TABLE I

BIS-(DIALKOXYPHOSPHINYL)-MERCURY, $[(RO)_2P(O)]_2Hg$

R	M.p., °C.	Yield, %	Formula	Mercury, % Calcd.	Mercury, % Found	Phosphorus, % Calcd.	Phosphorus, % Found
CH_3	121.6–123.0	83	$C_4H_{12}O_6HgP_2$	47.81	47.48	14.80	14.64
CH_3CH_2	56.8–58.2	91	$C_8H_{20}O_6HgP_2$	42.16	41.76	13.05	12.89
n-C_3H_7	35.6–36.8[a]	80	$C_{12}H_{28}O_6HgP_2$	37.70	36.46	11.67	11.62
i-C_3H_7	124.4–125.0	81	$C_{12}H_{28}O_6HgP_2$	37.70	37.22	11.67	11.70
n-C_4H_9	25.0–27.2[b]	92	$C_{16}H_{36}O_6HgP_2$	34.10	33.51	10.54	10.43
i-C_4H_9	132.0–133.5	88	$C_{16}H_{36}O_6HgP_2$	34.10	31.88	10.54	10.55

[a] Super-cooled liquid, $n^{20}D$ 1.5062. [b] Super-cooled liquid, $n^{20}D$ 1.4991.

the cold trap, 6.7 g. (0.37 mole) of water was isolated. The gray plates formed after removal of the low boiling materials were recrystallized three times from petroleum ether to give 216.1 g. (91.2% yield) of bis-(diethoxyphosphinyl)-mercury, m.p. 56.8–58.2°.

Anal. Calcd. for $C_8H_{20}O_6P_2Hg$: C, 20.24; H, 4.25; P, 13.05; Hg, 42.25; mol. wt., 474. Found: C, 20.32, 20.27; H, 4.74, 4.72; P, 12.90, 12.87; Hg, 42.25, mol. wt., 486 (Rast Method).

The Effect of Acid and Base on the Synthesis.—A vigorously stirred mixture of redistilled[6] diethyl phosphonate (0.1 mole), mercuric oxide (0.05 mole) and 100 ml. of dried benzene was refluxed for three hours under a reduced pressure of 200 mm. The quantities of recovered mercuric oxide, water collected and crude bis-(diethoxyphosphinyl)-mercury are given in Table II for the following runs using the above quantities and conditions: (1) with acid and base absent, (2) with triethylamine (0.7 g., 0.007 mole), and (3) with *p*-toluenesulfonic acid (1 g., 0.006 mole). It is evident from these results that acid is the best catalyst for the reaction.

TABLE II

EFFECT OF CATALYST

Catalyst	Moles	Water collected, mole	Mercuric oxide recovd., mole	Yield of crude product, mole
None		None	0.050	None
Triethylamine	0.007	Trace	.036	None
p-Toluenesulfonic acid	.006	0.039	.006	0.046

Reaction of Mercuric Chloride with Bis-(dialkoxyphosphinyl)-mercury.—Bis-(diethoxyphosphinyl)-mercury (4.7 g., 0.01 mole) was dissolved in 20 ml. of dried benzene, and 2.7 g. (0.01 mole) of mercuric chloride was added. The mixture was refluxed 15 minutes and allowed to cool to room temperature. An unidentified fine crystalline material (0.5 g., m.p. 145° dec.) was filtered from the benzene solution and 5.9 g. (78.6% yield) of crude diethoxyphosphinylmercuric chloride was obtained in two crops from the filtrate. Recrystallization first from carbon tetrachloride and then from water gave a product melting at 103–104°. A mixed melting point with the product previously reported[1] showed no depression.

WASHINGTON, D. C.

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(6) These runs were made under rigorously dry conditions, since a brief exposure of the phosphonates to atmospheric moisture results in the formation of traces of acidic hydrolysis products.

[CONTRIBUTION NO. 1975 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Coördination of Silver Ion with Unsaturated Compounds. VII. 3-Hexyne[1]

BY W. SMITH DORSEY AND HOWARD J. LUCAS[2]

RECEIVED MAY 21, 1955

The value of the argentation constant of 3-hexyne, as determined by a distribution method, is smaller than those of alkenes and greater than those of aromatic hydrocarbons. Oxygen must be rigorously excluded.

