Kinetics and mechanism of electrophilic bromination of acetylenes

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The rates of addition of molecular bromine in acetic acid to a number of acetylenes have been found to follow the general equation

$$-\mathrm{d(Br_2)}/\mathrm{d}t = [\text{acetylene}](k_2[\mathrm{Br_2}] + k_3[\mathrm{Br_2}]^2 + k_{\mathrm{Br}^-}[\mathrm{Br_2}][\mathrm{Br}^-])$$

In the absence of bromide ion and at low bromine concentrations ($< 2 \times 10^{-4}$ *M*), only the k_2 process is observable. These k_2 values for a series of ring-substituted phenylacetylenes are correlated well with σ^+ values and give a ρ value of -5.17 which is interpreted in terms of a transition state leading to a vinyl cation intermediate. As expected from this intermediate, both *cis* and *trans* dibromide products are formed and the bromoacetates are only of the Markownikoff type (1-acetoxy-1-phenylethylene derivatives). An ion pair scheme has been presented to account for the variation in product composition with substrate structure.

In contrast to these results for phenylacetylenes, a cyclic bromonium ion intermediate is postulated for alkyl acetylenes on the basis of only *trans* dibromide formation for 3-hexyne and 1-hexyne.

The k_{Br^-} values have also been obtained for the ring-substituted phenylacetylenes as well as 3-hexyne. For all the substrates studied, this k_{Br^-} process represents a bromide ion catalyzed attack of molecular bromine in an Ad_E3 mechanism. Thus only *trans* dibromide products are formed from this rate process. The non-linear σ^+ plot for these values has been interpreted in terms of change in transition state structure with substituent.

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Introduction

As recent reviews by de la Mare and Bolton (1) and Fahey (2) indicate, the electrophilic addition of bromine to acetylenes has received much less attention than the corresponding reaction with olefins. Furthermore, the results available are so incomplete and, in some cases contradictory, that little confidence can be placed in any of the postulated mechanisms. Thus, Robertson *et al.* (3) have suggested that the rate equation for the addition of bromine to several substituted acetylenes in acetic acid is similar to that observed for olefins (first order in substrate and both first and second order in bromine) and that the overall rates are in the expected order for an electrophilic process. In contrast, Sinn *et al.* (4) have measured rates for the bromination (by a process second order in bromine) of diphenylacetylenes in bromobenzene, that are best interpreted in terms of a nucleophilic reaction. Only slightly more information is available on the stereochemistry of the products of this addition reaction. Bergel'son and Nazarov (5) have reported that the addition of bromine to 3-hydroxypropyne, 3-hydroxy-3-methylbutyne, propyne, and acetylene gives exclusively *trans* addition under conditions that favor an ionic reaction. On the other hand, results for the bromination of diphenylacetylene by molecular bromine (6) and *N*-bromosuccinimide (7) in acetic acid indicate non-stereospecific addition.

As the limited results available demonstrate, a systematic examination of product stereochemistry under conditions of known kinetic control is necessary before any definite mechanism for the addition of bromine to acetylenes can be postulated. Therefore, in the present work, rates and product compositions are presented for the bromination of a number of phenyl and alkyl acetylenes in acetic acid with and without added bromide ion salts. The choice of this solvent system was made on the basis that the results would then be directly comparable with similar results for olefin substrates where the main details of the reaction are well understood (1, 2, 8, 9).

Results and Discussion

(1) Rates in the Absence of Bromide Ion Salts

Robertson *et al.* (3) have reported that the addition of bromine to acetylenes in acetic acid follows the rate eq. 1. In agreement with this

$$[1] \quad -\mathrm{d}[\mathrm{Br_2}]/\mathrm{d}t = [\text{acetylene}](k_2[\mathrm{Br_2}] + k_3[\mathrm{Br_2}]^2)$$

equation, curved rate plots were obtained when either simple first or second order dependence on bromine concentration was assumed for the

TABLE 1

Second order rate constants, k_2, for the bromination of acetylenes in acetic acid

Substrate	n*	Temperature (°C)	$k_2 \times 10^3$† (M^{-1} s^{-1})
3-Hexyne	3	17.9	4.18±0.20
	3	24.8	5.84±0.10
	3	39.8	12.4±0.5
1-Hexyne	3	24.8	0.174±0.011
t-Butylacetylene	3	24.8	0.285±0.013
4-Me PA‡	3	24.8	247±8
3,4-Benzo PA‡	3	24.8	153±1
4-F PA‡	3	24.8	11.3±0.3
3-Me PA‡	4	24.8	14.3±0.8
PA‡	3	24.8	4.33±0.06
	3	39.8	11.6±0.3
4-Cl PA‡	3	24.8	1.54±0.16
4-Br PA‡	3	24.8	1.13±0.03
	3	39.8	3.27±0.04
Methylphenyl-acetylene	2	17.3	1.37±0.02
	5	24.8	2.46±0.06
	3	29.9	3.63±0.07
	4	39.8	6.8±0.3

*n is the number of determinations.
†The errors quoted are the average deviations.
‡PA represents phenylacetylene.

bromination of methylphenylacetylene at a bromine concentration of approximately 1×10^{-2} M. However, by working at low bromine concentration (less than 3×10^{-4} M) only the first term in eq. 1 makes a significant contribution to the observed rate. Using pseudo-order conditions ([acetylene] $\gg$ [Br_2]), excellent first order plots of log $(A - A_\infty)$ values *vs.* time were obtained. The rate constants, k_2, for the acetylenes studied are listed in Table 1.

Using the values of k_2 for methylphenylacetylene, the rate constants, k_3, can be evaluated from kinetic runs at higher bromine concentration where both k_2 and k_3 contribute to the overall rate equation. Integration of eq. 1 and rearranging gives eq. 2, where $\log Y = k_2't/2.303$, $k_2' = k_2$ [acetylene], $k_3' = k_3$ [acetylene] and

$$[2] \qquad k_3' = \frac{k_2'\left(\frac{[Br_2]}{[Br_2]_0} Y - 1\right)}{[Br_2](1 - Y)}$$

$[Br_2]_0$ is the bromine concentration at $t = 0$. The k_3' values can be calculated for each value of [Br_2] and t. These values are then averaged to obtain k_3' and, hence, k_3 for any given run. The results for methylphenylacetylene are shown in Table 2. As the average deviations indicate, these are less reliable rate constants than those obtained by a graphical method. However, the accuracy is sufficient to justify accepting eq. 1 as the general rate expression for the bromination of acetylenes in acetic acid. Values of k_3 were not determined for the other acetylenes.

TABLE 2

Third order rate constants, k_3, for the bromination of methylphenylacetylene in acetic acid

Temperature (°C)	n*	k_3† (M^{-2} s^{-1})
17.3	3	2.3±0.2
24.8	7	2.6±0.2
29.2	3	3.2±0.2
39.8	3	3.6±0.1

*n is the number of determinations.
†The errors quoted are the average deviations.

The effect of substituents on the k_2 values of the bromination reaction can be evaluated from the Hammett plot in Fig. 1. The ρ value (*vs.* σ^+) is −5.17 (correlation coefficient, 0.997). The σ^+ values are those given by Brown and Okamoto (10). Their listing does not, however, include a value for the 3,4-benzo group (β-naphthylacetylene). In a recent study of substituent effects in polycyclic aromatic compounds (11), values of σ^+ ranging from −0.135 to −0.280 are quoted for this group, implying that the value may reflect the operation of variables that differ from reaction to reaction. Using the rate constant of 153×10^{-3} M^{-1} s^{-1} obtained for β-naphthylacetylene, a σ^+ value of −0.28 can be obtained from the log k_2 *vs.* σ^+ correlation for the other substituents. In effect, this determines a value of σ^+ for the 3,4-benzo substituent which will be used in a correlation described below. The value of −0.28 is similar to those for aromatic nitration (−0.28) and bromination (−0.27). Since the addition reaction is a side chain reaction, the lower values of −0.20 or −0.135 obtained for the solvolysis of side chain derivatives might seem more reasonable. However, the point would then deviate markedly from the correlation in Fig. 1.

