added 1 cc. (1.08 g., 0.0106 mole) of redistilled acetic anhydride and 3 cc. of anhydrous pyridine. The mixture was warmed on the steam-bath for about ten minutes, and set aside. Filtration after one day yielded 0.44 g. of crystals, m. p. 144–144.5° (reported[9] 144°). The filtrate was poured onto ice and the pyridine was neutralized with concentrated hydrochloric acid to yield an additional 0.68 g. of material, m. p. 141–142°, for a total yield of 1.12 g. (88%).

cis-**2-Benzamidocyclohexanol.**—16.12 g. (0.0735 mole) of *trans*-2-benzamidocyclohexanol (powdered in a mortar) was added in small portions to 15 cc. of thionyl chloride (cooled to 0°). Five cc. of thionyl chloride was added to bring a small amount of undissolved material into solution. The mixture was allowed to warm to room temperature and left for three hours. Then the mixture was carefully poured into *ca.* 400 cc. of distilled water. The resulting aqueous solution was filtered and the filtrate was refluxed for 10 minutes. After refluxing, the solution was cooled in an ice–salt-bath, filtered, and potassium hydroxide (6 *N*) was added to the filtrate to yield (after drying at 1 mm. over phosphorus pentoxide) 15.08 g. (93.5%) of material, m. p. 180–182°.

cis-**2-Benzamidocyclohexyl Tosylate.**—Ten grams (0.0457 mole) of *cis*-2-benzamidocyclohexanol, 10.0 g. (0.0527 mole) of *p*-toluenesulfonyl chloride, and 100 cc. of anhydrous pyridine were warmed on a hot-plate until all the solid material went into solution. The solution was set aside for a day. Then the pyridine solution was poured into ice, and the pyridine was neutralized by adding concentrated hydrochloric acid until the solution imparted a red color to methyl orange. The precipitate was filtered and taken up in benzene. The benzene layer was dried over potassium carbonate, and cooled to yield 7.92 g. (46.5%) of material, m. p. 162–163° (reported[9] m. p. 163–165°).

Rate Measurements in Absolute Ethanol.—The stock solution for a run was made up in a 100-cc. volumetric flask and distributed among 13 or 14 ampoules. The ampoules were sealed and inserted in the thermostat. At specified times, ampoules were removed from the thermostat, cooled for one minute in water at room temperature, and opened. A sample (4.723 cc.) was pipetted into 25 cc. of distilled water, and titrated with standard aqueous sodium hydroxide solution, using phenolphthalein as indicator. A blank was run to determine the titration correction. The absolute alcohol used in the rate runs and in all solvolyses in ethanol contained less than 0.01% water as shown by the paraffin oil test of Robertson.[39]

Rate Measurements in Glacial Acetic Acid.—These were performed according to the procedure of Winstein, Grunwald and Ingraham.[1]

Acknowledgment.—We are grateful to the Research Corporation for a grant-in-aid in support of this work.

Summary

Participation of certain so-called neighboring groups in nucleophilic replacement processes is briefly discussed, and qualitative and quantitative comparison between the neighboring benzamido and acetoxy groups is reported.

The rate of ionization of *trans*-2-benzamidocyclohexyl *p*-toluenesulfonate is *ca.* 200 times that of the corresponding acetoxy compound, brief treatment in glacial acetic acid or ethanol sufficing for nearly quantitative conversion to *cis*-2-phenyl-4,5-tetramethyleneoxazoline, which can be isolated as the *p*-toluenesulfonate, picrate or free base. The same steric result attends the conversion of *trans*-2-benzamidocyclohexanol to oxazoline by thionyl chloride.

Opening of the oxazolinium salt by aqueous acid or glacial acetic acid solutions gives the same stereochemical results previously observed with neighboring acetoxy. The opening by water, together with the treatment of *trans*-2-benzamidocyclohexanol with thionyl chloride make up a convenient method of preparation of *cis*-2-benzamidocyclohexanol.

[39] Robertson, "Laboratory Practice of Organic Chemistry," The Macmillan Co., New York, N. Y., 1943, p. 178.

