Kinetics, Mechanism, and Isotope Rate Effect of the Base-Catalyzed Formation of 1-Haloalkynes from Acetylenes and Sodium Hypohalites[1,2]

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Abstract: The formation of 1-haloalkynes in water at pH >11 and $[OH^-] > 2[X_2]$ follows third-order kinetics, $v_f = k_f[RC{\equiv}CH][OH^-][OX^-]$. The solvent isotope rate effects for the chlorination at 46.1° and bromination at 27.5° of phenylacetylene are essentially absent, *i.e.*, $k_{CH}{}^{H_2O}/k_{CD}{}^{D_2O} = 1.01$ and 1.07 (±0.04), respectively. For chlorination of phenylacetylene at 25.3°, $k = 9.5 \times 10^{-4}\ M^{-2}\ sec^{-1}$, $\Delta H^{\ddagger} = 13.0$ kcal/mol, and $\Delta S^{\ddagger} = -27$ eu. For bromination of four para-substituted phenylacetylenes (H, Cl, Br, and CH_3), $\Delta H^{\ddagger} = 7.5$–8.7 kcal/mol and $-\Delta S^{\ddagger} = 26$–28 eu; Hammett ρ values for this group were 0.72, 0.77, and 0.825 at 35.3, 25.3, and 15.3°, respectively, and the rate constants ($M^{-2}\ sec^{-1}$) depend on temperature and Hammett σ as follows: $\log k = -1.135\sigma - 1893/T + 574\sigma/T + 7.4$. Positive and specific salt effects on the rate of chlorination and on the activity coefficient of phenylacetylene were noted. Toward phenylacetylene, the reactivity of hypohalite is in the order $IO^- > BrO^- \gg ClO^-$. Rates of chlorination and bromination of an alkylacetylene, 3-methylbut-1-yn-3-ol, are within a factor of 5–10 of those for phenylacetylene. It is proposed that the mechanism of halogenation involves a fast preequilibrium to form $RC{\equiv}C^-$, a rate-determining step of this anion and hypohalite to yield the intermediate $RC{\equiv}CXO^{2-}$, and a rapid reaction of this intermediate with water to produce 1-haloalkyne and two hydroxide ions. One consequence of this mechanism is that the reverse process, 1-dehalogenation, probably has the form $v_r = k_r[RC{\equiv}CX]\cdot[OH^-]^2$, or its equivalent. In exploring the dehalogenation process, we found a rather different route with arsenious oxide; that is, the rate law is $v = k[C_6H_5C{\equiv}CBr][As_2O_3][OH^-]^2$. The general significance of this work in the area of positive halogen chemistry is indicated.

The base-catalyzed halogenation of weak carbon acids, *e.g.*, ketones, nitriles, sulfones, nitroalkanes, etc., has been extensively studied. This process is also of considerable synthetic importance for terminal acetylenes[3] but has been used only infrequently for hydrocarbons—the preparations of polychloro- and polybromocyclopentadienes or indenes seem to be unique.[3b] However, there seems to be no precedent for rate studies of base-catalyzed halogenation of hydrocarbons.[2] In this paper we demonstrate that this is possible with acetylenes.

$$RC{\equiv}CH + OX^- \rightleftharpoons RC{\equiv}CX + OH^- \qquad (1)$$

The mechanism of reaction 1 is unusual, first in that the halogenation is kinetically of the third order and second in that hypohalite ion is the attacking species.

$$v = k[RC{\equiv}CH][OH^-][OX^-] \qquad (2)$$

Among the hundreds of base-catalyzed halogenations studied,[4] there are perhaps two almost forgotten examples (hypochlorite with acetone or acetophenone) with the same rate law.[5] The rediscovery and investigation of this relatively obscure mechanism has uncovered problems and provided insights in several important areas. We investigated the reaction of hypochlorite or hypobromite ions with diisopropyl ketone and found that rate law 2 applied at high pH.[6] As a result, conclusions drawn by previous workers on mechanism, isotope effects, and tunneling effects in this system will probably have to be revised.[6] We examined the reaction of hypochlorite with nitroethane and found a novel rate law in which there was an inverse dependence in hydroxide ion at pH >11.[7] In this paper, the focus turns to several aspects of positive halogen chemistry. Appropriately, recent reports on apparently unrelated reactions also involve hypohalite and carbanions analogous to those in both forward and reverse reactions of eq 1, *e.g.*, the complex conversion of picric acid to bromopicrin with a rate law similar to that of eq 2[8] and several base-catalyzed halogen abstractions from polyhaloaromatics, haloalkynes, propargyl halides, etc.[9,10] We shall touch on some of these aspects of positive halogen chemistry later.

It will be recalled that in the description of base-catalyzed halogenation, say of a ketone, one usually sees the following scheme.[4,6]

$$\begin{aligned} CH + B &\underset{-a}{\overset{a}{\rightleftharpoons}} C^- + BH^+ \\ C^- + X^+ &\xrightarrow{b} CX \end{aligned} \qquad (3)$$

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[1] (a) This work, supported in part by Public Health Service Grant GM 7021, was abstracted from R.-R. Lii's Ph.D. thesis, Illinois Institute of Technology, May 1971; (b) presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 8–12, 1969, Paper 213.