The coördination of the olefinic double bond with silver ion has been fairly well investigated.[3-5] Although a number of complexes of acetylene with silver and cuprous salts have been known for a long time, acetylene and propyne are not the proper types of substances for investigating coördination of the acetylenic triple bond because an acidic hydrogen atom on a triply bound carbon atom can be replaced by a metal atom. 3-Hexyne is the simplest symmetrical non-acidic alkyne having a convenient boiling point. Failure of others[6] to observe complexing of dialkylacetylenes may be due to the limitations of visual methods when only slight changes in solubility are involved.

Method.—The distribution method of the earlier papers[3] was followed and the immiscible solvents were water and carbon tetrachloride. The mutual solubilities of the two solvents are low, and the extent to which the hexyne–silver nitrate complex dissolves in carbon tetrachloride is so small that its presence in solution could not be detected. The presence of oxygen even in low concentration was very troublesome. It was only after 99.9% pure nitrogen became available[7] that satisfactory analyses became the rule.

Materials.—The 3-hexyne was in part supplied by H. Lemaire of these laboratories (synthesized by the method of Bried and Hennion),[8] b.p. 80.0–80.6° (746 mm.), $n^{25}D$

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(1) Previous paper of this series, unnumbered, R. E. Kofahl and H. J. Lucas, THIS JOURNAL, **76**, 3931 (1954).

(2) To whom requests for reprints should be sent.

(3) F. R. Hepner, K. N. Trueblood and H. J. Lucas, THIS JOURNAL, **74**, 1333 (1952). Herein are cited a number of references.

(4) R. N. Keller, *Chem. Revs.*, **28**, 229 (1941).

(5) J. Chatt, "Cationic Polymerizations," edited by P. H. Plesch, W. Heffer and Sons, Ltd., Cambridge, Eng., 1953, pp. 41–48; G. Salomon, *ibid.*, pp. 57–64.

(6) H. J. Taufen, M. J. Murray and F. C. Cleveland, THIS JOURNAL, **63**, 3500 (1941).

(7) From Linde Air Products Company.

(8) E. A. Bried and G. F. Hennion, THIS JOURNAL, **59**, 1310 (1937).

1.4087, and in part by Farchan Research Laboratories, b.p. 80.0–80.3° (744 mm.), $n^{25}\text{D}$ 1.4089.[9,10] It was distilled under nitrogen and was transferred by a hypodermic syringe into previously weighed small bulbs, 0.05 to 0.3 g. per bulb. Each bulb was sealed and weighed.

Carbon tetrachloride was purified as described earlier.[11]

Inorganic Reagents.—Potassium bromide, potassium bromate, mercuric sulfate, mercuric oxide and mercuric nitrate were reagent grade. Mercuric nitrate was dried in a desiccator containing phosphorus pentoxide before weighing. Potassium iodide was satisfactory as USP grade. Solutions containing 2 to 4% (by weight of total solids content)[12] of sodium carbonate were stable over the two or three weeks period required to consume them.

Stopcock Lubricant.—Most commercial lubricants absorb bromine. A satisfactory although rather stiff paste was prepared by melting together 20 g. of No. 7 mineral oil, 1.0 g. of zinc oxide (J. T. Baker analyzed) and 40 g. of stearic acid. The last had stood 24 hours in the dark with acidified bromide–bromate solution, was then melted, and while molten was washed with water. The mineral oil absorbed 0.0038 meq. of bromine per ml., the treated stearic acid, 0.0082 meq. per gram. The maximum error is 2.4% on the assumption that the 3-hexyne sample is 0.017 meq. and that as much as 0.05 g. of lubricant is dissolved. This probably is the extreme condition.

Later Fluorolube Light Grease[13] was found satisfactory though relubrication was necessary after every extraction operation owing to removal of the grease by carbon tetrachloride. One gram absorbed 0.0051 to 0.0081 meq. of bromine. On the aforementioned basis the maximum error would be 2.4%, the same as for stearic acid paste.

Oxygen-free Water.—Distilled water at about 40° was evacuated (aspirator) in a 2-l. bottle until bumping took place with formation of very large bubbles. Nitrogen was admitted to the flask as the contents cooled. Transferals of water and of solutions in general were accomplished by nitrogen pressure, using two nitrogen lines at different pressures.

