\log\left(-\dfrac{\mathrm{d}(B - X)}{\mathrm{d}t}\right)_1 - \log\left(-\dfrac{\mathrm{d}(B - X)}{\mathrm{d}t}\right)_2}{\log B_1 - \log B_2} \qquad (21)$$

where B_1 and B_2 are initial concentrations of the variable reactant in runs 1 and 2, respectively, and $(\mathrm{d}(B - X)/\mathrm{d}t)_1$ and $(\mathrm{d}(B - X)/\mathrm{d}t)_2$ are the slopes of the acetylene *vs.* time curves for runs 1 and 2, respectively, both measured at same time. Because of stoichiometry, $\mathrm{d}X/\mathrm{d}t = -\mathrm{d}(B - X)/\mathrm{d}t$. As in section C, plots of acetylene *vs.* time were made for runs 1, 3, and 4. Normals to the curves were taken at 5-min intervals and logarithms were taken of the slopes calculated as above in section C. By averaging the first five values (0–25 min), the order in triphenylaluminum was 0.58 and the order in the acetylene 0.99

Attempted Carbalumination in Cineole. Under a nitrogen atmosphere 3.65 g (4.06 ml) of cineole, 0.77 g (3.69 mmol) of *p*-methoxydiphenylacetylene, and 1.00 g (3.87 mmol) of triphenylaluminum were heated for 4 hr at 180 ± 0.1°. After 3 min a homogeneous solution was attained, but after 1 hr most of the reaction mixture had solidified into a colorless mass and remained so throughout the heating period. After hydrolysis with 8 ml of water and 6 ml of 1:1 hydrochloric acid all solids had disappeared. The hydrolysate was extracted with 25 ml of benzene and extracts were dried over anhydrous calcium sulfate. Removal of solvent left 0.82 g of pale yellow needles whose infrared spectrum showed only the bands of the starting material.

Calculation of Equilibrium Constants for the Dimerization of Triphenylaluminum. Although equilibrium constants have not been reported, the constant for 80° can be calculated from data available in the literature.[19,20] For the equilibrium

$$[(C_6H_5)_3Al]_2 \rightleftharpoons 2(C_6H_5)_3Al \qquad (22)$$

K_{eq}(naphthalene) = 7.11×10^{-4} and K_{eq}(benzene) = 5.65×10^{-4}. By use of the standard formula relating K_{eq} and T and the heat of dimerization of 7–10 kcal/mol, the K_{eq} (120°, mesitylene) is estimated to be 2.3×10^{-3}. This value is used in calculating k_2, the bimolecular rate constant at 120° (Table I).

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