[2] Preliminary communication: R.-R. Lii and S. I. Miller, *J. Amer. Chem. Soc.*, **91**, 7524 (1969). All of the rate constants in this paper should be doubled; the factor 2 was inadvertently omitted in the analysis for free halogen.

[3] (a) S. Y. Delavarenne and H. G. Viehe in "The Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, Chapter 10; (b) F. Straus, L. Kollek, and W. Heyn, *Chem. Ber.*, **63**, 1868 (1930); (c) S. I. Miller, G. R. Ziegler, and R. Wielesek, *Org. Syn.*, **45**, 86 (1965).

[4] (a) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapters X, XI; (b) R. P. Bell and B. G. Cox, *J. Chem. Soc. B*, 652 (1971); (c) F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, **93**, 2829 (1971).

[5] P. D. Bartlett and J. R. Vincent, *ibid.*, **57**, 1596 (1935).

[6] R.-R. Lii and S. I. Miller, *J. Chem. Soc. B*, 2269 (1971).

[7] R.-R. Lii and S. I. Miller, *ibid.*, 2271 (1971).

[8] A. R. Butler and H. F. Wallace, *ibid.*, 1758 (1970).

[9] Numerous citations to positive halogen abstraction are given by J. F. Bunnett, *Accounts Chem. Res.*, **5**, 139 (1972).

[10] (a) A. Fujii, J. I. Dickstein, and S. I. Miller, *Tetrahedron Lett.*, 3435 (1970); (b) A. Fujii and S. I. Miller, *J. Amer. Chem. Soc.*, **93**, 3694 (1971).

If the steady-state assumption applies to the intermediate C^-, one obtains the general rate law 4. In most

$$v = k_a k_b[CH][B][X^+]/(k_{-a}[BH^+] + k_b[X^+]) \qquad (4)$$

cases, $k_{-a}[BH^+] \ll k_b[X^+]$ and second-order (eq 5)

$$v = k_a[CH][B^-] \qquad (5)$$

kinetics applies. One can, of course, elicit the other alternative by making $k_{-a}[BH^+] \gg k_b[X^+]$. Bell and Long did this simply by having $[X^+] \rightarrow 0$ and halogenation proceed *via* molecular bromine or tribromide ion.[4] In our work, we did this by suppressing the concentrations of all halogenating species but the least active one, namely, hypohalite ion. Admittedly, there are rate laws other than (4) and schemes other than (3) that may apply to a given halogenation; the steady-state condition, for example, need not hold and the halogenating agent may prefer to attack an isomeric form of CH, etc. Here we consider the alternatives in eq 3 and 4 with special reference to acetylenes.

Experimental Section

The following instruments were used routinely: Beckman IR-8 for infrared (ir) spectra; Varian A-60 for nuclear magnetic resonance (nmr) spectra; Varian MAT CH7 for mass spectra; Aerograph Models 20 and 700 for gas chromatography. Spectral checks were made on neat compounds, unless otherwise indicated; tetramethylsilane was used as an internal reference for nmr. All melting points and boiling points listed are uncorrected.

Our acetylenes were prepared by established methods and most of them have been described recently.[10] Here we add 4-bromophenylacetylene, mp 64–65° (lit.[11] 63–63.5°), ir ν (CCl_4) 2090 cm^{-1}, nmr δ (CCl_4) 2.99 (1 H, s); mercuric 4-bromophenylacetylide, mp 255–256° (lit.[12] 256–256.5°), ν(CCl_4) 2130 cm^{-1}; 4-bromophenylbromoacetylene, mp 96–97° (lit.[13] mp 93–95°), ν (CCl_4) 2180 cm^{-1}; 4-nitrophenylacetylene, mp 149° (lit.[11] 148–149°). Phenylacetylene-*d* was prepared from sodium phenylacetylide and deuterium oxide in ether; nmr analysis indicated ~90 atom % deuteration.

α,β-Dichlorostyrene.[14] Phosphorus pentachloride (10.4 g) and ω-chloroacetophenone (7.7 g) were warmed at *ca.* 100° until a clear yellow melt was obtained. Distillation at 1 atm yielded a fraction which had bp 210°; ir ν (neat) 3070 cm^{-1}; nmr δ 6.45 (1 H, s, trans), 6.63 (1 H, s, cis); uv $\lambda_{max}{}^{H_2O}$ 256 nm; mass spectrum *m/e* 172 $(P)^+$, 137 $(P - 35)^+$, 102 $(P - 70)^+$. The cis and trans designations are tentative but are based on a fairly reliable chemical shift relationship for alkenes of this type.[15]

Hypohalites. Reagent grade chlorine, bromine, and iodine (resublimed) were used. Stock solutions of hypochlorite were prepared by distilling an appropriate amount (1 or 2 ml) of liquefied chlorine into a cooled (~0°) solution of sodium hydroxide (250 ml, 4–8 *M*). Hypobromite or hypoiodite solutions were prepared by adding the halogen to a cooled (~0°) solution of sodium hydroxide (20 ml, 0.45–0.9 *M*). These solutions were diluted with distilled water and used immediately, except for the sodium hypochlorite which was stored in a refrigerator.