Solutions for Analysis.—These were prepared with ordinary distilled water. Sulfuric acid, 9 *M*, catalyst solution, 1.00 *M* in mercuric sulfate and 3 *M* in sulfuric acid, and glacial acetic acid were degassed by heating under a pressure of about 20 mm. as described earlier and were stored under nitrogen. The standard bromide–bromate solutions[11] had a bromide–bromate molal ratio of 5.00 and were 0.02 to 0.12 *N* in bromine. Thiosulfate was 0.01 to 0.02 *N*.

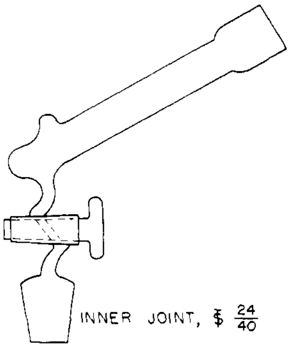

Fig. 1.—Tube for introducing 3-hexyne into the equilibration flask.

Aqueous Solutions for Distributions.—Solutions of silver nitrate and/or potassium nitrate, prepared under oxygen-free conditions in a 1.2-l. mixing cylinder, were transferred to the distribution flask with a maximum error of about 0.5%. The volume was 700 to 1,000 ml., usually fairly close to 1,000 ml.

Apparatus.—The equilibration flask, usually 1 l., had a well at the bottom approximately 2.5 cm. deep by 2.5 cm. o.d., capacity about 15 ml. This served to collect the carbon tetrachloride phase and facilitate sampling. There were five ₸ 24/40 necks, for the following: a stirrer (center neck), a nitrogen inlet tube, a sample removal tube extending into the well, an inclined tube for introducing hexyne and carbon tetrachloride, and a venting tube to allow escape of nitrogen as liquids flowed in. Samples of the aqueous phase were forced out through one of the two necks later available and into a pipet calibrated to contain.[14]

The stirrer (Patterson)[15] was mercury sealed and was driven by a Palo–Meyers variable speed motor. Good mixing without pick-up of gas bubbles was achieved by reducing the wing spread from about 10 cm. to about 3 cm. By regulation of the speed the carbon tetrachloride was well dispersed as an opaque suspension in which the droplets were for the most part individually visible but not so fine as to produce a misty or foggy appearance. The phases separated nicely and sampling could be done in about 20 minutes after stirring ceased.

Temperature was maintained by a constant temperature glass jar bath equipped with a stirrer, a 100-watt immersion heater, a "Cenco–de Khotinsky" thermoregulator and a thermometer (15 to 30°, divisions 0.1°), calibrated by comparison with a U. S. Bureau of Standards thermometer. The equilibration flask and thermostat assembly were mounted as a separate unit and could be removed *in toto* by disconnecting the electricity, nitrogen and compressed air supply lines.

Dissolving the Hexyne.—This was done by breaking an ampoule of 3-hexyne in a special slanting tube, Fig. 1, i.d. *ca.* 14 mm., capacity about 25 ml., provided with a stopcock and a standard taper joint for connection to the equilibration flask. The tube was expanded in one place to a dome so that gas in the ampoule on rising would be dissolved in the solvent. The tube was first flushed out by nitrogen and about 5 ml. of carbon tetrachloride was added, an amount sufficient to bring the level above that of the dome. Trapped air was removed from the dome before attaching the tube to the flask, and before breaking the ampoule. Solution and washings, total volume 5 to 15 ml., entered the flask on top of the aqueous solution already present. A slight positive pressure was maintained from here on. The maximum error was ±0.4 ml., or 2 to 8%.

Equilibration.—Stirring time was usually 30 minutes. The time of stoppage was called "zero time."

Sampling.—The carbon tetrachloride was blown out into a storage cylinder. As soon as possible two analyses were made by sampling as before.[14] This required about 0.5 hour. Sampling[14] and analysis[11] of the aqueous phase, now clear and free of all droplets of carbon tetrachloride, followed. Samples of the carbon tetrachloride and aqueous phases were taken alternately until the desired number had been obtained, at least three of each. Elapsed time was recorded from zero time to the beginning of bromination. If any trend with time was noted more samples were taken, in some cases as many as seven. The data were extrapolated back to zero time. As the procedure was improved the number of samples in general approached the minimum of three. A material balance was obtained from the volume of each phase and the concentration of hexyne in each phase.