Although Sinn *et al.* have concluded that the bromination of diphenylacetylene derivatives is a nucleophilic reaction (4), the large negative ρ value and the good σ^+ correlation clearly demonstrate that the bromination of phenylacetylenes in acetic acid is an electrophilic reaction. The two cases are, however, not strictly comparable since in bromobenzene the reaction

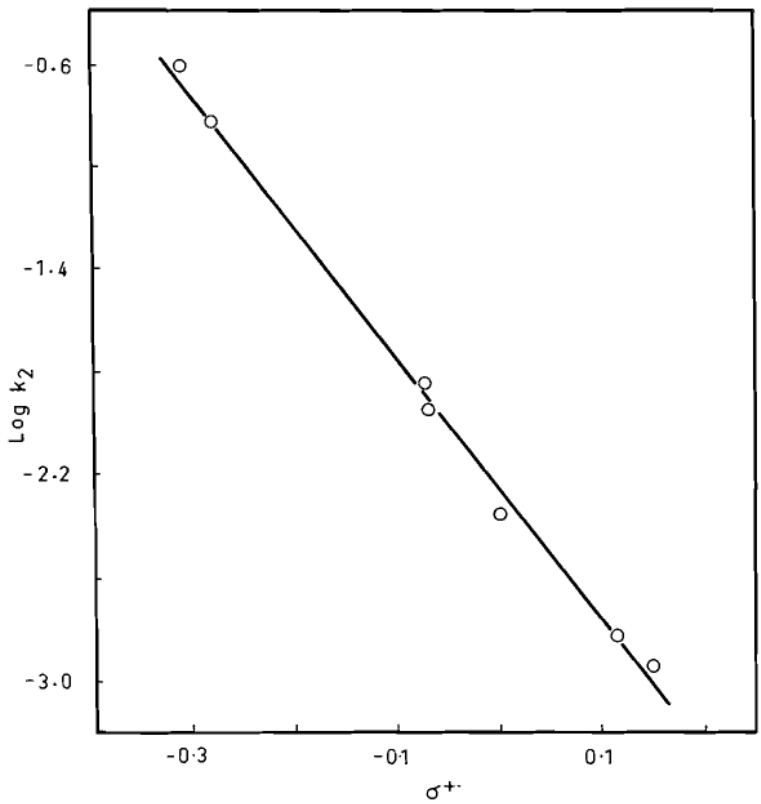


FIG. 1. Plot of log k_2 *vs.* σ^+ for the bromination of phenylacetylenes in acetic acid.

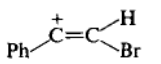
is second order in bromine whereas the rate constants obtained in this work are for the simpler first order in bromine process. In the corresponding olefin systems, the ρ^+ values are also quite different. Thus, for the bromination of styrenes in acetic acid ρ^+ value for the k_2 rate constants is approximately -4.5 (9, 12) whereas for the stilbenes the values for the k_3 process (13) are -0.67 in carbon tetrachloride and -1.99 in bromobenzene.

The ρ^+ value of -5.2 for the bromination of acetylenes in acetic acid can be compared with values for similar systems. The hydration of acetylenes has a ρ^+ value of approximately -4.5 (14, 15). As well, a ρ^+ value of -3.6 has been obtained by Miller and Kaufman (16) for the solvolysis of triaryliodoethylenes. These reactions have been interpreted in terms of transition states leading to vinyl cation intermediates. The similarity of these ρ^+ values to that for the bromination of acetylenes is therefore strongly indicative of rate determining formation of a vinyl cation **2** through a transition state resembling **1**, as shown in eq. 3. The bromination of olefins in acetic acid is also believed to proceed by a mechanism involving rate determining formation of a carbonium ion (1). The two systems, olefins and acetylenes, might therefore be expected to exhibit a similar substituent dependence. The ρ^+ value of approximately -4.5 (9, 12) for styrenes is therefore in agreement with the suggested rate determining step in eq. 3.

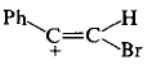
[3] $$\mathrm{Ph{-}C{\equiv}C{-}R} \xrightarrow[\mathrm{HOAc}]{\mathrm{Br_2}} \left[\mathrm{Ph{-}C^{+\delta}{\equiv}C{-}R \quad Br \quad Br^{-\delta}}\right] \xrightarrow{-\mathrm{Br}^-} \mathrm{Ph{-}\overset{+}{C}{=}C(R)(Br)}$$

1 **2**

As the great number of recent publications indicate (17, 18), there has been a considerable upsurge in interest in the structure, reactivity and stability of vinyl cations. The results available imply that linear structures of the type **2** with sp hybridization at the cationic center are favored

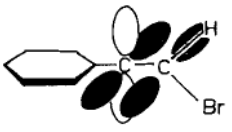


3a

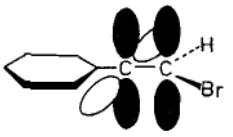


3b

over either of the bent forms ***3a*** or ***3b*** with sp^2 hybridization. This has been confirmed by theoretical molecular orbital calculations which show the bent structure to be less stable than the linear one by approximately 50–60 kcal/mole (19, 20). As well, the high negative ρ^+ values for reactions where vinyl cations are generated adjacent to phenyl rings (*vide supra*) suggests that the phenyl ring is directly conjugated with the positive charge on the α-carbon atom as in ***4a*** rather than with the remaining π-bond of the vinyl system as in ***4b***. In the discussion that



4a



4b

follows, therefore, the structure of the cationic intermediate is assumed to be ***4a*** although, for simplicity, it will be drawn as shown in **2**.

The activation parameters for several of the acetylenes are shown in Table 3. These values are obtained from a least-squares fit of the data to a plot of log (k_2/T) *vs.* $1/T$ according to eq. 4 (21). For the phenylacetylenes, the entropy values

$$[4]\quad \log\frac{k_2}{T} = \left[\log\frac{k}{h} + \frac{1}{2.303}\frac{\Delta S^{\ddagger}}{R}\right] - \frac{\Delta H^{\ddagger}}{2.303R}\left(\frac{1}{T}\right)$$

of approximately −30 e.u. are consistent with the rate determining step proposed earlier (eq. 3). Thus, Wiberg (22) has estimated that, for a bimolecular reaction, an entropy change of −20 e.u. is expected because of loss of translational and rotational degrees of freedom. The excess over this estimate is presumably a result of restriction of solvent motion because of solvation changes as the reaction proceeds from neutral ground state molecules to a dipolar transition state. Similar values of −28 e.u. have been reported for the corresponding styrene substrates (23) but revised values of approximately −40 e.u. have been obtained more recently (12). A similar decrease to that observed for the entropy and enthalpy values of the k_3 process for methylphenylacetylene ($\Delta H^{\ddagger} = 3.0$ kcal/mole and $\Delta S^{\ddagger} = -51$ e.u. compared with $\Delta H^{\ddagger} = 12.3$ kcal/mole and $\Delta S^{\ddagger} = -29$ e.u. for the k_2 process) has also been previously observed for olefin substrates (24). Both these changes can be explained in terms of the usual mechanism postulated for this third order process: a bromine-assisted heterolysis of the bromine–bromine bond as in eq. 5 (1). The more negative entropy value is a reflection of the unfavorable nature of such a termolecular transition state. As well, the second molecule of bromine is acting as a catalyst in the breaking of the bromine–bromine bond and, hence, dispersing the negative charge of the bromide ion released. This should give a lower enthalpy of activation as observed. The

TABLE 3

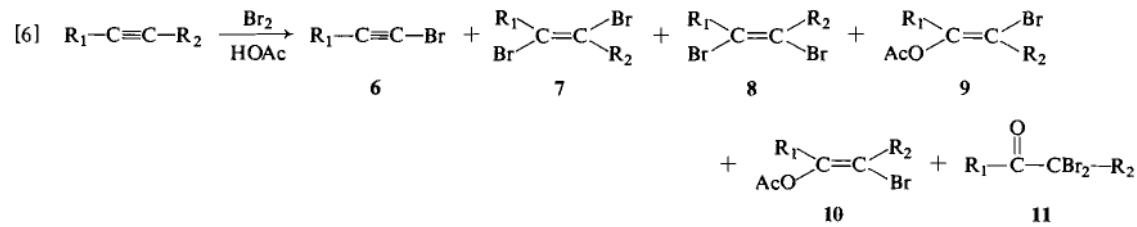
Activation parameters for acetylenes

Substrate	$\Delta H\ddagger$* (kcal/mole)	$\Delta S\ddagger$* (e.u.)
Methylphenylacetylene, k_2	12.3±0.3	−(29±1)
PA,† k_2	11.7	−31
4-Br PA,† k_2	12.5	−30
3-Hexyne, k_2	8.4±0.2	−(41±1)
Methylphenylacetylene, k_3	3.0±0.2	−(51±1)

*Values quoted with no error are from rate constants at only two temperatures. The errors quoted are evaluated from the standard deviations of the slope and intercept of the least-squares line.
†PA represents phenylacetylene.

$$[5]\quad \mathrm{Ph{-}C{\equiv}C{-}R} \xrightarrow[\mathrm{HOAc}]{\mathrm{Br_2}} \left[\mathrm{Ph{-}C{\equiv}C(R)(Br)}\ (+\delta)\ \cdots\ (-\delta)\ \mathrm{Br}\ \cdots\ (-\delta)\ \mathrm{Br_2}\right] \xrightarrow{-\mathrm{Br_3^-}} \mathrm{Ph{-}C^{+}{=}C(R)(Br)}$$

5

[6] 

lower value of -40 e.u. for 3-hexyne compared to those of -30 e.u. for the phenylacetylenes will be discussed later.