The kinetics of decomposition of our hypohalites have been investigated,[16-19] but we also checked two of them briefly. Hypochlorite (λ_{max} 292 mμ) and hypobromite (λ_{max} 330 mμ) were monitored spectrophotometrically. For the hypochlorite, there was no significant decomposition within 1 week; for the hypobromite, decomposition was detectable in 2 days. Judging from the reported rate law for the decomposition of hypoiodide,[18] its half-life is *ca.* four to eight times longer than that we found for the iodination of phenylacetylene at p*K* > 11; in any case, we found no trends in our kinetic data.[1a]

Sodium Deuterioxide. Fifty milliliters of 99.8% (Diaprep Inc.) deuterium oxide was placed in a 500 ml three-neck round-bottom flask equipped with a reflux condenser connected with a calcium chloride tube and a nitrogen inlet. While the flask was chilled in an ice bath and swept with nitrogen, an appropriate amount of small pieces of sodium metal, which had been freshly cut and washed with pentane, was added. The concentration of base was determined with standard hydrochloric acid.

Analyses. A Corning 10 pH meter, equipped with a glass combination electrode, was used for acid–base titrations. The sodium hydroxide solutions were determined with standard (0.1000 *M*) hydrochloric acid. Hypohalites were estimated iodimetrically: a known volume of hypohalite was treated with an excess of standard sodium arsenite, stirred, appropriately buffered, and back-titrated to the starch end point with standard iodine solution.[20] These titrimetric results were occasionally checked spectrophotometrically. In order to avoid the interference and presence of halate (XO_3^-), the hypohalites were used and analyzed before their decomposition became significant.

Kinetics. Process 1 was followed by uv spectroscopy in quartz cells (0.5, 1.0, or 5.0 cm path length). Beckman DK-2 and Cary 11 recording spectrophotometers equipped with thermostated cell compartments were used. Since the temperature within the cell was often slightly different (±0.5°) from that of the external constant-temperature bath which was used to control the temperature of the cell compartment, both were checked. The stock solutions were left in the external bath (>10 min) and then suitable volumes were mixed in the cell. Then the cell was quickly transferred to the cell compartment and absorbance readings were started. The reference cell normally contained the same solution as the sample cell, except for the substance being measured.

For the halogenation of the arylacetylenes, the appearance of the product phenylhaloacetylenes was followed; for 3-methylbutyn-3-ol (MB), the disappearance of sodium hypohalite was followed. Detailed spectral data are found in the thesis[1a] and are summarized in Table I. We found, for example, that Beer's law (eq 6) held for

$$OD = \log I_0/I = \epsilon bc \qquad (6)$$

phenylchloroacetylene, phenylbromoacetylene, and sodium hypochlorite from 0 to 10^{-4}, 10^{-3}, and 10^{-2} *M*, respectively.

Table I. Ultraviolet Spectral Data of Arylacetylenes, 4-$YC_6H_4C{\equiv}H$, and Their Halogenation Products, 4-$YC_6H_4C{\equiv}CX$, in Methanol

Y	X	λ_{max}, nm	$10^4\epsilon$, M^{-1} cm^{-1}
H	H	244.5	0.91[a]
H	Cl	250	0.98
H	Br	253	1.15
H	I	256	
CH_3	H	249.5	1.59
CH_3	Cl	253.5	1.72
CH_3	Br_2	256	1.95
Cl	H	252	2.07
Cl	Br	260	2.30
Br	H	254.5	1.92
Br	Br	262	2.11
NO_2	H	292	
NO_2	Br	300[b]	

[a] This value is not significantly changed in water. [b] Reference 13.

All of the kinetic runs were carried out under pseudo-first-order conditions. That is, for the conditions $[OH]_0 > [ClO^-]_0 \gg [ArC{\equiv}CH]$, the pseudo-first-order expression

$$\text{rate} = k_\psi[ArC{\equiv}CH] \qquad (7)$$

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(12) T. H. Vaughn and J. A. Nieuwland, *J. Amer. Chem. Soc.*, **56**, 1207 (1934).

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(14) R. Dyckeroff, *Chem. Ber.*, **10**, 119 (1877).

(15) R. Tanaka, M. Rodgers, R. Simonaitis, and S. I. Miller, *Tetrahedron*, **27**, 2651 (1971).

(16) M. W. Lister, *Can. J. Chem.*, **34**, 465 (1956).

(17) B. Perlmutter-Hayman and G. Stein, *J. Phys. Chem.*, **63**, 734 (1959).

(18) C. H. Li and C. F. White, *J. Amer. Chem. Soc.*, **65**, 335 (1943).

(19) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Wiley, New York, N. Y., 1966, p 570; (b) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. I, Oxford University Press, London, 1965, Chapter 12.

(20) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed, London, Macmillan, New York, N. Y., 1952, chapter XXXIX.