LOS ANGELES 24, CALIF. RECEIVED APRIL 25, 1950

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

The Interaction of Bromine with Benzene and Certain of its Derivatives

BY R. M. KEEFER AND L. J. ANDREWS

Two interesting examples of the basic nature of the aromatic nucleus have been considered in recent publications concerning complex formation of certain aromatic substances with iodine[1] and with silver ion.[2] Recently it has been reported that the ultraviolet absorption spectra of solutions of bromine[3] in certain aromatic compounds display maxima very similar to those described[1a,b] for the interaction of iodine and benzenoid systems. The present investigation was undertaken to see whether the absorption spectra reported by Bayliss[3] could be explained by bromine–aromatic complex formation. Spectrophotometric methods similar to those used by Benesi and Hildebrand[1a,b] have been employed to evaluate the equilibrium constants for the formation of bromine addition complexes of benzene and several of its derivatives in carbon tetrachloride solution. The results are of interest not only because of their relationship to the findings of the studies with iodine and silver ion but are also potentially useful in connection with proposed experiments concerning the mechanism of substitution of bromine in the aromatic nucleus.[4]

Experimental

Materials.—All organic compounds were of the best grade available from Eastman Kodak Co. The carbon tetrachloride was dried over calcium chloride and distilled.

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[1] (a) Benesi and Hildebrand, THIS JOURNAL, **70**, 3978 (1948); (b) Benesi and Hildebrand, *ibid.*, **71**, 2703 (1949); (c) Fairbrother, *Nature*, **160**, 87 (1947); (d) Fairbrother, *J. Chem. Soc.*, 1051 (1948).

[2] (a) Andrews and Keefer, THIS JOURNAL, **71**, 3644 (1949); (b) Andrews and Keefer, *ibid.*, **72**, 3113 (1950).

[3] Bayliss, *Nature*, **163**, 764 (1949).

[4] Robertson, *J. Chem. Soc.*, 933 (1949), has postulated a bromine–mesitylene addition compound as an intermediate in the formation of bromomesitylene.

Benzene, toluene and the xylenes were washed three times with concentrated sulfuric acid, with water and dilute sodium hydroxide. After drying, the hydrocarbons were fractionated and samples of the following b. p. collected: benzene (80.2°), toluene (110.0°), *o*-xylene (144.0–144.3°), *m*-xylene (139.1°), *p*-xylene (137.1°). Chlorobenzene (b. p. 132.0°), bromobenzene (b. p. 156.3°) and anisole (b. p. 153.4–153.8°) were fractionated after drying over calcium chloride. The iodobenzene (b. p. 188.3°) was washed with dilute sodium thiosulfate solution to remove traces of iodine and was dried and fractionated. Mallinckrodt Chemical Works Anal. Reagent grade bromine was used in the experiments described.

The Ultraviolet Absorption Spectra.—All reagents or solutions were brought to 25.0° before analysis or before dilution to provide the final solutions for spectrum measurement. In general, measured volumes of the aromatic substances or of their carbon tetrachloride solutions of known concentration were mixed with measured volumes of standard solutions of bromine in carbon tetrachloride. Particularly with toluene, the xylenes and anisole it was desirable to avoid prolonged exposures of the aromatic substances even to dilute bromine solutions since slow reaction to yield substitution products occurred. The optical densities of the resulting solutions were measured immediately in 1-cm. absorption cells over a wave length range of 280–400 mμ using a Beckman spectrophotometer. The blank in each case consisted of a carbon tetrachloride solution of the aromatic substance of the same concentration as that of the solution the spectrum of which was being measured. In each case the cell housing was maintained at 25.0° by circulating around it water from a constant temperature bath. In the measurements of solutions of low concentrations of aromatic substance the bromine concentration had to be raised sufficiently high to obtain a measurable concentration of complex so that it was necessary to correct the measured optical densities for the absorption due to the free bromine itself. All extinction coefficients reported are calculated from the expression $d = \log_{10} I_0/I = \epsilon lc$ where d is the optical density of a solution l cm. in length and c is the concentration of light absorbing substance in moles/liter.