The relative reactivity of olefins and acetylenes in electrophilic bromine additions can be estimated from the rate constants in Table 1 and those available in the literature for olefins.[1] Thus, the ratio for styrene:phenylacetylene is 2×10^3 and for 3-hexene:3-hexyne is 1.4×10^5. Perrin (25) has suggested that, for substrates that react via open ions rather than cyclic "bromonium" ion transition states, the reactivity of olefins and acetylenes might be similar. The reactivity factor of 2×10^3 for styrene over phenylacetylene does not agree with this hypothesis. However, the two substrates, 3-hexene and 3-hexyne, are believed to react via cyclic ions (*vide infra*) and in this case the reactivity ratio is 1.4×10^5. Perhaps this extra factor of approximately 10^2 may be accounted for in terms of Perrin's argument.

(2) Products of the Addition of Bromine to Acetylenes

The products for the addition of bromine to acetylenes in acetic acid are outlined, for the general case, in eq. 6. The bromoacetylene **6** is only formed if the acetylene is a terminal one, i.e. R_2 is H. The bromoacetates **9** and **10** are regiospecific in the Markownikoff sense so that for phenylacetylene derivatives only 1-acetoxy-1-phenyl products were observed. The dibromoketone (**11**) is formed by the reaction of bromine with the bromoacetates **9** and **10** and consequently can be regarded as a secondary reaction product. Fahey and Lee (26) have observed a similar reaction of the enol acetates formed from the addition of HCl to methylphenylacetylene in acetic acid. The bromoacetates themselves were not well characterized because they could not be separated by g.l.c. methods. Because of this problem, as well as the secondary reaction with bromine to form the ketone **11**, all three of the products, **9**, **10**, and **11**, are classified under one heading as solvent-incorporated (SI) products.

The results for methylphenylacetylene are shown in Table 4 and for the other acetylenes in Table 5. All of the products are formed under conditions of kinetic control since no isomerization or reaction of the dibromides (to form either bromoacetates or tetrabromides) was observed under the reaction conditions.

The results for methylphenylacetylene in Table 4 will be discussed first since the experimental results for this substrate are more complete. At the bromine concentrations shown, both the terms first order in bromine and that second order in bromine from eq. 1 are contributing to product formation. From the integrated form of eq. 2, one can derive eq. 7, where P_2 is

$$[7] \quad \frac{P_2}{P_2 + P_3} = \frac{k_2}{k_3[\mathrm{Br_2}]_0} \ln \frac{k_2 + k_3[\mathrm{Br_2}]_0}{k_2}$$

amount of product formed from the k_2 process and P_3 the amount from the k_3 process. In other words, the fraction of the product from the k_2 process, $P_2/(P_2 + P_3)$, is determined only by the rate constants k_2 and k_3 and $[\mathrm{Br_2}]_0$. Over the range of $[\mathrm{Br_2}]_0$ shown in Table 4 this ratio varies from 0.24 to 0.40 (using $k_2 = 2.46 \times 10^{-3}\ M^{-1}\ \mathrm{s}^{-1}$ in Table 1 and $k_3 = 2.7\ M^{-2}\ \mathrm{s}^{-1}$ in Table 2). Since no change in the product ratio (within experimental error) is observed, both k_2 and k_3 must lead to the same product distribution. This is also confirmed by the observation that the product distribution remains effectively constant for samples taken at 50, 75, and 100% conversion with initial bromine concentration of $6.66 \times 10^{-3}\ M$ even though the fraction of products from each rate process will be different for each sample. These results imply that the product forming intermediate is the same for both k_2

[1]The k_2 value for styrene is from ref. 9 at zero bromide ion concentration. The k_2 value for 3-hexene is estimated from data obtained by R. S. McDonald in this laboratory.

TABLE 4

Product distribution for the bromination of methylphenylacetylene

$[MPA]_0$ ($M \times 10^2$)	$[Br_2]_0$ ($M \times 10^3$)	Salt 0.10 M	T*	C*	SI*
			(%) by g.l.c.†		
11.1	10.3	—	59	14	27
8.55	8.4	—	56	13	31
10.6	6.3	—	56	14	30
8.96	4.56	—	58	12	30
3.34	3.78	—	59	14	27
1.40	6.66‡	—	62	12	26
	§	—	61	13	26
	‖	—	59	13	28
7.61	5.14	LiBr	97	<0.5	3
3.37	3.78	LiBr	98	<0.5	2
10.0	5.82	$LiClO_4$	49	10	41
7.91	3.96	$LiClO_4$	53	10	37

*T is *trans* dibromide, C is *cis* dibromide and SI is solvent-incorporated products **9**, **10**, and **11**.
†All results are from areas of g.l.c. peaks. Estimated accuracy is ±1 to ±2%.
‡, §, ‖All from the same reaction at 50, 75, and 100% reaction respectively.

TABLE 5

Product distribution for the bromination of acetylenes

Substrate and conditions*		BrA†	T†	C†	SI†
			(%) by g.l.c.‡		
4-Me phenylacetylene, HOAc		—	56	44	—
0.10 LiBr	—	—	81	19	—
0.06 LiBr,	0.04 $LiClO_4$	—	73	27	—
0.02 LiBr,	0.08 $LiClO_4$	—	59	41	—
—	0.10 $LiClO_4$	—	42	58	—
Phenylacetylene, HOAc		25	42	19	14
0.10 LiBr	—	—	>99	—	—
—	0.10 $LiClO_4$	—	52	21	27
3-Hexyne, HOAc		—	72§	—	—
0.10 LiBr	—	—	>99	—	—
1-Hexyne, HOAc		—	>99	—	—

*Salt values are in molarity.
†BrA is bromoacetylene, T is *trans* dibromide, C is *cis* dibromide and SI is solvent-incorporated products **9**, **10**, and **11**.
‡All results are from areas of g.l.c. peaks. Estimated accuracy is ±1 to ±2%.
§28% of the product was an unknown compound which was not BrA, C, or SI.

and k_3 as has been postulated for olefins (1). For the other substrates in Table 5 the ratio of $P_2/(P_2 + P_3)$ cannot be calculated because k_3 is unknown. However, by analogy with methylphenylacetylene, the products are assumed to be the same for both rate processes.

The product results in the absence of lithium bromide will be discussed first. For the phenylacetylene derivatives, the non-stereospecific formation of dibromides as well as the formation of large amounts of solvent-incorporated products clearly point to a reactive intermediate, the vinyl cation, which reacts in a fast step with either bromide ion or the solvent acetic acid. This is in agreement with the kinetic results. The ratio of the various products will be dependent on the structure and reactivity of this intermediate cation. In a non-dissociating solvent, like acetic acid, ion pairing phenomena are extremely important as the early work of Winstein *et al.* on solvolysis demonstrated (27). Recently, several authors (26, 28, 29) have had some success in explaining product composition for addition reactions in terms of the various ion pairs possible. Figure 2 shows the completely general approach for the addition of bromine to phenylacetylenes.

The advantage of this type of scheme is, of

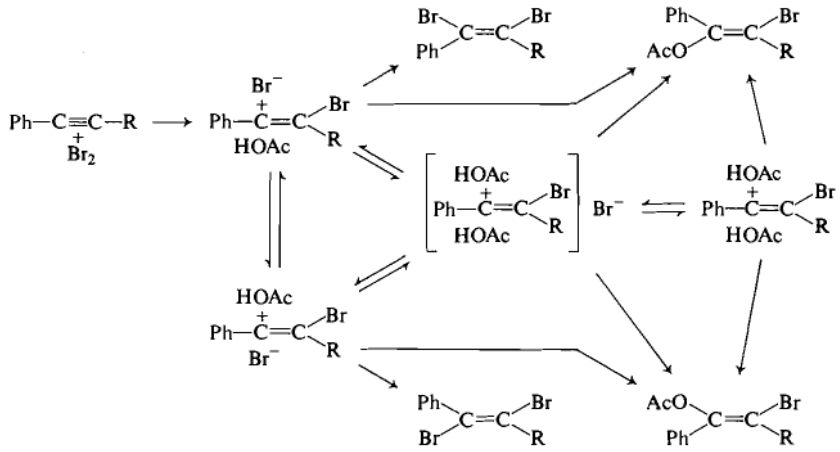
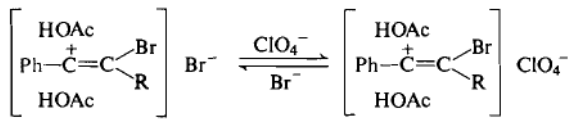


FIG. 2. General ion pair scheme for the addition of bromine to phenylacetylenes in acetic acid.