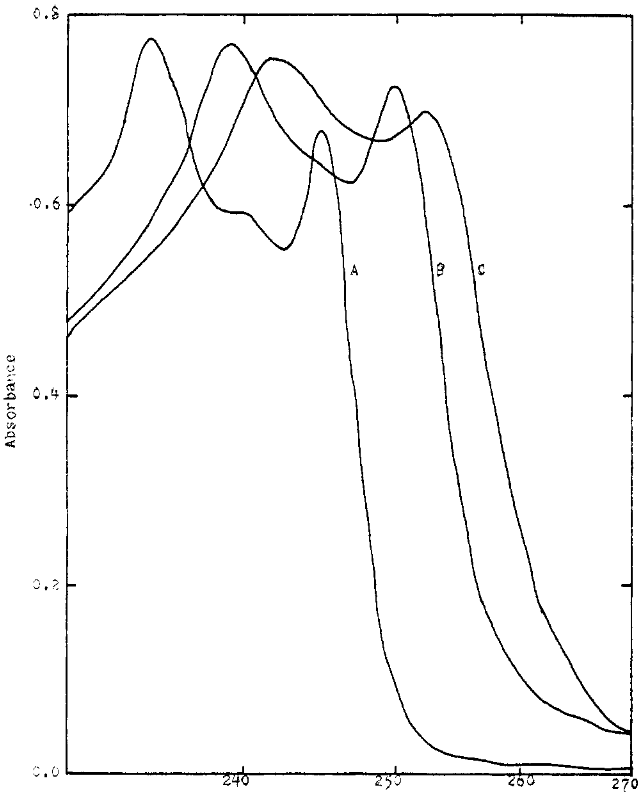

Figure 1. The ultraviolet spectra of phenylacetylene (A) and its halogenation products, phenylchloroacetylene (B) and phenylbromoacetylene (C) in methanol.

applied. By combining eq 6 and the integrated form of eq 7, we obtain

$$2.303 \log (\mathrm{OD}_\infty - \mathrm{OD}) = -k_\psi t + B \qquad (8)$$

in which OD is the optical density of the solution, t is the time, and B is a constant. An analogous procedure was followed when hypohalite was monitored. Note that unless OD_∞ depends on it, the initial concentration of the substance being monitored does not need to be known precisely.

The kinetic runs proceeded for *ca.* 4 half-lives. When the disappearance of a reactant was followed, the optical density at "infinite" time was taken after at least 10 half-lives. Since this OD_∞ was usually small (~0.02–0.06), this leads to a difference of 3–8% in the rate constants as calculated for the observed OD_∞ and the expected $\mathrm{OD}_\infty = 0$. When the appearance of the haloalkynes was followed, the observed OD_∞ was found to be somewhat low, as compared with the value expected from the known ϵ value. The discrepancy in $(\mathrm{OD})_\infty$, which presumably arises because of the lability of the haloalkynes, leads to ~10% difference in the estimates of the rate constants for a single run.

Two compounds of interest to us were not suitable for study by our techniques. The bromination of *p*-nitrophenylacetylene appeared to have the right stoichiometry according to eq 1, but $\lambda_{\max}$ of reactant and product overlapped; since the solubilities of these compounds were low ($<10^{-4}$ *M*), it was difficult to devise an alternate to the uv method. With respect to *p*-methoxyphenylacetylene, bromine addition to the triple bond[21] or perhaps attack on the ring[22] appear to compete with process 1, so that this system too was not studied kinetically.

For each system, at least five runs were made at different concentrations of reagents. The mean rate constant was then corrected for volume changes from the temperature at which the solutions were made up (25.0°) to t at which the run was carried out. Because we ended up with a third-order rate law, the adjustment is given by

$$k_{\mathrm{cor}} = k_{\mathrm{obsd}}(d_{25}/d_t)^2 \qquad (9)$$

in which d was taken as the density of water.

The activation parameters were determined from a least-squares treatment of log k/T *vs.* $1/T$ according to the standard relation[23]

$$k = (kT/h)e^{\Delta S^{\ddagger}/R}e^{-\Delta H^{\ddagger}/RT} \qquad (10)$$

Products of the Arylacetylene–Hypohalite Reaction. Under the conditions of the kinetic studies, namely $[\mathrm{OH^-}]_0 > 2[\mathrm{Cl_2}]_0$, an aqueous solution of phenylacetylene (1.74×10^{-4} *M*), sodium hydroxide (0.65 *M*), and sodium hypochlorite (0.04 *M*) at 25° developed an OD at λ 250 nm which indicated essentially quantitative conversion (~95%) to phenylchloroacetylene. Likewise, bromination runs of the arylacetylenes yielded solutions whose uv spectra were identical in shape with those of the expected arylbromoacetylenes; the calculated yields usually exceeded 90%. At least some of the deviation from the theoretical yield may be ascribed to the side reactions of the following paragraphs.

At comparable hydroxide and chlorine concentrations, $[\mathrm{OH^-}]_0 \simeq [\mathrm{Cl_2}]_0$, the yield of phenylchloroacetylene was reduced. A solution of phenylacetylene (1.5×10^{-4} *M*), sodium hydroxide (0.21 *M*), and chlorine (0.1 *M*) at 46.1° gave a maximum of ~25% phenylchloroacetylene, which then decreased slowly with time, according to uv analysis at 250 nm. Judging by the uv spectrum of authentic benzoic acid ($\lambda_{\max}$ 226.5 nm), this compound appeared in the reaction solution after 40 hr. As a check, the above reaction was scaled up to 1.5 l. and the product mixture worked up. The presence of benzoic acid was established by tlc.