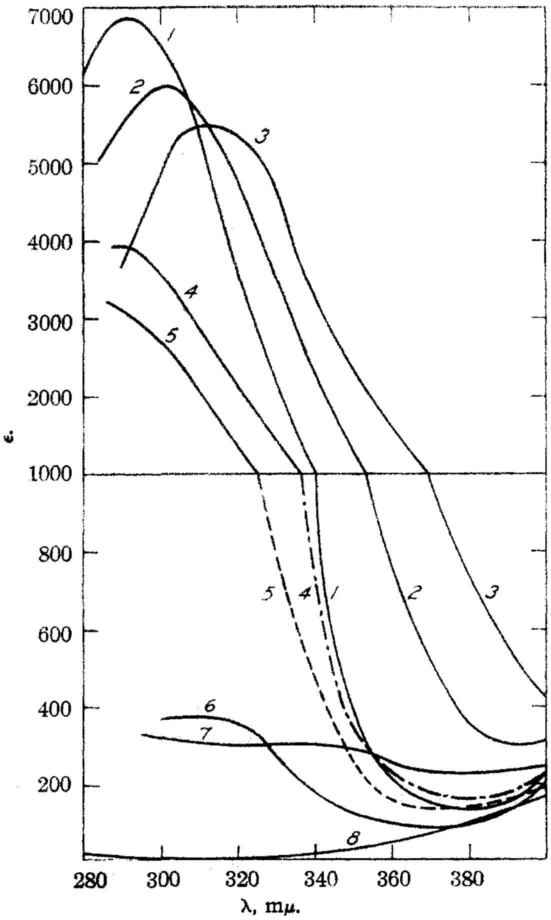

Fig. 1.—The absorption spectrum of bromine in various solvents[a]: (1) pure benzene, (2) toluene and carbon tetrachloride, $N_{C_6H_5CH_3} = 0.901$, (3) *o*-xylene and carbon tetrachloride, $N_{C_6H_4(CH_3)_2} = 0.890$, (4) bromobenzene and carbon tetrachloride, $N_{C_6H_5Br} = 0.902$, (5) chlorobenzene and carbon tetrachloride, $N_{C_6H_5Cl} = 0.9047$, (6) iodobenzene and carbon tetrachloride, $N_{C_6H_5I} = 0.01391$, (7) anisole and carbon tetrachloride, ($N_{C_6H_5OCH_3}$) = 0.366, (8) pure carbon tetrachloride. [a] The molecular extinction coefficients are based on total bromine present.

Results

The absorption spectra of bromine in benzene and in carbon tetrachloride solutions of some substituted benzenes are given in Fig. 1. In all solutions involving benzene or substituted benzenes and bromine high absorption peaks were obtained in the vicinity of 300 mμ which are similar to the absorption peaks obtained with iodine and benzene.[1b] For solutions containing iodobenzene and bromine the absorption peak occurs at 310 mμ as shown in curve 6 of Fig. 1. Since iodobenzene shows marked light absorption in this range, measurements could be made only on solutions of low iodobenzene concentration. Consequently the maximum extinction coefficient in curve 6 is much lower than that for certain of the other solvents. Measurements on anisole were also restricted to dilute solutions owing to the susceptibility of anisole to bromine substitution. The absorption curve in this case (curve 7) showed no discrete maximum in the neighborhood of 300 mμ, but instead indicated a pronounced absorption, over the wave length range measured. Table I summarizes the wave lengths and extinction coefficients for maximum absorption of the several systems investigated. The values $\lambda_{max.}$ 293 mμ and $\epsilon_{max.}$ 6800 for bromine in benzene as reported by Bayliss[3] are in good agreement with those reported here. For bromine in toluene and in chlorobenzene Bayliss lists values of $\lambda_{max.}$ 297.5

Table I

Extinction Coefficient[a] of Bromine in Benzene and Substituted Benzenes

Aromatic substance	N_A, mole fraction	$\lambda_{max.}$ mμ	$\epsilon_{max.}$
Benzene	1.000	292	6880
Toluene	0.901	301	5980
o-Xylene	.890	313	5490
m-Xylene	.759	312	5500
p-Xylene	.887	306	4940
Chlorobenzene	.905	286	3240
Bromobenzene	.902	288	3940
Iodobenzene	.00278	310	78

[a] Molecular extinction coefficients are based on total bromine present.

mμ, $\epsilon_{\max.}$ > benzene and $\lambda_{\max.}$ 296 mμ, $\epsilon_{\max.}$ < benzene, respectively. These values are at variance with the results of the present investigation.