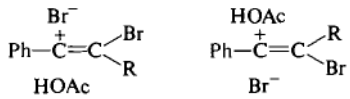
[8] 

12 **13**

course, that any combination of products can usually be rationalized although there may only be rather tenuous arguments for invoking the particular ion pairs necessary. Perhaps the best approach would be to realize that, on the basis of the limited results available, any conclusions must be considered as speculative. The results for the phenylacetylenes will illustrate the difficulties involved.

The first point to note is that 4-methylphenylacetylene behaves quite differently from phenylacetylene and methylphenylacetylene. Thus, the 4-methyl compound gives no solvent-incorporated or elimination products. Furthermore, added $LiClO_4$ has little effect on the *trans*:*cis* dibromide ratio for the unsubstituted compounds (52:21 changes to 42:19 for phenylacetylene) whereas the ratio is significantly altered for the 4-methyl case (56:44 becomes 42:58 on addition of $LiClO_4$).

$LiClO_4$ is believed (27) to interact with solvent-separated ion pairs as shown in eq. 8. The perchlorate ion pair **13** is more likely to yield solvent-incorporated products than the bromide ion pair **12**. Consequently, the addition of $LiClO_4$ might be expected to increase the amount of bromoacetate product if solvent-separated ion pairs are important in these reactions. This effect is observed for the unsubstituted phenylacetylenes. However, this increased reaction with the solvent does not affect the *trans*:*cis* dibromide ratio for these substrates. There seem to be two possible interpretations of this result. First, there may be no return of solvent-separated ion pairs to intimate ion pairs. Thus, once dissociation occurs, the only product is a bromoacetate and the formation of dibromides is determined only by the relative reactivity of **14** and **15**. The effect of $LiClO_4$ must then be



14 **15**

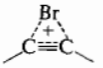
visualized as enhancing the dissociation of intimate ion pairs to solvent-separated ion pairs by increasing the polarity of medium. The capture of solvent-separated ion pairs by $LiClO_4$ would only be a secondary effect and not the major contributor to increased bromoacetate production. The second possibility is that there is return from solvent-separated ion pairs to intimate ion pairs. In this case, the same behavior must be exhibited by ions that are returning as those that did not dissociate. In other words **14** and **15**

equilibrate faster than they react to form dibromides. It is interesting to note at this point that Poutsma and Kartch (28) have concluded that an initially formed "*cis*" ion pair like **14** can rearrange to a "*trans*" ion pair like **15** without the intervention of solvent-separated ion pairs. This type of rearrangement is, of course, necessary in this second hypothesis.

The first of these interpretations seems preferable on the basis of the results for 4-methylphenylacetylene. The 4-methylphenylvinyl cation is more stable than the corresponding unsubstituted ions. Thus, it only reacts with bromide ion and not with the less nucleophilic acetic acid. However, since it is a more stable ion, solvent-separated ion pairs must also be important in its reaction scheme. Therefore, some of the dibromides must be formed from intimate ion pairs that are the result of return from solvent-separated ion pairs. Since the ratio of *trans*:*cis* dibromide changes on the addition of $LiClO_4$, ions returning from **13** through **12** to the intimate ion pairs give a different ratio of dibromides than those initially formed. This observation would seem to preclude complete equilibration of the intimate ion pairs.

In summary then, for phenylacetylene and methylphenylacetylene, the dibromides are probably formed from collapse of the initially formed intimate ion pairs. A similar conclusion has been reached for the bromination of β-methylstyrenes where added $LiClO_4$ also increases the bromoacetate products but does not affect the *trans*:*cis* ratio (8). The opposite conclusion has been reached by Fahey and Lee (26) for the addition of HCl to methylphenylacetylene since their scheme indicates that return of solvent-separated ion pairs to intimate ion pairs is important. This situation is more comparable to the scheme suggested here for 4-methylphenylacetylene.

On the basis of the results available, there seems to be no simple explanation for the observed dibromide ratios for these phenylacetylenes. More information is necessary on the stereochemistry of bromoacetate formation which presumably affects the amount of dibromide formed from the intimate ion pairs **14** and **15**. As well, the formation of bromophenylacetylene is more probable from **15** since the basic bromide ion is better situated for hydrogen abstraction than in **14**. This side reaction may well interfere with the "normal" reactivity of the two ion pairs.



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The results in Table 5 for the alkyl acetylenes are quite different than those for the phenylacetylenes. For both 3-hexyne and 1-hexyne only *trans* dibromides are observed. This is in agreement with the results of Bergel'son and Nazarov (5) for some other alkyl acetylenes and is good evidence that these alkynes react via an Ad_E2 (2) cyclic "bromonium" ion mechanism with an intermediate like **16**. This type of mechanism has been firmly established for the addition of sulfenyl halides since no *cis* addition has ever been observed (30, 31). There are several factors in favor of this interpretation. First of all, from solvolysis studies, alkyl vinyl cations are less stable than phenyl vinyl cations (17, 18) and, therefore, participation by bromine should be more favorable in the alkyl case. Second, the more negative entropy of activation value of −40 e.u. (Table 3) for 3-hexyne compared to that of −30 e.u. for the phenylacetylenes is consistent with a loss of degrees of freedom because of a more ordered transition state. Finally, the complete absence of solvent-incorporated products is also observed for the bromination of *cis*- and *trans*-2-butene in acetic acid (8). These olefins also react via cyclic bromonium ion intermediates.

The final point to be mentioned in this discussion of the products of addition is the change on the addition of LiBr. There is a marked decrease in bromoacetate product and a large increase in *trans* dibromide formation. An examination of the kinetics under these conditions is necessary before a mechanistic interpretation can be made.

(3) Rates in the Presence of Bromide Ion Salts

As the review by de la Mare and Bolton indicates (1), the kinetics of bromine addition to olefins in the presence of added bromide ion have been interpreted in a number of ways. More recent work (9, 32), although providing more results, has done little to clarify the problem. Before discussing this more fully, the main details of the kinetics will be briefly outlined.

If both tribromide ion and molecular bromine are electrophiles, the rate of consumption of bromine is given by eq. 9 where $[Br_2]_T$ is the total

TABLE 6

Second order rate constants,* $k_0 \times 10^3$, for the bromination of phenylacetylenes with added LiBr

LiBr (M)	$LiClO_4$ (M)	4-Me PA†	3,4-Benzo PA†	4-F PA†	PA†	4-Br PA†	3-Cl PA†	MPA‡
0.10	—	211±4	87.6±0.2	19.5±0.6	14.2±0.1	6.75±0.12	2.46±0.05	29.3±1.0
0.08	0.02	210±2	89.6±0.6	19.7±1.1	13.6±0.2	6.49±0	—	27.8±0.8
0.06	0.04	229±2	92.3±0.3	19.1±0.6	12.9±0.2	6.48±0.06	—	25.4±0.6
0.04	0.06	263±3	98.0±0.7	18.1±0.3	12.8±0.3	6.27±0.15	—	24.6±0.3
0.02	0.08	313±1	116±6	16.0±0.1	11.7±0.2	5.11±0	—	19.2±0.4

*k_0 values in units of $M^{-1}s^{-1}$.
†PA stands for phenylacetylene.
‡MPA stands for methylphenylacetylene.

TABLE 7

Second order rate constants* for the bromination of 3-hexyne and t-butylacetylene with added LiBr

LiBr (M)	$LiClO_4$ (M)	K (M^{-1})	$[1 + K(Br^-)]$	$k_0 \times 10^3$ 3-Hx†	$k_0 \times 10^3$ TBA‡
0.10	—	92	10.2	474±7	1.01±0.02
0.08	0.02	93.7	8.50	494±6	—
0.07	0.03	95.6	7.69	491±5	0.981±0.002
0.06	0.04	99.4	6.96	488±2	0.983±0
0.04	0.06	108	5.31	471±2	0.948±0.02
0.03	0.07	114	4.41	448±1	—
0.02	0.08	120	3.40	396±3	0.780±0.01
0.01	0.09	128	2.28	329±1	—

*k_0 values are in units of $M^{-1}s^{-1}$.
†3-Hexyne.
‡t-Butylacetylene.

[9] $$-d[Br_2]_T/dt = [\text{acetylene}](k_2[Br_2]_F + k_{Br_3^-}[Br_3^-])$$

bromine concentration and $[Br_2]_F$ is the free bromine, uncomplexed as tribromide ion. The two are related by eq. 10 where K is the equilibrium

[10] $$[Br_2]_T = (1 + K[Br^-])\,[Br_2]_F$$

constant for tribromide ion formation. Substitution of eq. 10 into eq. 9, integrating and rearranging gives eq. 11 where k_0 is the observed second order rate constant.