Chlorine solutions that are deficient in base, $[\mathrm{OH^-}]_0 < [\mathrm{Cl_2}]_0$, do not give process 1. Solutions of phenylacetylene (~8×10^{-5} *M*) and chlorine (~0.05 *M*), with and without sodium hydroxide (~0.05 *M*), present at 46.1°, yielded a product solution whose uv spectrum resembled that of α,β-dichlorostyrene ($\lambda_{\max}$ 257.5 nm). A preparative scale reaction of phenylacetylene (2 ml), chlorine (2 ml), and 0.02 *M* sodium hydroxide (250 ml) as a heterogeneous mixture was carried out at ~25° on a shaking device. The product was worked up and identified by uv and nmr spectra as *cis*- and *trans*-α,β-dichlorostyrene.

Results and Discussion

Stoichiometry. The preparation of *some* 1-haloalkynes from terminal alkynes according to eq 1 is well documented.[3] Phenylbromoacetylene (80% yield) and 11 of its ring-substitution products (unspecified yields) were obtained routinely in this way.[13] Under conditions similar to those of our kinetic runs, we established that phenylchloroacetylene was produced in essentially quantitative yield, and four arylbromoacetylenes and phenyliodoacetylene were produced in yields ⩾90%, as determined by uv spectral analysis.

The halogenation process 1 is favored only under specified conditions. Depending on the pH, one might have to contend with one or more of the following forms of halogen, *e.g.*, $\mathrm{X_2}$, $\mathrm{X_3^-}$, HOX, and $\mathrm{OX^-}$ (and perhaps others), each of which has its characteristic reactivity. In strongly basic aqueous solutions (pH >11), it is possible to have hypohalite ion as the dominant halogenating species. For here the pertinent equilibrium is

$$2\mathrm{OH^-} + \mathrm{X_2} \rightleftharpoons \mathrm{XO^-} + \mathrm{X^-} + \mathrm{H_2O} \qquad (11)$$

and the equilibrium constants at 25° are $K \simeq 10^{15}$, 10^8, and 30 for $\mathrm{X_2} = \mathrm{Cl_2}$, $\mathrm{Br_2}$, and $\mathrm{I_2}$, respectively.[19] One cannot suppress any one of these species completely, and if its reactivity is sufficiently high, it will compete with hypohalite for the alkyne. Such competition was probably present in the *p*-methoxyphenylacetylene–hypobromite system, where electrophilic attacks on the

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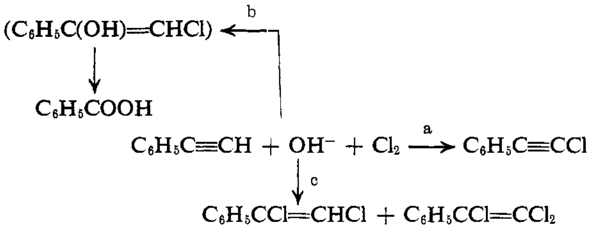
[21] (a) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970); (b) P. B. DeLaMare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966, Chapters 6 and 7.

[22] L. M. Stock and H. C. Brown, *J. Amer. Chem. Soc.*, **82**, 1942 (1960). The partial rate factor for bromination of the para position of anisole is 10^{10}.

[23] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, Chapter 5.

double bond or ring are expected to be fast.[21,22,24]

Now consider our findings for phenylacetylene in reaction 12 in three situations: a, $[OH^-]_0 > 2[Cl_2]_0$; b, $[OH^-]_0 \simeq 2[Cl_2]_0$; c, $[OH^-]_0 < 2[Cl_2]_0$. Condition a was used in our kinetic studies. Condition b led to reduced yields of phenylchloroacetylene at short reaction times and to benzoic acid over a long period. Condition c led to α,β-dichlorostyrene. It is clear that solutions deficient in base give characteristic addition reactions of chlorine or hypochlorous acid to an unsaturated compound.[21,24] This is in contrast to the behavior of many weak carbon acids, *e.g.*, ketones, in which a change in pH merely alters the mechanism, not the process. In this work, a drop in pH can be catastrophic.



$$C_6H_5C\equiv CH + OH^- + Cl_2 \xrightarrow{a} C_6H_5C\equiv CCl \qquad \xrightarrow{b} (C_6H_5C(OH){=}CHCl) \rightarrow C_6H_5COOH \qquad \xrightarrow{c} C_6H_5CCl{=}CHCl + C_6H_5CCl{=}CCl_2 \quad (12)$$

Kinetics and Base Mechanism. The arylacetylenes and arylhaloacetylenes are sparingly soluble ($<10^{-3}$ *M*) in water. Fortunately the uv spectra (Table I, Figure 1) of reactant and product of eq 1 did not overlap appreciably so that this method of following the reaction could be used. In the case of *p*-nitrophenylacetylene, however, the λ_{max} of it and its product overlapped strongly; in addition, its low solubility rendered other methods impracticable. Unlike ordinary alkylacetylenes, methylbutynol (MB) had fair solubility in water. We could therefore follow its reaction by monitoring hypohalite ion by uv. The kinetics of chlorination of this compound, which had some unusual features, will be discussed separately in the Appendix.