Analysis.—The procedure for hexyne analysis by bromide–bromate[11] as finally developed[16] gave results as follows: 99 to 102% with an average deviation of 1% for 0.02 to 1.41 meq. in carbon tetrachloride, and of 98 to 101% with an average deviation of 1% for 0.06 to 0.55 meq. in aqueous solution. A blank was always run. This usually was 1 to 2%, sometimes as high as 3%.

No interference by oxygen was noted in the analysis of carbon tetrachloride solutions, but oxygen must be excluded

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(9) (a) A. L. Henne and K. W. Greenlee, THIS JOURNAL, **67**, 484 (1945), give b.p. 81° (760 mm.) and $n^{20}\text{D}$ 1.4115 (from which $n^{25}\text{D}$ is calculated to be 1.4089 with dn/dt of −0.0005237); G. Egloff, "Physical Constants of Pure Hydrocarbons," Vol. 1, A.C.S. Monograph 78, Reinhold Publishing Corp., New York, N. Y., 1939, p. 366. (b) K. N. Campbell and L. T. Eby, THIS JOURNAL, **63**, 2683 (1941), give $n^{20}\text{D}$ 1.4110 ($n^{25}\text{D}$ calcd. 1.4084).

(10) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg and F. L. Howard, *J. Research Natl. Bur. Standards*, **52**, 51 (1954), give b.p. 81.43° (760 mm.), $n^{20}\text{D}$ 1.4112.

(11) H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938).

(12) M. E. Stansby, *ibid.*, **13**, 627 (1941).

(13) A polymer of trifluoroethylene kindly supplied by the Hooker Electrochemical Co.

(14) W. F. Eberz and H. J. Lucas, THIS JOURNAL, **56**, 1232 (1934).

(15) J. A. Patterson, *Ind. Eng. Chem., Anal. Ed.*, **6**, 171 (1934).

(16) It is planned to present elsewhere the details of this investigation and the data on the solubility of 3-hexyne.

during the analysis of aqueous solution, even during the final titration with sodium thiosulfate. It was necessary to direct a stream of nitrogen into the titration flask until the final end-point was reached.

Constants Evaluated.—These are K_D, K_1, K_2, K_0 and K_E, eq. 1 to 5, the respective constants[3,17-19] (except K_E) for the reactions shown by eq. 1a to 4a. Here (Un), (Un_t), (Ag^+) and (Ag_t^+) refer to concentrations in the aqueous phase at constant ionic strength $\mu = 1$, and $(Un)_c$ to concentrations in carbon tetrachloride.

$$K_D = (Un)_c/(Un) \tag{1}$$

$$K_1 = (Un{\cdot}Ag^+)/(Un)(Ag^+) \tag{2}$$

$$K_2 = (Un{\cdot}2Ag^+)/(Un{\cdot}Ag^+)(Ag^+) \tag{3}$$

$$K_0 = (Un{\cdot}Ag^+)/(Un)_c(Ag^+) = K_1/K_D \tag{4}$$

$$K_E = K_D[(Un) - (Un)_c/K_D]/(Un)_c[(Ag^+_t) - (Un_t) + (Un)_c/K_D] \tag{5}$$

$$Un_w \rightleftarrows Un_c \tag{1a}$$

$$Un + Ag^+ \rightleftarrows Un{\cdot}Ag^+ \tag{2a}$$

$$Un{\cdot}Ag^+ + Ag^+ \rightleftarrows Un{\cdot}2Ag^+ \tag{3a}$$

$$Un_c + Ag^+ \rightleftarrows Un{\cdot}Ag^+ \tag{4a}$$

None of these constants are thermodynamic constants since they are formulated with concentrations rather than activities.

K_D.—The distribution of 3-hexyne between carbon tetrachloride and 1 N potassium nitrate, Table I, gave K_D values of 2190 to 2480, the higher values occurring at the lower concentrations of 3-hexyne, Fig. 2. The straight line shown in Fig. 2 was fitted by the method of least squares and gave for K_D at zero concentration of 3-hexyne a value of 2600. On the assumption that this method of extrapolation is justified, this value would be the thermodynamic distribution constant of 3-hexyne between carbon tetrachloride and 1.00 N aqueous potassium nitrate because at infinite dilution the activity coefficient of dissolved 3-hexyne is regarded as unity in each solvent.