A series of measurements of the spectra of carbon tetrachloride solutions of varying concentrations of bromine and of the several aromatic compounds were made. The results, as were those obtained in the iodine studies,[1b] may be explained on the assumption that the following equilibrium is established in these solutions, where A represents the aromatic compound.

$$\mathrm{Br_2 + A = Br_2{\cdot}A} \quad K = (\mathrm{Br_2{\cdot}A})/(\mathrm{Br_2})(\mathrm{A}) \qquad (1)$$

Since in these experiments the relative concentrations of reactants and product are in the order $(\mathrm{A}) \gg [(\mathrm{Br_2}) + (\mathrm{Br_2{\cdot}A})]$ the equilibrium constant may be closely approximated by the expression

$$K = (\mathrm{C})/[(\mathrm{Br_2})_i - (\mathrm{C})]N_\mathrm{A} \qquad (2)$$

in which (C) and $(\mathrm{Br_2})_i$ are, respectively, the molar concentrations of $\mathrm{Br_2{\cdot}A}$ and of added bromine, and N_A is the mole fraction of aromatic substance in the solvent. On the assumption that the absorption maxima of these solutions in the vicinity of 300 mμ are characteristic of $\mathrm{Br_2{\cdot}A}$, (C) may be evaluated from the expression $d = (\mathrm{C})\epsilon_\mathrm{c}l$, where d is the maximum optical density, ϵ_c is the molecular extinction coefficient of $\mathrm{Br_2{\cdot}A}$ and l is the length of the light path in cm. It then follows that

$$\frac{(\mathrm{Br_2})_i l}{d} = \frac{1}{K\epsilon_\mathrm{c}}\,\frac{1}{N_\mathrm{A}} + \frac{1}{\epsilon_\mathrm{c}} \qquad (3)$$

The data as shown in Fig. 2 give straight lines when $(\mathrm{Br_2})l/d$ is plotted *versus* $1/N_\mathrm{A}$, indicating that a 1:1 complex is formed through the range of mole fractions used. The values of ϵ_c were obtained from the reciprocals of the ordinate intercepts of such plots. The slopes of these lines, which according to eq. 3 are equal to $1/K\epsilon_\mathrm{c}$, were measured to evaluate K. The values of ϵ_c and K thus obtained are given in Table II.

TABLE II

EQUILIBRIUM CONSTANTS FOR THE BROMINE–AROMATIC COMPLEXES (25°) IN CARBON TETRACHLORIDE SOLUTIONS

	ϵ_c	K
Benzene	13,400	1.04
Toluene	10,500	1.44
o-Xylene	8,200	2.29
m-Xylene	10,100	2.16
p-Xylene	7,300	2.26
Chlorobenzene	7,300	0.90
Bromobenzene	7,600	1.18
Iodobenzene	17,000	1.59

The conformity of the experimental values to the linear plot demanded by eq. 3 is good considering the assumptions involved in evaluating the data: namely, that N_A is equal to the activity of A; that $(\mathrm{C})/[(\mathrm{Br_2})_i - (\mathrm{C})]$ is equal to the ratio of the activities of $\mathrm{Br_2{\cdot}A}$ and $\mathrm{Br_2}$; and that ϵ_c remains constant as the solvent is changed from carbon tetrachloride solutions to the pure aromatic substance. The assumptions regarding activities are probably close.[1b] As regards the third assumption, it should be noted that the molar extinction coefficient and the wave length of maximum absorption of a compound frequently varies with the solvent used. In fact in the present series of experiments the position of maximum absorption was shifted slightly to shorter wave lengths as N_A was decreased. In all calculations the maximum optical density of the solutions was used.[5]