Since we were not committed to any particular rate law, we sought the kinetic order in each reagent. In the uv method, it is convenient to use pseudo-first-order conditions. Our concentration ranges were, therefore, $[OH^-]_0 > 2[X_2]_0 > 100[ArC\equiv CH]_0$. However, we did change the initial concentrations in order to establish the kinetic order in each of the participants.

Typical runs (Figure 2, Table II) establish reaction 1 as first order in acetylene. The variation in acetylene concentration leaves the pseudo-first-order rate constant unchanged, as it should, and incidentally indicates the precision in k_ψ. By keeping the $[NaOH]_0$ constant and varying $[OX^-]$, we found the order in hypohalite to be unity (Figure 3, Table II). Then by keeping hypohalite constant and varying the sodium hydroxide, we found the kinetic order in NaOH to be unity (Figure 4). Rate law 2 applies to our systems. (If one postulates $[X_2]$ or $[HOX]$ as the halogenating agent in place of $[OX^-]$, one will end up inevitably with the wrong rate law.) Our rate data are given in Tables III and IV.

As a result of these kinetic studies, we shall take as our working hypothesis that eq 3 applies; a pre-equilibrium step, for which $K_a = k_a/k_{-a}$ and the base is hydroxide ion, is followed by a rate-determining halogen transfer from hypohalite ion. The observed rate constant is composite

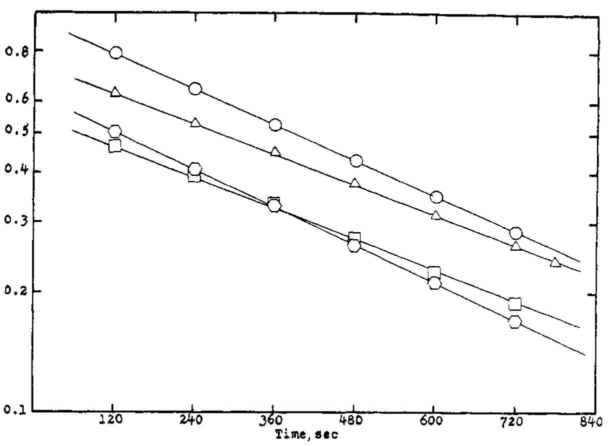


Figure 2. Typical pseudo-first-order plots for the reaction of $4\text{-}YC_6H_4C\equiv CH$ with bromine in aqueous sodium hydroxide: ○, Y = H, 27.5°; △, Y = CH_3, 35.3°; ○, Y = Cl, 25.3°; □, Y = Br, 25.3°. Only *ca.* 2 of the *ca.* 4 half-lives followed are shown.

Table II. A Test of the Third-Order Dependence of the Reaction of Sodium Hypochlorite with Phenylacetylene at ~25°

$10^5 \cdot [C_6H_5C\equiv CH]$, *M*	[NaOH], *M*	$10^3 \cdot [OCl^-]$, *M*	$10^4 k_\psi$, min^{-1}	$10^5 k$, M^{-2} min^{-1}
5	1.77	47	122	147
18	1.77	47	114	137
25	1.77	47	120	144
31	1.77	47	120	144
32	1.77	47	122	147
19	1.73	46	121	152
13	1.77	24.5	60	138
12	1.79	16.5	42	143
18	1.80	9.2	23	139
			Mean[a]	143 ± 4
15	0.230	46.7	6.0	55.9
16.5	0.069	46.5	1.9	59.0
17	0.640	39.7	14.9	58.5
16	0.309	19.9	3.2	51.7
17	0.680	22.7	9.0	58.6
16	0.890	23.2	12.4	60.2
16	0.518	9.9	2.89	56.7
			Mean[b]	57 ± 2

[a] At 25.5°. Since the ionic strengths in these solutions were high, these *k*'s are larger than those below and in Table III. See text for a discussion of medium effects. [b] At 25.3°.

$$k_{obsd} = k_b K_a/[H_2O] \qquad (13)$$

The kinetic implications are easily derived. From the p*K*'s of water, 15.7, and phenylacetylene, 21,[25a] and $k_a \simeq 3 \times 10^3\ M^{-1}\ sec^{-1}$ (from exchange of labeled phenylacetylene),[25b] we can make the following estimates: $K_a \simeq 10^{-5.3}$, $k_{-a} \simeq 6 \times 10^8\ M^{-1}\ sec^{-1}$, and $k_b \simeq 10^8\ M^{-1}\ sec^{-1}$ for the bromination of phenylacetylene at 25°. In several succeeding sections we shall see how useful this over-all mechanism is.

Structure and Reactivity. The ratio of the third-order rate constants at 25.3° for the reaction of hypohalites with phenylacetylene is $k_{(IO^-)}:k_{(BrO^-)}:k_{(ClO^-)} = 3.4:1.2:1.2 \times 10^{-4}$. This gives the reactivity of hypohalite ions with phenylethynyl anion as $IO^- > BrO^- \gg ClO^-$. Although maxima and minima in the properties of

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(24) (a) S. Goldschmidt, R. Endres, and R. Dirsch, *Chem. Ber.*, **58**, 572 (1925); (b) R. O. Norris, R. R. Vogt, and G. F. Hennion, *J. Amer. Chem. Soc.*, **61**, 1460 (1939); (c) J. Koenig and V. Wolf, *Tetrahedron Lett.*, 4629 (1970).