[11] $$k_0 = \frac{k_2 + k_{Br_3^-}K[Br^-]}{1 + K[Br^-]}$$

An alternative equation can be derived assuming that molecular bromine is the only electrophile but a bromide ion catalyzed process is possible as in eq. 12. Substituting eq. 10 into eq. 12, again integrating and rearranging gives eq. 13. As shown, eqs. 11 and 13 are kinetically indistinguishable, with $k_{Br^-} = Kk_{Br_3^-}$.

[12] $$-\frac{d[Br_2]_T}{dt} = [\text{acetylene}](k_2[Br_2]_F + k_{Br^-}[Br_2]_F[Br^-])$$

[13] $$k_0 = \frac{k_2 + k_{Br^-}[Br^-]}{1 + K[Br^-]}$$

Dubois *et al.* have discussed in considerable detail (32*b*) the problems in obtaining the rate constants k_2 and k_{Br^-} (or $k_{Br_3^-}$) from these equations using the usual plots of $(1 + K[Br^-])\,k_0$ *vs.* $[Br^-]$. However, there should be little difficulty if salt concentrations of up to only 0.10 M are used. Thus, the $k_{Br_3^-}$ values at either variable ionic strength or constant ionic strength agree well for the styrenes studied by Rolston and Yates (9).

The k_0 values for the phenylacetylene derivatives are given in Table 6. The values for 3-hexyne and t-butylacetylene are shown in Table 7 along with the K values (9) and the derived parameters necessary for $(1 + K[Br^-])\,k_0$ *vs.* $[Br^-]$ plots. The rate constants were obtained from the excellent linear plots of log $(A - A_\infty)$ values at

TABLE 8

Separated rate constants for the phenylacetylene derivatives

Substrate	k_{Br^-}* (M^{-2} s^{-1})	$k_2 \times 10^3$* (M^{-1} s^{-1})	$\frac{k_{Br^-}[Br^-]}{k_2}$§
4-Me PA†	12.8±0.9	826±61	1.5
3,4-Benzo PA†	7.85±0.47	128±31	6.1
4-F PA†	1.80±0.06	21.9±3.6	8.2
PA†	1.29±0.03	14.2±2.2	9.1
4-Br PA†	0.625±0.027	6.51±1.78	9.6
3-Cl PA†	0.251±0.005	—	—
MPA‡	2.88±0.03	8.1±7.6	35

*Errors quoted are obtained from the standard deviations of the least-squares line.
†PA represents phenylacetylene.
‡MPA represents methylphenylacetylene.
§Calculated at 0.10 *M* LiBr.

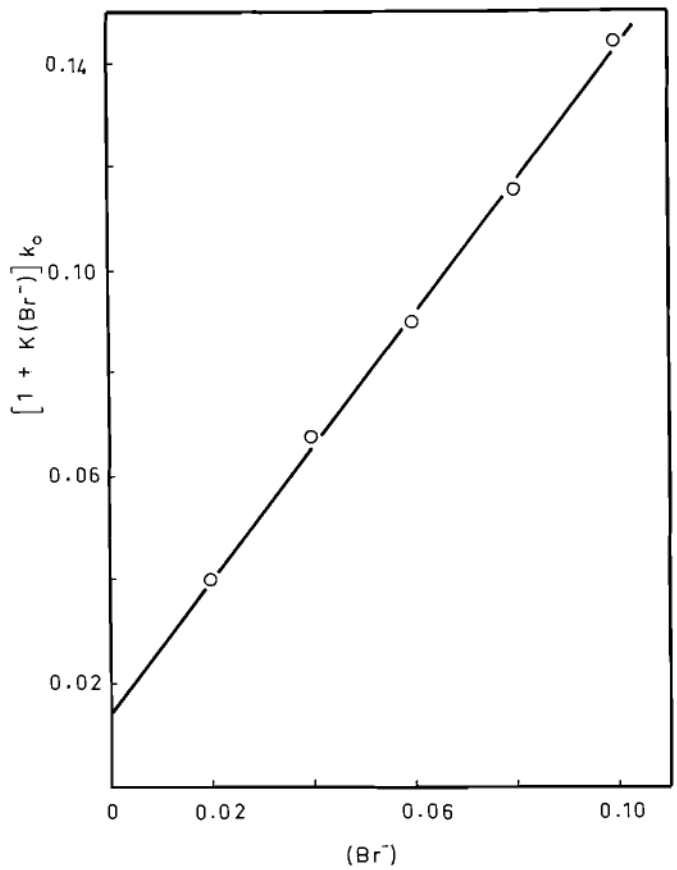


FIG. 3. Plot of $[1 + K(Br^-)]\, k_0$ *vs.* (Br^-) for phenylacetylene.

320 mμ vs. time. The values listed are the average of two runs and the error quoted is the average deviation.

The least-squares slope (k_{Br^-}) and intercept (k_2) for the $(1 + K[Br^-])\, k_0$ *vs.* $[Br^-]$ plots are shown in Table 8 for the phenylacetylenes. A sample plot for phenylacetylene is shown in Fig. 3. In general, the errors in the intercepts (k_2) are quite large because they are so close to the origin. Since these values have already been independently measured (Table 1) no attempt was made to use those obtained by extrapolation.

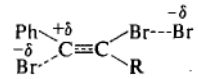
Now that the rate constants are known for the two rate processes occurring in the presence of added bromide ion, the ratio of the products obtained from each can be calculated. This ratio is equal to $k_{Br^-}[Br^-]/k_2$ for the bromide ion catalyzed case. These values are shown for the phenylacetylenes in Table 8 (bromide ion concentration is 0.10 M).

In view of the magnitude of this ratio for some substrates ($k_{Br^-}[0.10]/k_2 = 9.1$ for phenylacetylene) it is no longer surprising that the product ratios shown in Tables 4 and 5 change in the presence of added bromide ion. The reaction is now being dominated by a different kinetic process and the molecular bromination, k_2, is only a minor contributor.

The problem of distinguishing between the above two mechanisms (the tribromide ion and the bromide ion catalyzed) has been discussed in some detail in a preliminary communication on this work (33) and only the more recent results will be mentioned here. The data obtained by Rolston and Yates (8, 9) for the bromination of styrenes in acetic acid have been interpreted in terms of an electrophilic attack by tribromide ion mainly on the basis of product composition. The major objection to this conclusion is that for unreactive substrates, like 3- and 4-nitrostyrene, $k_{Br_3^-} > k_2$. It is surprising that tribromide ion becomes a better electrophile than molecular bromine, especially for unreactive substrates. Conversely, one would expect the bromide ion catalyzed process to become more favorable as the reactivity decreased. Finally, Dubois *et al.* (32) have given a lengthy discussion of this problem for the kinetics of a series of substituted olefins in methanol. The possibility of tribromide as an electrophile was rejected for the same reason mentioned above, that for unreactive compounds its reactivity would be equal to that of bromine.

Furthermore, the bromide ion catalyzed process as proposed here was also rejected. However, the argument used in this case assumes that the rate determining step of the molecular bromination is the formation of the π-complex between the olefin and bromine. All other authors (1) and even Dubois in other papers (34) have postulated a rate determining break-down of this complex. The reason for not considering the bromide ion catalyzed mechanism is therefore far from convincing. At any rate, Dubois *et al.* conclude that for the more reactive substrates the process with an order in bromide ion is simply a salt effect on the molecular bromine process. For the less reactive cases, a mechanism involving pre-equilibrium formation of a complex between the olefin and bromide ion followed by an electrophilic attack of molecular bromine on the negatively charged complex in the rate determining step is suggested.

As discussed previously for methylphenylacetylene (33), the case for acetylenes seems to be much more definite. The marked decrease in bromoacetate formation and the increase in *trans* dibromide in the presence of bromide ion is consistent with a bromide ion catalyzed process proceeding through a transition state like **17**. This



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type of change in dibromide and solvent-incorporated products would not be expected for electrophilic attack by tribromide ion. Of particular interest is the product distribution for 4-methylphenylacetylene where both k_2 and k_{Br^-} are competitive even at 0.10 M LiBr. The ratio of *trans*:*cis* dibromide of 42:58 in 0.10 M $LiClO_4$ can be used for the product distribution of k_2 at ionic strength of 0.10. Assuming k_{Br^-} gives only *trans* dibromide, as is reasonable, a comparison of the calculated $k_{Br^-}[Br^-]/k_2$ ($k_{Br^-} = 12.8\ M^{-2}\,s^{-1}$ and $k_2 = 0.826\ M^{-1}\,s^{-1}$ in Table 8) and the observed ratio is shown in Table 9. The agreement is very good considering the errors involved in the rate constant and product composition determinations.