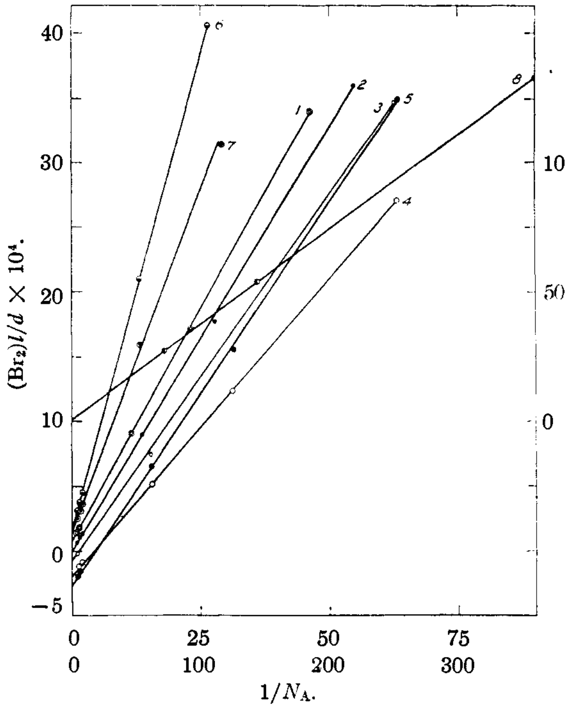

Fig. 2.—The evaluation of ϵ_c and K. Curves 1–8 present, respectively, data for benzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene, chlorobenzene, bromobenzene and iodobenzene. For curves 1–7 read ordinates on left-hand axis and abscissas using upper series of numerals. For curve 8 read ordinates on right-hand axis and abscissas using lower series of numerals. To $(\mathrm{Br_2})l/d$ values for toluene, *o*-xylene, *m*-xylene and *p*-xylene add, respectively, 1, 2, 3 and 4 to obtain the correct readings.

In certain cases where data are not available for solutions more concentrated than $N_\mathrm{A} = 0.1$ the accuracy of the recorded K values is further limited by the error inherent in the extrapolation process to obtain ϵ_c. Thus in the cases of iodobenzene and *m*-xylene the ϵ_c and K values must be considered as less accurate than those reported for other compounds. Although the spectrum of bromine in *m*-xylene–carbon tetrachloride solutions was measured over a wide range of *m*-xylene concentrations, it was found that the

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[5] Benesi and Hildebrand, private communication, report that similar shifts in the position of the absorption maximum were observed in the measurements on the iodine complexes. They also used the maximum optical density values in the calculation of K and ϵ values for the complexes.

data for solutions for which N_A was near unity did not yield points which fit accurately the straight line obtained in the graphical interpretation of equation 3. The reason for this discrepancy is not clear. It may in part be ascribed to the occurrence of a slow substitution reaction to form bromoxylene.

The Structure of the Complexes.—In discussing the structures of the iodine–aromatic complexes Benesi and Hildebrand[1a,b] have likened the role of the benzene ring in forming $A{\cdot}I_2$ to that of iodide ion in the formation of triiodide ion. The results of the present study indicate that bromine can interact with aromatic substances by accepting electrons from the benzene ring in much the same manner as does iodine. One might predict that bromine in this sense would be a weaker acid than iodine. This belief is strengthened by a comparison of the K values for the formation of $C_6H_6{\cdot}I_2$ and $C_6H_6{\cdot}Br_2$ which are 1.72[1b] and 1.04, respectively.

In a recent publication Mulliken[6] has discussed several possible structures for the $A{\cdot}I_2$ complexes and has chosen as most likely a type in which the center of the iodine molecule is on the six-fold symmetry axis of the ring and the axis of the iodine molecule is parallel to the plane of the ring. The possible structural resemblance of these complexes to those formed by silver ion with benzene and its derivatives should not be overlooked. These silver complexes have been described in terms of a structure in which silver ion is bonded to the ring from a position on the six-fold symmetry axis of the ring.[2,7] On this basis the benzene–halogen complex would be described as a resonance hybrid of the many different resonance forms based on the general formula

$$(C_6H_6^+):\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}::\underset{\cdot\cdot}{\overset{\cdot\cdot}{X}}:^-$$

in which the centers of the benzene ring and the two halogen atoms (X) lie on a straight line. Mulliken[6] regards this as an unlikely structure since he believes that the intense absorption bands of these complexes in the neighborhood of 300 mμ may in part be explained in terms of a loss of symmetry by the benzene ring on forming the complex. On the other hand, Bayliss[3] attributes this absorption of bromine and iodine in benzene around 300 mμ to a shift in the strong transition normally occurring in the free halogen molecules below 200 mμ. The similarity in the spectra of these halogen complexes to that[8] of the linear[9] triiodide ion might be regarded as evidence in favor of the structure preferred at this writing by the present authors.[10]

It has been observed (see Table II) that as hydrogens on the ring are replaced by methyl groups, the K values for bromine complex formation are increased. As was noted in connection with the studies of iodine[1b] this increase may be attributed to the electron-donor character of the methyl group relative to hydrogen. In the case of the silver ion complexes[2a] the methyl group effect seems to be counteracted by steric effects when more than one methyl group is substituted on the aromatic ring.