(25) (a) A. Streitwieser, Jr., and D. M. E. Reuben, *J. Amer. Chem. Soc.*, **93**, 1794 (1971); (b) E. A. Halevi and F. A. Long, *ibid.*, **83**, 2809 (1961).

Table III. Rate Data for the Halogenation of Substituted Phenylacetylenes ($4\text{-}YC_6H_4C{\equiv}CH$) or 3-Methylbut-1-yn-3-ol (MB) with Sodium Hypohalite (NaOX) in Aqueous Sodium Hydroxide

X (concn, *M*)	Y (10^5 concn, *M*)	[NaOH], *M*	Temp, °C ± 0.1°	No. of runs	k,[a] M^{-2} sec^{-1}
Cl	H	0.07–0.89	25.3	7	$(95 \pm 3) \times 10^{-5}$
(0.01–0.047)	(10–17)		36.0	7	$(211 \pm 5) \times 10^{-5}$
			46.1	8	$(431 \pm 17) \times 10^{-5}$
Cl	H[b]	0.3–0.63[b]	46.1	4	$(428 \pm 10) \times 10^{-5}$ [b]
(0.026–0.076)	(15–21)				
Br	H	0.034–0.175	5.8	4	3.75 ± 0.23
((38–525) × 10^{-5})	(1.4–9.5)		16.0	8	6.89 ± 0.21
			27.5	14	11.34 ± 0.42
			36.0	8	17.36 ± 0.48
Br	H[b]	0.026–0.76[b]	27.5	5	10.57 ± 0.24
((8–28) × 10^{-4})	(7–8)				
Br	CH_3	0.04–0.045	15.3	4	4.40 ± 0.03
((98–405) × 10^{-5})	(4–9.1)		25.0	5	7.31 ± 0.18
			35.3	5	12.74 ± 0.3
Br	Cl	0.04–0.047	15.3	5	9.63 ± 0.35
((4–8) × 10^{-4})	(3.1–6.9)		25.3	4	15.11 ± 0.37
			35.3	6	24.25 ± 0.45
Br	Br	0.04–0.045	15.3	6	10.02 ± 0.2
((7–43) × 10^{-4})	(3.2–4.3)		25.3	5	15.67 ± 0.5
			35.3	5	25.26 ± 0.55
I	H	0.043–0.098	25.3	6	32.12 ± 0.70
((5–28) × 10^{-4})	(7–11)				
Br	MB	0.036–0.14	25.3	6	2.02 ± 0.01
((8–30) × 10^{-4})	(11–60) × 10^{-8}				
Cl	MB	0.29–1.15	25.3	3	$(2.12 \pm 0.11) \times 10^{-4}$
(0.012–0.015)	(12–31) × 10^{-7}				

[a] The average deviation, which is <5%, is indicated. These figures have not been rounded off so that our activation parameters may be reproduced. [b] This run had $C_6H_5C{\equiv}CD$ and NaOD in D_2O. The isotope rate effect was for chlorination, $k_{CH}{}^{H}/k_{CD}{}^{D} = 1.01 \pm 0.04$; for bromination, $k_{CH}{}^{H}/k_{CD}{}^{D} = 1.07 \pm 0.04$.

Table IV. Activation Parameters at 25.3° for the Reaction of Arylacetylenes, $4\text{-}YC_6H_4C{\equiv}CH$, with Halogens ($X_2$) in Aqueous Sodium Hydroxide[a]

Y	X	k, M^{-2} sec^{-1}	Log A, M^{-1} sec^{-1}	ΔE_a, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$-\Delta S^{\ddagger}$, eu
H	Cl	95×10^{-5}	6.9 ± 0.4	13.7 ± 0.4	13.0 ± 0.4	27
H	Br	10.4	7.3 ± 0.3	8.6 ± 0.2	8.0 ± 0.2	27
CH_3	Br	7.5	7.7 ± 0.3	9.3 ± 0.3	8.7 ± 0.2	26
Cl	Br	15.1	7.1 ± 0.3	8.1 ± 0.3	7.5 ± 0.3	28
Br	Br	15.7	7.2 ± 0.3	8.1 ± 0.3	7.6 ± 0.3	28

[a] The probable errors of the activation parameters are included.

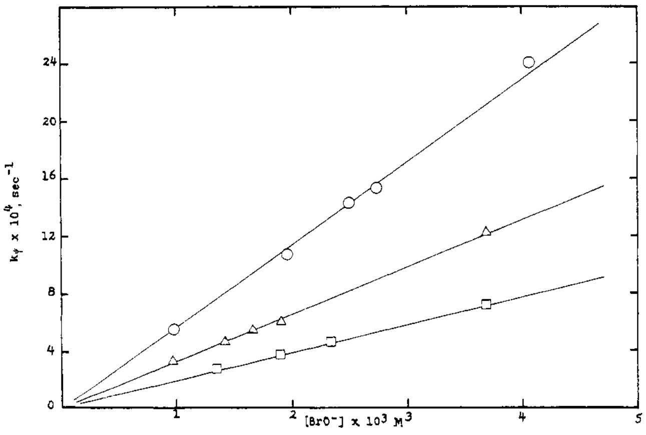

Figure 3. The reaction of 4-methylphenylacetylene with sodium hypobromite in water at a fixed $[NaOH]_0 = 0.045$ *M*: □, 15.3°; Δ, 25.0°; ○, 35.3°.