TABLE I

DISTRIBUTION OF 3-HEXYNE BETWEEN CARBON TETRACHLORIDE AND 1.00 M AQUEOUS POTASSIUM NITRATE AT 25°

Stirring time, min.	M.B.[a]	3-Hexyne in CCl_4 M	3-Hexyne in H_2O $M \times 10^4$	K_D
15	100.1	0.0990	0.412	2400
15	89.3	.2185	.965	2260
30	100.7	.1985	.832	2380
30	95.3	.2505	1.088	2300
30	102.9	.1462	0.590	2480
20	95.3	.3198	1.460	2190
20	104	.2100	1.24	1690[b]

[a] Material balance: percentage found of hexyne taken. [b] K_W, the distribution constant in pure water.

The drop in values of K_D with increasing concentration of 3-hexyne is to be expected since the activity coefficient rises more rapidly in aqueous solution than in a carbon tetrachloride solution. The maximum concentration of 3-hexyne in the aqueous phase during the determination of K_D was never greater than one-fifteenth the solubility of 3-hexyne in 1.00 N potassium nitrate.[16]

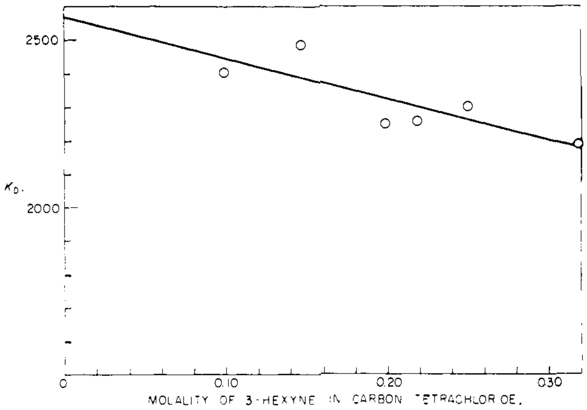

Fig. 2.—Distribution coefficient K_D of 3-hexyne between 1.00 N aqueous potassium nitrate and carbon tetrachloride at 25°.

Metallic Salts.—Distributions were made with a number of metallic salts at 25° and ionic strength $\mu = 1$ obtained by the addition of potassium nitrate. The data are shown in Table II. The material balance was in most cases imperfect. This was due in part to the use of 99.7% nitrogen, and in part to difficulties in the analysis of aqueous solutions containing colored ions. The observed values of K_D were those calculated from the observed concentrations of hexyne. The limiting values were calculated from the observed concentrations in the carbon tetrachloride phase and concentrations for the aqueous phase calculated on the assumptions that the concentration of the carbon tetrachloride phase was correct, and that no hexyne was lost during the distribution. The limiting values of K_D agree reasonably well with K_D obtained during good material balance (Table I); thus in general the limiting K_D is better than the observed K_D.

Of the metallic salts, silver nitrate and cuprous chloride are the only ones showing pronounced ability to coördinate, as evidenced by the low K_D values. The results with cuprous chloride were inconclusive. There was little or no tendency of cadmium, cobaltous, cupric, nickelous or zinc ion to coördinate with the triple bond in aqueous solution. A similar condition was found years ago with alkenes.[18]

K_E.—The data of distributions of 3-hexyne with aqueous silver nitrate are shown in Table III. In all cases except two the material balance error did not exceed 10%, and in one case it was not determined. Values of K_E decrease with a drop in the concentration of silver nitrate. There is also a relationship between the values at a given silver concentration and the concentration of hexyne, as shown by the curves of Fig. 3, where K_E is plotted against $(Un)_c$. As the ratio $(Ag)^+/Un$ increases, K_E becomes larger. This would be a normal behavior if one Un should complex with more than one Ag^+. In drawing the curve for 0.25 N silver nitrate, three values of Table III were given less than normal weight because of a feeling that a change of nitrogen cylinders may have had some effect (footnote c).

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[17] W. F. Eberz, H. J. Welge, D. M. Yost and H. J. Lucas, THIS JOURNAL, **59**, 45 (1937).

[18] S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).