One might anticipate that the substitution of a halogen atom on the benzene ring should diminish the tendency for ring–halogen molecule complex formation. This was observed in the studies with silver ion,[2b] except in the case of iodobenzene which appears to coördinate silver ion at the iodine atom. The K value for the addition of bromine to chlorobenzene is slightly smaller than that for benzene. It is possible that the equilibrium constants reported for bromo- and iodobenzene may account in part for the formation of complexes in which the bromine molecule is coördinated with the halogen atom of the halobenzenes.[11]

The spectrum for the anisole complex is sufficiently different from those of the other complexes studied in this investigation as to suggest that with the aromatic ether a bromine-ring complex is not formed uniquely. It is possible that at least a portion of the complex formation may be described in terms of a coördination of the bromine molecule with the oxygen atom of the ether. However, iodine in diethyl ether does not show major absorption in the region of 300–400 mμ in which the anisole–bromine solution was investigated.[1b] Although iodine in ethanol has been reported to display absorption maxima in the neighborhood of 290 and 350 mμ[6,8] it should be noted that it has been suggested[12] that this absorption may result from impurities in such solutions.

Acknowledgment.—The authors wish to express their appreciation to Prof. Joel H. Hildebrand and to Dr. Hans A. Benesi for the many courtesies extended them during the course of this research and for their helpful comments in connection with the preparation of this manuscript.

Summary

It has been found that solutions of bromine in aromatic solvents, like those of iodine, display a major absorption peak in the neighborhood of 300 mμ. A detailed spectrophotometric study of carbon tetrachloride solutions of bromine and several simple aromatic compounds has been made, and the data have been used to calculate equilibrium constants for the formation of one to one complexes of the type $C_6H_6{\cdot}Br_2$.

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(6) Mulliken, THIS JOURNAL, **72**, 600 (1950).

(7) Winstein and Lucas, *ibid.*, **60**, 836 (1948).

(8) Custer and Natelson, *Anal. Chem.*, **21**, 1005 (1949), report that aqueous triodide solutions show an absorption maximum at 289 mμ, $\epsilon_{max.}$ = 35000 with a peak of less intensity at 350 mμ.

(9) Wells, "Structural Inorganic Chemistry," Oxford University Press, Amen House, E. C. 4, London, England, 1945, p. 270.

(10) Preliminary measurements indicate that in aqueous solution tribromide ion displays a major absorption maximum at 265 mμ.

(11) Such complexes should be closely related to iodobenzene dichloride.

(12) Ref. 5, p. 607.

It has been suggested that these complexes are closely related structurally to those of the complexes formed by silver ion and aromatic substances. At the present time a structure is favored for the product of interaction of bromine and the aromatic ring in which the centers of the ring and the two halogen atoms lie on a straight line.

DAVIS, CALIFORNIA RECEIVED MARCH 6, 1950

[CONTRIBUTION NO. 101 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Copolymerization. XV.[1] Copolymerization of Acetylene Derivatives with Olefins. Retardation by Radicals from Acetylenes

BY KENNETH W. DOAK

Much work has been done to determine the relative reactivities, in free radical copolymerization, of various olefinic monomers with different radicals. Mayo, Lewis and Walling[2] have established a general reactivity series based on a consideration of monomer reactivity ratios. A polarity series, in which monomers are placed according to their ability to donate or accept electrons, has been established by a consideration of the products of the reactivity ratios. No quantitative data have been determined for the radical copolymerization of acetylene derivatives which would enable this class of monomers to be placed in the reactivity and polarity series for olefins. It was the objective of this work to determine the reactivity ratios for the copolymerization of the representative acetylenes, hexyne-1, phenylacetylene, and diphenylacetylene, with the olefins acrylonitrile and methyl acrylate. The copolymerization of styrene and phenylacetylene was also studied. In order to compare the reactivity of the double and triple bond, hexene-1 was copolymerized with acrylonitrile and methyl acrylate.