In summary this is one of the few cases where a clear-cut decision can be made between these two mechanisms. The bromide ion catalyzed process is obviously preferred for acetylenes over direct electrophilic attack by tribromide ion.

In view of the quite different transition state,

TABLE 9

Calculated and observed % *trans* dibromide for the bromination of 4-methylphenylacetylene

LiBr (M)	$LiClO_4$ (M)	(%) *trans* (observed)	(%) *trans* (calculated)
0.10	—	81	79
0.06	0.04	73	70
0.02	0.08	59	56

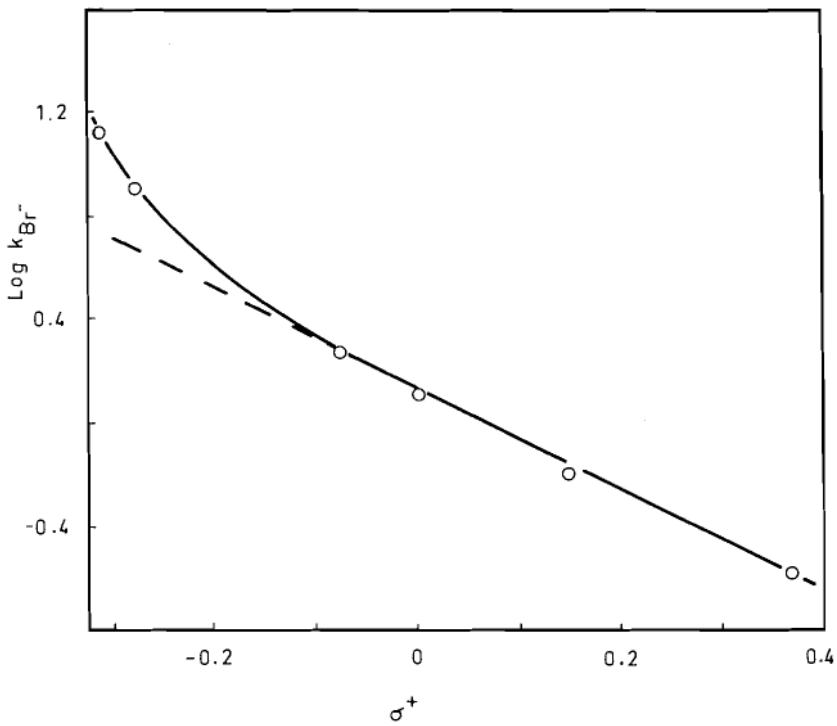

FIG. 4. Plot of log k_{Br^-} *vs.* σ^+ for bromination of phenylacetylenes in acetic acid.

17, postulated for the k_{Br^-} process compared to the molecular bromine, k_2, process substituent effects should also be quite different. This is shown by the Hammett $\rho\sigma^+$ plot shown in Fig. 4 for the k_{Br^-} values from Table 8. (As mentioned above the σ^+ value for the 3,4-benzo substituent was determined as -0.28 from the linear log k_2 *vs.* σ^+ correlation (Fig. 1).) The plot is curved and furthermore the effect of substitution is much less than for the k_2 process since the slope is approximately -1.9 for four substrates of lower reactivity.

Non-linear Hammett plots have generally been regarded as a criterion for a change in mechanism (35). However, this cannot be the case here since the product distribution for the 4-methyl compound is successfully explained by assuming the same Ad_E3 (2) *trans* mechanism (Table 9) as the unsubstituted compound. The curvature may be explained by another approach. The transition state **17** involves synchronous bond formation with both an electrophile (bromine) and a nucleophile (bromine ion). Presumably, as the substituent becomes more electron donating, bond formation between the electrophile and the substrate may have proceeded further than bond formation between the nucleophile and the substrate because positive charge build-up on the α-carbon atom is more favorable. Conversely, for electron withdrawing substituents nucleophile–substrate bonding may have proceeded further. The overall result would be that both types of substituent would have a rate accelerating effect and the Hammett plot would be concave upwards. This type of behavior has been observed previously for the reaction of benzyl halides with nucleophiles (36, 37). Unfortunately, this explanation is not certain because over the range of substituents used no minimum was reached. The possibility is currently being examined further in this laboratory.

As a final point on the reactivity of acetylenes in the presence of bromide ion, the rate constants for the alkyl acetylenes in Table 7 should be mentioned. The results for *t*-butylacetylene are quite straight-forward and a plot of $(1 + K[Br^-])\,k_0$ *vs.* $[Br^-]$ gives the two rate constants, $k_{Br^-} = (8.31 \pm 0.26) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_2 = (18.5 \pm 1.8) \times 10^{-4}\ M^{-1}\ s^{-1}$. Bergel'son and Nazarov (5) have observed that *t*-butylacetylene gives exclusively *trans* dibromide in the presence of LiBr in acetic acid so this substrate

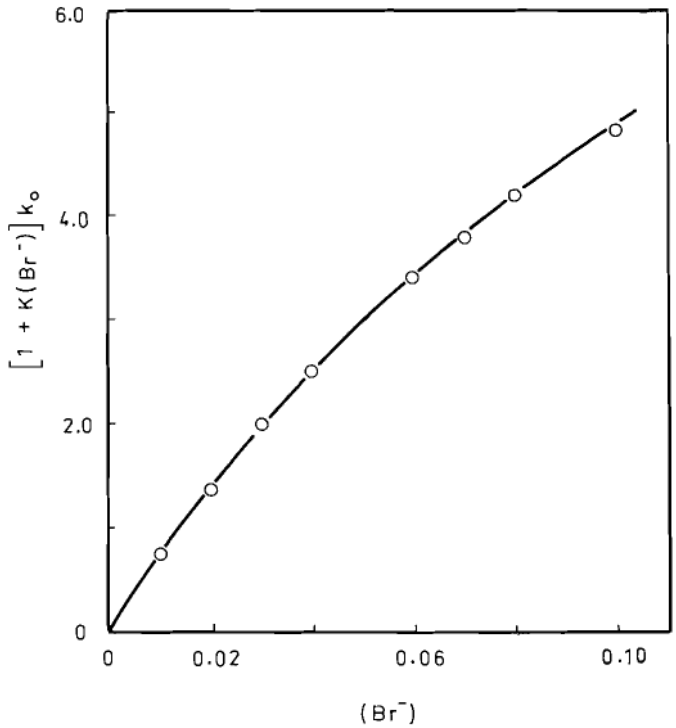

FIG. 5. Plot of $[1 + K(Br^-)]\ k_0$ *vs.* (Br^-) for 3-hexyne.

seems completely analogous to the phenylacetylenes for the bromide ion catalyzed case. The rate constants for 3-hexyne are somewhat different. Thus, a plot of $(1 + K[Br^-])\ k_0$ *vs.* $[Br^-]$ is decidedly curved as shown in Fig. 5. There are no changes in product composition for 3-hexyne in the presence of bromide ion since in both cases only *trans* dibromide is formed (Table 5). We have not as yet arrived at a completely satisfactory explanation for this curvature.

Experimental

All melting points and boiling points are uncorrected. The i.r. spectra were recorded on a Perkin–Elmer model 137B spectrophotometer: spectra of liquids were taken as thin films on sodium chloride discs and those of solids as solutions in CCl_4. Only bands used for identification purposes are reported. The n.m.r. spectra were recorded on a Varian model A-60 spectrometer. Samples were approximately 20% in CCl_4, with 1% tetramethylsilane as reference. Line positions (δ) are in p.p.m. downfield from this reference. The g.l.c. was carried out on either a Wilkens model A-705 "Autoprep" instrument or a Wilkens model 600D "Hy-Fi" instrument both equipped with flame ionization detectors. Peak areas were measured with a disc integrator on the former instrument and by the product of height times width at half peak height on the latter. Columns and conditions (column temperature, flow rate) will be outlined for the individual cases. Microanalyses were performed by A. Gygli, Toronto, Ontario.

Dipole moments were measured on a Wissenschaftliche–Technische Werkstätten Type DMO1 Dipolmeter as used previously in this laboratory (38). The instrument was not recalibrated but the measured dielectric constant of benzene (2.2726 to 2.2735) was in good agreement with that quoted (2.2730) in the previous work. The Halverstadt–Kumler equation (39) was used to obtain total molar polarizations, and electron polarizations were estimated from Vogel's values (40). No correction was made for atom polarization. The dipole moments were then obtained from the Debye equation (41).