[19] H. J. Lucas, R. S. Moore and D. Pressman, *ibid.*, **65**, 227 (1943).

Table II

Distribution of 3-Hexyne Between Carbon Tetrachloride and Aqueous Metallic Salts with Imperfect Material Balance; $\mu = 1.00$, $T = 25°$

Aqueous phase	Concn, *M*.	M.B.[a]	Time of Stir., min.	Time of Analysis, hr.	3-Hexyne in[b] CCl_4, *M*	3-Hexyne in[b] H_2O, $M \times 10^4$	K_D Obsd.	K_D Calcd. limit[c]
KNO_3	1.00	79	14	6	0.218[d]	1.42[d]	1640	2080
		71	15	5.5	.195	1.25[d]	1560	2200
		78	15	4	.129	0.48	1900	2440
$AgNO_3$	0.20	61	14	5.5	.152	5.97[d]	255	420
$Cd(NO_3)_2$[e]	.20	60	14	5.5	.187[d]	1.58[d]	1180	1970
$Co(NO_3)_2$	.01	61	15	6	.195	1.26	1560	2560
$CuSO_4$[f]	.00043	76	15	2	.24	1.65	1400	1840
$CuSO_4$[f]	.20	30	10	3.5	.094	0.43	2170	..
$Ni(NO_3)_2$	.20	64	12	5.5	.203	1.42	1425	2230
$Zn(NO_3)_2$	.20	67	14	5	.190	1.24	1530	2280
CuCl[g]		69	11	3	.196	4.06	481	700
CuCl[g]		63	12	3	.192	1.27	1507	2390
H_2O[h]		61	15	5	.188	1.61	1170	1920
H_2O[h]		78	15	5	.126	0.96	1310	1680

[a] Material balance. [b] Mean values, except when extrapolated to zero time. [c] Calculated on the assumption that all error is in the analysis of the aqueous phase. [d] Extrapolated to zero time. [e] $\mu = 0.80$. [f] H_2SO_4, 0.01 *N*; KNO_3, 0.00 *N*. [g] Saturated aqueous solution; KNO_3 = 0.00 *N*. [h] $\mu = 0.00$.

Table III

Distribution of 3-Hexyne Between Carbon Tetrachloride and Aqueous Silver Nitrate at 25°, $\mu = 1.00$

$AgNO_3$, *M*	M.B.[a]	3-Hexyne in CCl_4, *M*	3-Hexyne in H_2O, $M \times 10^4$	K_E
1.000	104	0.1180	12.27	24.2
	108	.1837	19.43	24.0[b]
	82	.0477	6.02	30.5
	109	.0690	7.32	25.3
	110	.0632	6.72	25.4
	112	.0565	6.75	26.5
0.500	107	.2037	10.1	21.3[b]
0.250	109	.2065	5.40	20.4[b]
	107	.0575	1.48	21.7
	110	.0520	1.32	21.5
	107	.0427	0.287	23.1
	108	.1418	3.82	22.0[c]
	..	.0975	2.63	22.5[c]
	107	.0930	2.45	22.0[c]
	104	.1035	2.55	20.0
	102	.0995	2.5	21.4
0.250[d]	108	.1948	6.45	20.0

[a] Material balance; percentage found of hexyne taken. [b] Selected for calculation of K_1 and K_2. [c] Not weighted normally in drawing curve of Fig. 3, owing to change in conditions of experiment. [d] $\mu = 0.25$.

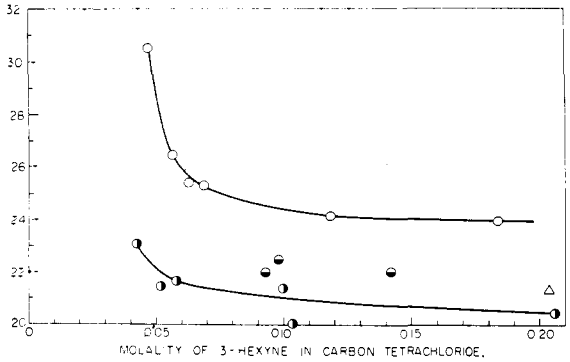


Fig. 3.—K_E at 25° and $\mu = 1$ *vs.* concentration of 3-hexyne in carbon tetrachloride $(Un)_c$: ○, 1.00 *N* silver nitrate; △, 0.50 *N* silver nitrate; ◑, 0.25 *N* silver nitrate; ◒, 0.25 *N* silver nitrate, footnote *c*, Table III.