Since the acetylene derivatives caused marked retardation in most copolymerizations, some experiments were carried out in order to gain some information upon the mechanism of chain termination. The rate of polymerization of three systems was determined as a function of the catalyst concentration, in order to test for the formation of radicals which do not propagate the kinetic chain. Thus, it was shown by Bartlett and Altschul[3] that the rate of polymerization of allyl acetate is proportional to the catalyst concentration, instead of being a square root function, as occurs for most polymerizations. This presumably is due to the formation of allyl radicals which do not propagate the chain. The molecular weight of the polymers is independent of the catalyst concentration.

Experimental

Monomers.—The acetylene derivatives were obtained commercially. The diphenylacetylene (m. p. 59–61°) was used without further purification. Hexyne-1 and phenylacetylene were carefully fractionated before being used. The physical constants were: hexyne-1, b. p. 71.8–72.0 (760 mm.), n^{20}D 1.3993; phenylacetylene, b. p. 75.2 (90 mm.), n^{20}D 1.5485. Styrene, acrylonitrile and methyl acrylate were commercial samples, redistilled before use. Physical constants closely checked literature values.

Copolymerization for Reactivity Ratios.—Copolymerizations were carried out in evacuated tubes, with benzoyl peroxide as catalyst, as previously discussed by Mayo and Lewis.[4] The amount of peroxide used was 0.1 mole %,

TABLE I

COPOLYMERIZATION OF ACETYLENES

Expt.	$[M_1]_0$[a]	$[M_1]$[a]	$[M_2]_0$[a]	$[M_2]$[a]	Time, hr.	Polymer analysis
Methyl Acrylate (M_1)–Phenylacetylene (M_2)						
1	85.22	71.53	14.20	11.25	70	63.66, 63.49% C
2	85.23	71.73	14.32	11.38	70	63.61, 63.71
3[b]	40.42	37.68	57.27	54.72	145	75.97, 75.89
4[b]	40.62	37.95	55.35	52.72	145	76.41, 76.44
Acrylonitrile (M_1)–Phenylacetylene (M_2)						
5	83.46	76.42	14.09	11.40	97	15.40, 15.19% N
6	84.63	77.54	14.09	11.23	97	14.96, 14.73
7[b]	39.13	36.87	54.72	51.96	145	7.90
8[b]	39.58	37.32	54.99	52.22	145	7.88
Acrylonitrile (M_1)–Diphenylacetylene (M_2)						
9	80.44	72.78	20.17	20.03	15	25.0, 24.7% N
10	50.62	46.48	50.04	49.76	160	21.56
11	51.02	47.96	49.85	49.63	160	21.31
Methyl Acrylate (M_1)–Diphenylacetylene (M_2)						
12	79.67	65.58	19.980	19.913	15	56.11, 56.26% C
13	50.95	42.48	49.92	49.74	48	57.57, 57.33
14	50.91	42.07	50.01	49.84	48	57.26, 57.25
Acrylonitrile (M_1)–Hexyne-1 (M_2)						
15	121.13	114.68	73.74	73.05	54	22.65% N
16	120.14	114.27	73.91	73.26	54	22.51
17	49.94	48.42	45.82	45.61	32	21.80
Acrylonitrile (M_1)–Hexene-1 (M_2)						
18	59.29	44.11	38.02	37.19	3.5	24.30% N
19	59.75	47.12	37.97	37.20	3.5	24.08
Methyl Acrylate (M_1)–Hexyne-1 (M_2)						
20	50.54	33.39	46.72	45.35	75	58.10% C
21	35.59	16.51	31.64	29.49	115	58.90
22	35.23	14.83	34.72	32.31	115	59.03
Methyl Acrylate (M_1)–Hexene-1 (M_2)						
23	50.02	18.56	43.41	38.72	4.5	59.59% C
24	49.66	17.71	43.27	39.22	4.5	59.08
25	49.49	18.39	43.32	39.36	4.5	59.09
Phenylacetylene (Homopolymerization)						
26[b]			45.31	44.28	160	

[a] Millimoles. [b] 0.2 mole % benzoyl peroxide.

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[1] This paper was presented at the Atlantic City Meeting of the American Chemical Society, September, 1949. For paper XIV in this series, see Walling, Cummings, Briggs and Mayo, THIS JOURNAL, 72, 48 (1950).

[2] Mayo, Lewis and Walling, *ibid.*, 70, 1529 (1948).

[3] Bartlett and Altschul, *ibid.*, 67, 816 (1945).

[4] Mayo and Lewis, *ibid.*, 66, 1594 (1944).