Bromine – Acetic Acid Solutions

Acetic acid was purified by the method used previously in this laboratory (9). Bromine (Mallinckrodt) was used without further purification. Anhydrous LiBr and $LiClO_4$ were dried at 100 °C and 1 mm over P_2O_5 for at least 48 h. Stock 1.0 *M* solutions of these salts were prepared by weighing in a dry box to prevent the absorption of atmospheric water. Aliquots of the stock solutions were then used to prepare solutions of the desired concentration for kinetic and product studies.

Bromine concentrations in acetic acid were determined by titration with $Na_2S_2O_3$ (standardized against KIO_3) as described by Vogel (42) using the "dead-stop" end point technique (43). For more convenient work, as well

as for some of the kinetics, extinction coefficients in acetic acid were determined. The values at 490 mμ and the temperatures given are: 17.2 °C, 58.6 ± 0.1; 24.8 °C, 60.5 ± 0.3; 29.9 °C, 61.3 ± 0.1; 39.8 °C, 63.6 ± 0.3. The errors quoted are the average deviation for at least five points.

Kinetic Measurements in Acetic Acid

(a) Spectrophotometric Method

The rates of molecular bromination, k_2, for the acetylenes were measured on a Cary 16 spectrophotometer by following the change in bromine absorbance with time at 490 mμ. The maximum of this band (405 mμ) was not used for the reason described previously (12). Since low concentrations of bromine were necessary (less than 3×10^{-4} *M*) a 10 cm cylindrical cell equipped with a circulating jacket was used. The temperature of the cuvette was controlled to ±0.1 °C with circulating water.

The kinetics for methylphenylacetylene bromination were also measured at higher bromine concentration (2.0 to 5.0 $\times 10^{-3}$ *M*) using 1 cm cuvettes and the Cary 16 constant temperature cell holder for thermostatting.

(b) Spectrophotometric Method: Added Salts

The rates for the acetylenes were also measured on the Cary 16 spectrophotometer at LiBr concentrations varying from 0.01 to 0.10 *M*. Ionic strength was kept constant at 0.10 by addition of $LiClO_4$. The 1 cm cuvette was used and the change in absorbance at 320 mμ (335 mμ for β-naphthylacetylene and 380 mμ for *t*-butylacetylene) was followed.

Preparation and Purification of Acetylenes

Methylphenylacetylene, phenylacetylene, 3-hexyne, 1-hexyne, and *t*-butylacetylene were commercial compounds and were purified by distillation in a 24″ Nester-Faust spinning band still. The substituted phenylacetylenes (except β-naphthylacetylene) were prepared by the methods described previously (44). β-Naphthylacetylene was also prepared by the treatment of β-naphthylmethyl ketone with PCl_5 followed by base catalyzed dehydrohalogenation with KOH in ethanol. The product was purified by sublimation to give a white crystalline solid: m.p. 37–38 °C. The n.m.r. spectrum showed peaks at 3.0 (s, 1.0H) and 7.1–8.0 δ (multiplet, 7.4H).

Anal. Calcd. for $C_{12}H_8$: C, 94.70; H, 5.30. Found: C, 94.80; H, 5.33.

Products of Acetylene Bromination

(a) Methylphenylacetylene(MPA)

Bromine (6.9 g, 0.043 mole) in 50 ml of acetic acid was dropped into 5 g (0.043 mole) of MPA in 50 ml of acetic acid. The reaction mixture was left stirring for 10 h, then poured into 200 ml of water and extracted with two 50 ml portions of pentane. The extract was washed with 5% $NaHCO_3$ and then dried over $MgSO_4$. Concentration on the rotary evaporator gave 9.6 g of a mixture consisting of *trans*-1,2-dibromophenylpropene (81%), *cis*-1,2-dibromophenylpropene (8%), *trans*- and *cis*-1-acetoxy-2-bromo-1-phenylpropene, and 1,1-dibromoethylphenyl ketone (the last three combined are 10%) plus some unreacted acetylene. The ratio of the products was determined by g.l.c. on a 1/4″ × 5′ 5% DEGS on Chromosorb G column (140 °C, 60 ml/min).

The compounds were characterized as follows. The dibromides could be separated from the ketone and bromoacetates by column chromatography on Florisil with pentane eluant. Pure samples of the dibromides were then obtained by preparative g.l.c. on a 3/8″ × 12′ 5% Carbowax on Chromosorb G column (170 °C, 150 ml/min).

Anal. Calcd. for $C_9H_8Br_2$: C, 39.17; H, 2.92; Br, 57.91. Found for *trans* dibromide: C, 39.57; H, 2.99; Br, 57.86. Found for *cis* dibromide: C, 39.47; H, 3.07; Br, 57.55.

The stereochemistry of the dibromides was established by the measured dipole moment values of 0.1 D for the *trans* compound and 2.2 D for the *cis* isomer. This corresponds well with values given by McClelland (45) of 1.77 D for *cis*-1,2-dibromoethylene and 0.0 D for *trans*-1,2-dibromoethylene. This agreement is substantiated by the n.m.r. spectra. The *trans* dibromide shows 2.58 (s, 3.0H), and 7.33 δ (s, 5.2H) while the *cis* dibromide gives 2.22 (s, 3.0H) and 7.33 δ (s, 5.3H) in agreement with the observation that, for β-methylstyrene derivatives, methyl groups *cis* to phenyl absorb at higher field than those *trans* to phenyl (30). In addition the i.r. spectrum of the *cis* isomer has a band at 6.18 μ whereas the *trans* dibromide has only a very weak absorbance in this C=C stretch region.

1,1-Dibromoethylphenyl ketone was synthesized by acid catalyzed bromination of propiophenone. This sample had identical spectral properties to one obtained from the reaction mixture. The ketone could also be prepared by the reaction of bromine with a mixture of *trans* and *cis*-1-acetoxy-2-bromo-1-phenylpropene. This mixture was obtained by molecular distillation of the appropriate fraction from the column chromatography of the crude products from the bromination of MPA.

Anal. Calcd. for $C_{11}H_{11}O_2Br$: C, 51.78; H, 4.35; Br, 31.33. Found for mixture: C, 51.93; H, 4.21; Br, 31.29.

The n.m.r. spectrum of this mixture showed 2.10 (s, 1.8), 2.15 (s, 1.2H), 2.33 (s, 1.9H), 2.37 (s, 1.3H), and 7.25–7.45 δ (m, 5.0H) and indicated the two bromoacetates were there in the ratio of 1.85:1.25 but no assignment of stereochemistry was made. Unfortunately the two isomers could not be separated by g.l.c. The bromoacetates could also be synthesized by the addition of NBS to MPA in acetic acid as described by Jovtscheff (7). This reaction gave a mixture of the dibromoketone (57%) and the *trans* and *cis* bromoacetates (43%) as determined by n.m.r. analysis.

To establish that the products reported in Table 4 are kinetically controlled, a check for dibromide isomerization was made. Neither the *trans* or the *cis* dibromide showed any sign of reaction or isomerization when subjected to the reaction conditions. However, as mentioned above the bromoacetates do react with bromine. Because of this problem and the difficulty in separating and identifying the bromoacetates, these three products were combined as "solvent-incorporated" products (Table 4).

(b) Phenylacetylene (PA)

Bromine (12.0 g, 0.075 mole) in 50 ml of acetic acid was added slowly to 7.5 g (0.075 mole) of PA in 50 ml of acetic acid. The reaction was left to stand for 3 h and then poured into water and extracted with two 50 ml

portions of pentane. The extract was washed with 5% $NaHCO_3$ and dried over Na_2SO_4. After removal of the pentane, analysis on a 1/4″ × 5′ 5% DEGS on Chromosorb G column (150 °C, 50 ml/min) gave four products: bromophenylacetylene (26%), *trans*-1,2-dibromophenylethylene (43%), *cis*-1,2-dibromophenylethylene (17%), and 1-acetoxy-2-bromophenylethylene (14%). The bromoacetate could again be separated from the other components by column chromatography on Florisil with pentane eluant. Pure samples of the bromoacetylene and the dibromides were then prepared by preparative g.l.c. on a 3/8″ × 12′ 5% Carbowax on Chromosorb G column (175 °C, 175/min).

A sample of bromophenylacetylene was prepared independently by the reaction of PA with NaOBr (46). This compound had identical retention time, n.m.r. and i.r. spectra with the compound from the addition reaction.

The dibromides were characterized as follows.

Anal. Calcd. for $C_8H_6Br_2$: C, 36.68; H, 2.31; Br, 61.01. Found for *trans* dibromide: C, 36.66; H, 2.43; Br, 61.37. Found for *cis* dibromide: C, 36.81; H, 2.45; Br, 61.02.