K_1, K_2 and K_0.—A plot of K_E against (Ag^+) at $(Un)_c$, approximately 0.2 *M*, shows an upward curvature, Fig. 4. This indicates that in addition to $Un{\cdot}Ag^+$ there is at least one other complex in which one Un complexes with more than one Ag^+. On the assumption that there are only two complexes, namely, $Un{\cdot}Ag^+$ and $Un{\cdot}2Ag^+$, the expression relating the respective constants, K_1 and K_2, to K_E is given by eq. 6.

$$K_E = \frac{K_1 + K_1K_2(Ag^+)}{1 + K_1K_2(Un)(Ag^+)} \qquad (6)$$

Values of K_1 and K_2 were obtained from three different pairs of experiments by a trial and error method and found to be: K_1, 18.8, 19.2 and 19.4: K_2, 0.22, 0.25 and 0.21. There is satisfactory agreement here with 19.7, the extrapolated zero-silver-concentration value of K_1 in Fig. 4. The values of K_1 and K_2 are taken to be, respectively, 19.1 ± 0.5 and 0.23 ± 0.05, under these conditions: 25.0°, 1 atm. (nitrogen), solvents, carbon tetrachloride and aqueous $AgNO_3$–KNO_3 at $\mu = 1.00$, $(Un)_c$ approx. 0.20 *M*. In calculating K_0 from K_1, K_D was taken as 2330, the value at $(Un)_c$ = 0.2 *M*, Fig. 2. K_0 is 8.2×10^{-3}. K_0 probably is a better measure of

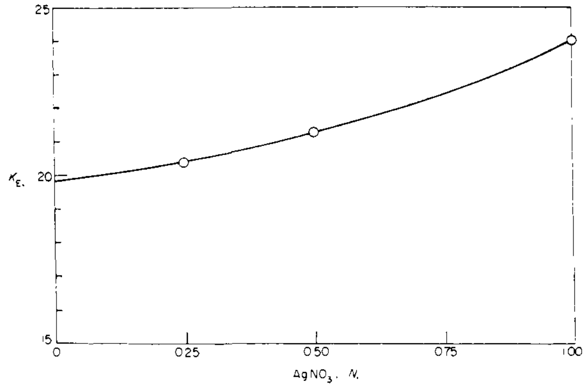


Fig. 4.—K_E *vs.* silver nitrate concentration at μ = 1.00 and $(Un)_c \approx 0.20$ *M*.

complexing power than K_1, because the activity coefficient of Un in water, eq. 2, deviates from unity very much more than it does in carbon tetrachloride, eq. 4.

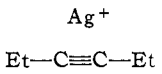
TABLE IV

COMPARISON OF ARGENTATION CONSTANTS AT 25°

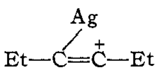
Hydrocarbon	K_1	K_2	$K_0 \times 10^3$
3-Hexyne	19.1	0.23	8.2
cis-2-Pentene[19]	112.5		31.2
trans-2-Pentene[19]	62.2		11.1
Cyclohexene[18]	79.3		18.4
Benzene[20]	2.41	0.212	
Naphthalene[1]	2.94	.91	
Phenanthrene[1]	3.55	.99	

3-Hexyne complexes less strongly with silver than do the 2-pentenes[19] and cyclohexene[18] and more strongly than aromatic hydrocarbons[1,20] as shown by the data in Table IV. The fact that alkyl groups depress the argentation reaction in alkenes,[18] in spite of electron release by these groups, may be due in large part to steric factors. Steric effects may well account for the lower constants of *trans*-2-butene[3] and *trans*-2-pentene[19] as compared to their *cis*-isomers.[21] In 3-hexyne the steric effect presumably would be more than in a corresponding *cis*-alkene,[4] and probably comparable to that in the *trans* isomer.

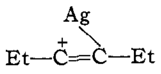
Nature of the Complex.—The 3-hexyneargentonium ion,[22] like the silver–olefin and mercury–hexyne[23] complexes, is a resonance hybrid. The main contributing forms are I, II, III and IV; other forms, presumably less important, arise from hyperconjugation, V.[24] Other ways of representing the complex are based on the formulations of Dewar, VI,[25] and Winstein, VII.[26] The structure of the 3-hexyne–silver ion complex is similar to that of the 3-hexyne-acetoxymercurinium ion,[23] the intermediate in the mercury-catalyzed reaction of 3-hexyne with acetic acid.


$\overset{Ag^+}{Et{-}C{\equiv}C{-}Et}$

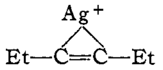
I



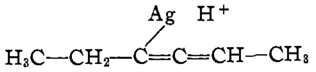
II



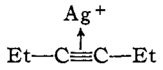
III



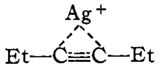
IV



V



VI



VII

The 3-hexyne–silver complex is less stable than the complex of cyclohexene, but probably is more stable than that of a *trans*-hexene, for which an approximate value of 5 to 7 × 10^{-3} is reached by considering the respective values of *cis*- and *trans*-2-pentene, Table IV, those of *cis*- and *trans*-2-butene[3] (73.0 × 10^{-3} and 25.2 × 10^{-3}, respectively), the trend in these values, and the *cis/trans* ratios of 2.8 and 2.9 for the pentenes and butenes, respectively. This rough estimate, 5 to 7 × 10^{-3}, is substantiated by a second estimate from cyclohexene, $K_0 = 18.4 \times 10^{-3}$, by assuming a *cis/trans* ratio of 2.7 for the hexenes. This gives a value of 6.8 × 10^{-3} for the K_0 of a *trans*-hexene.

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(20) L. J. Andrews and R. M. Keefer, THIS JOURNAL, **71**, 3644 (1949).

(21) M. J. S. Dewar, *Bull. soc. chim.*, C71 (1951), believes that an alkyl group lessens the stability of a complex through its effect on the anti-bonding π-molecular orbitals of an olefin in the formation of the second bond between a heavy metal and an olefin.

(22) According to N. Koenig, Ph.D. Thesis, California Institute of Technology, 1950, this would be silver(I)-3-hexynium ion. The salt in solution would be silver(I)-3-hexynium nitrate.

(23) H. Lemaire and H. J. Lucas, THIS JOURNAL, **77**, 939 (1955).

(24) Proposed by A. E. Comyns.

(25) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); see also A. D. Walsh, *Nature*, **159**, 165, 712 (1947).

(26) S. Winstein and co-workers, THIS JOURNAL, **74**, 1133, 1160 (1952).

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[CONTRIBUTION FROM THE RESEARCH CENTER, THE B. F. GOODRICH CO.]

Vinylidene Cyanide. VII. Copolymerization[1a]

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Vinylidene cyanide copolymerizes readily with a wide range of common monomers. The Mayo–Lewis copolymerization equation is solved for 15 systems. The relative reactivities of the comonomers toward the vinylidene cyanide free radical are listed. The most active comonomers are styrene, chlorobutadiene, dichlorostyrene, and methyl methacrylate. The least active comonomers are acrylic acid, vinyl chloride, dichloroethylene and maleic anhydride. Vinyl ether–vinylidene cyanide systems give a novel autocatalytic ionic polymerization. The styrene–vinylidene cyanide system exhibits a rapid free radical cross-initiation. The Price–Alfrey Q and e parameters for vinylidene cyanide are calculated. The near-quantitative nature of the Q–e concept is rather strongly confirmed by the data.

The homopolymerization of vinylidene cyanide (I) has been reported previously.[2] The present paper describes the copolymerization of I with sixteen vinyl monomers and one diene. Another objective of this work was to check the quantitative nature of the Price–Alfrey[3] "Q" and "e" method for correlating resonance stabilization and polarity with relative reactivities of monomers toward free radicals.

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(1) (a) This paper was presented before the Division of Polymer Chemistry at 126th Meeting of the American Chemical Society in New York, N. Y., September 14, 1954. (b) B. F. Goodrich Chemical Co., Avon Lake, Ohio.

(2) H. Gilbert, F. F. Miller, S. J. Averill, R. F. Schmidt, F. D. Stewart and H. L. Trumbull, Part III, THIS JOURNAL, **76**, 1074 (1954).

(3) C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).