The dipole moments were 0.6 D for the *trans* isomer and 2.1 D for the *cis* in agreement with the observation that *cis* dibromides have considerably higher dipole moments than the *trans* forms (*vide supra*). This assignment is also verified by n.m.r. spectra. The *trans* isomer gave 6.72 (s, 1.0H), 7.1–7.6 δ (m, 5.2H) whereas the *cis* isomer showed 6.90 (s, 1.0H), 7.0–7.5 δ (m, 5.1H). Again, protons *cis* to phenyl appear at lower field than those *trans* to phenyl for styrene derivatives (30).

1 - Acetoxy - 2 - bromophenylethylene was prepared independently by the reaction of NBS with PA in acetic acid (7). This reaction gave 52% of the bromoacetate product and 48% of α,α-dibromoacetophenone. A pure sample of the bromoacetate was obtained by preparative g.l.c. on a 3/8″ × 12′ 5% Carbowax or Chromosorb G column (175 °C, 175 ml/min). This sample was identical to that obtained from the addition of Br_2 to PA.

Anal. Calcd. for $C_{10}H_9Br_2O_2$: C, 49.82; H, 3.76; Br, 33.15. Found: C, 50.02; H, 3.7; Br, 32.97.

The n.m.r. spectrum for the bromoacetate was 2.20 (s, 3.1H), 6.50 (s, 1.0H), and 6.7–7.5 δ (m, 5.3H). The g.l.c. and n.m.r. analysis indicated only one of the bromoacetate isomers but its stereochemistry is unknown.

A check of both the *trans* and *cis* dibromides in acetic acid under the reaction conditions indicated no isomerization or reaction to form either tetrabromides or bromoacetates.

(c) 4-Methylphenylacetylene (4-Me PA)

Bromine (2.07 g, 0.013 mole) in 15 ml of CCl_4 was dropped slowly into 1.5 g (0.013 mole) of 4-Me PA in 15 ml of CCl_4. The solvent was then removed on the rotary evaporator. The g.l.c. analysis on the 1/4″ × 5′ 5% DEGS on Chromosorb G column (150 °C, 50 ml/min) showed only two compounds: *trans*-1,2-dibromo-(4-methylphenyl)ethylene (30%) and *cis*-1,2-dibromo-(4-methylphenyl)ethylene (70%). The two isomers could not be separated completely by preparative g.l.c. because they isomerized under the high temperatures required (190 °C) for reasonable retention times on the preparative column. However, a sample containing 43% *trans* and 57% *cis* was sent for analysis.

Anal. Calcd. for $C_9H_8Br_2$: C, 39.16; H, 2.92; Br, 57.91. Found: C, 38.85; H, 2.89; Br, 57.98.

This sample was obtained by distillation, t = 108–111 °C (1 mm). The stereochemistry of the two isomers was established by n.m.r. only. The olefinic proton of the *cis* isomer is at 6.93 δ; that of the *trans* isomer at 6.70 δ in agreement with the previous assignment for the phenylacetylene dibromides (*vide supra*).

No other products were obtained for the addition of Br_2 to 4-Me PA in either acetic acid or CCl_4.

(d) 3-Hexyne

Bromine (10.0 g, 0.061 mole) in 20 ml of acetic acid was dropped slowly into 5 g (0.061 moles) of 3-hexyne in 20 ml of acetic acid. The reaction mixture was poured into water, extracted with pentane, washed with 5% $NaHCO_3$ solution, and dried over $MgSO_4$. Removal of the pentane gave 13.5 g (90% yield) of product that by g.l.c. analysis was greater than 99% *trans*-3,4-dibromo-3-hexene. Analysis was carried out on the 1/4″ × 5′ 5% DEGS on Chromosorb G column (105 °C, 55 ml/min). Preparative g.l.c. on a 3/8″ × 13′ Tide (8) column (155 °C, 100 ml/min) gave the pure compound.

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.78; H, 4.18; Br, 66.05. Found: C, 30.31; H, 4.18; Br, 65.39.

The i.r. spectrum showed an absorption band in the C=C region. The n.m.r. spectrum was 1.10 (t, J = 7.5 c.p.s., 3.0H), 2.65 δ (q, J = 7.5 c.p.s., 2.0H).

In order to confirm that no *cis*-3,4-dibromo-3-hexene was being formed, a sample was prepared by acetophenone photo-sensitized isomerization of the *trans* compound in benzene. The g.l.c. analysis indicated a *trans*:*cis* ratio of 3.9 after 48 h. The dibromides were separated by preparative g.l.c. on a 3/8″ × 12′ 5% DEGS on Chromosorb G column (160 °C, 120 ml/min). The i.r. spectrum of the *cis* isomer showed a band at 6.3 μ in the C=C region and the n.m.r. spectrum was 1.16 (t, J = 7.5 c.p.s., 3.0H), 2.57 δ (q, J = 7.5 c.p.s., 1.9H).

Samples of 4,4-dibromo-3-hexanone and 3-acetoxy-4-bromo-3-hexene was also prepared by the reaction of NBS with 3-hexyne in acetic acid (7). Neither of these compounds were found to be formed in the molecular bromine reaction.

(e) 1-Hexyne

Bromine (20.0 g, 0.125 mole) in 30 ml of acetic acid was dropped slowly into 10 g (0.125 mole) of 1-hexyne in acetic acid and the reaction was left stirring for 12 h. The reaction was then poured into water and extracted with pentane. The extract was washed with 5% aqueous $NaHCO_3$, dried over Na_2SO_4, and then the pentane removed on the rotary evaporator. The yield was 24.4 g (80%) of a mixture of *trans*-1,2-dibromo-1-hexene (72%) and *cis*-1,2-dibromo-1-hexene (28%). The analysis was carried out on the 1/4″ × 5′ 5% DEGS on Chromosorb G column (105 °C, 50 ml/min).

Anal. Calcd. for $C_6H_{10}Br_2$: C, 29.99; H, 4.12; Br, 66.39. Found for the mixture: C, 29.78; H, 4.12; Br, 66.05.

The dibromides were separated by preparative g.l.c. on a 3/8″ × 12′ 5% DEGS on Chromosorb G column (120 °C, 100 ml/min). The i.r. spectrum of the *cis* isomer had a C=C stretch band at 6.23 μ whereas the *trans* isomer showed only a very weak band. The n.m.r. spectrum of the *trans* isomer was 1.00 (3, J = 7 c.p.s.,

3.3H), 1.2–1.8 (m, 4.2H), 2.60 (t, $J = 7$ c.p.s., 2.0H), and 6.20 δ (s, 1.0H). That of the *cis* was 0.92 (t, $J = 7$ c.p.s., 3.2H), 1.2–1.8 (m, 4.2H), 2.50 (t, $J = 7$ c.p.s., 2.1H), and 6.55 δ (t, $J = 1$ c.p.s., 1.0H). The coupling across the double bond between the vinyl and methylene protons is therefore somewhat larger for the *cis* compound (1 c.p.s.) than for the *trans* case (negligible). This effect has been observed previously (47, 48).

No other products were observed for the bromination of 1-hexyne in acetic acid.

Product Ratio Determinations

The procedures involved in the characterization of the reaction products were, in general, large scale reactions where the bromine concentrations are quite high. However, for accurate product determinations this procedure is undesirable because the k_3 kinetic process which would be dominant under these conditions is only well characterized for methylphenylacetylene (Table 2). Two procedures were used to ensure lower bromine concentration.

For reactive acetylenes, an acetic acid – bromine solution was dropped slowly into an acetylene solution so that the bromine concentration remained low because of rapid reaction. This procedure has the advantage that enough product can be obtained to compare g.l.c. and n.m.r. analysis. In all cases where this was possible, good agreement was obtained. As an example, for 4-methylphenylacetylene, 0.740 g of Br_2 in 10 ml of acetic acid was added slowly to 0.507 g of acetylene in 10 ml of acetic acid. Work-up yielded 1.06 g (85% yield). The g.l.c. analysis gave a *trans*:*cis* ratio of 1.31 whereas n.m.r. analysis indicated 1.25.

For less reactive acetylenes, stock solutions of known concentration were mixed and reaction allowed to go to completion. Since again bromine concentrations were kept low ($< 1.0 \times 10^{-2}$ *M*), only enough product for g.l.c. analysis was obtained.

In either case the reactions were worked-up by pouring into water, extracting with pentane, washing the extract with 5% $NaHCO_3$, drying over $MgSO_4$, filtering, and evaporating at room temperature on a rotary evaporator. For all the acetylenes the product ratios were determined on the 1/4″ × 5′ 5% DEGS on Chromosorb G column. Column conditions and retention times are given in the section on preparation and characterization of the compounds. Ratios are determined by peak areas, and reproducibility of the results in any given run or from run to run is estimated at ±1 to ±2%.

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