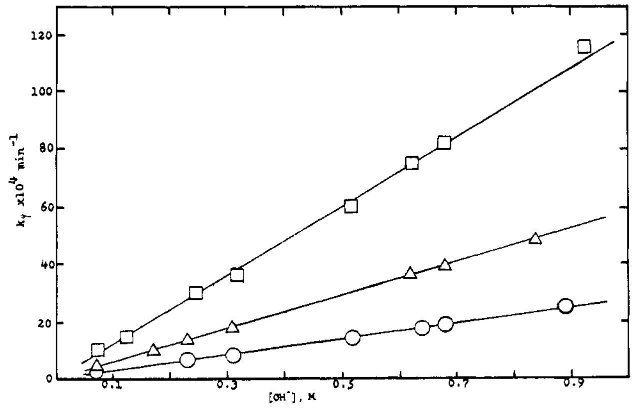

Figure 4. The reaction of phenylacetylene (*ca.* 10^{-4} *M*) with sodium hypochlorite in water at a fixed $[NaOCl]_0 = 0.047$ *M*: ○, 25.3°; Δ, 36.0°; □, 46.1°.

halogen species are known,[19,26] the preceding is the order of bimolecular disproportionation rate constants (to halide and halate ions)[16–18] and of polarizabilities, etc., but the reverse of the usual order as oxidants based on standard potentials.[19] Probable trends in the reactivity of carbanions with free halogens and with trihalides are $I_2 > Br_2 > Cl_2$ and $I_3^- > Br_3^- > Cl_3^-$;[27] it

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(26) M. Eigen and K. Kustin, *J. Amer. Chem. Soc.*, **84**, 1355 (1962).

(27) (a) R. P. Bell and P. Engel, *J. Chem. Soc.*, 247 (1957); (b) R. P. Bell and D. C. Vogelsong, *ibid.*, 243 (1958).

does appear that rates toward enolate anions[6,27] are in the order $X_2 > X_3^- > OX^-$ or that hypochlorite is the least reactive of this group.

To compare aliphatic with arylacetylenes, we also investigated the base-catalyzed halogenation of MB. The ratio of the third-order rate constants at 25.3° of phenylacetylene to MB for chlorination and bromination is $k(\mathrm{ArC{\equiv}CH}):k(\mathrm{RC{\equiv}CH}) \simeq 5$. This is a modest effect. Recall that the overall rate constant is composite (eq 13). Any inductive and resonance effects which favor the aryl group in step 1 (K_a) would retard the halogenating step (k_b). Judging from our results, the effects on the two steps are roughly compensatory.

Turning to the activation parameters (Table IV), one must again take into account the composite nature of k_{obsd} (eq 13). We shall show that the interesting as-

$$\Delta S^{\ddagger}_{\mathrm{obsd}} = \Delta S_{\mathrm{a}} + \Delta S^{\ddagger}_{\mathrm{b}} \tag{14}$$

$$\Delta H^{\ddagger}_{\mathrm{obsd}} = \Delta H_{\mathrm{a}} + \Delta H^{\ddagger}_{\mathrm{b}} \tag{15}$$

pects of the observed parameters, except possibly for a constant term, may be identified with those obtained for the second-order process, the rate-determining step k_b. The equilibrium process in eq 3 may be regarded as deriving from the two dissociations

$$\mathrm{ArC{\equiv}CH} \rightleftharpoons \mathrm{ArC{\equiv}C^-} + \mathrm{H^+} \tag{16}$$

$$\mathrm{H_2O} \rightleftharpoons \mathrm{OH^-} + \mathrm{H^+} \tag{17}$$

Since $\Delta S_{17} = -19.2$[28] and ΔS_{16} is probably $\simeq -20$ also,[28] we guess that $\Delta S_a = \Delta S_{16} - \Delta S_{17} \simeq 0$ eu. On this basis, it would be expected that $\Delta S^{\ddagger}_{\mathrm{obsd}}$ should be characteristic of second-order, negative ion–negative ion associations. Judging from both similar and different charge types,[28] *e.g.*, $\mathrm{ClO^-} + \mathrm{ClO^-}$ with $\Delta S^{\ddagger} = -19.6$, $\mathrm{HSO_5^-} + \mathrm{Br^-}$ with $\Delta S^{\ddagger} = -24.8$, $\mathrm{BrCH_2COO^-} + \mathrm{S_2O_3^{2-}}$ with $\Delta S^{\ddagger} = -28.3$ eu, and $\mathrm{ArC{\equiv}CT} + \mathrm{OH^-}$ with $\Delta S^{\ddagger} \simeq -42$,[29] our values of $\Delta S^{\ddagger}$ in Table IV are quite reasonable.

The chlorination and bromination of phenylacetylene have about the same $\Delta S^{\ddagger}$, but differ by ~5 kcal/mol in $\Delta H^{\ddagger}$. This could be taken to mean that the mechanisms are identical but that the reactivities of hypochlorite and hypobromite are very different.

For the bromination of the four phenylacetylenes the variations in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are quite small. Nevertheless, a good fit to the Hammett equation was obtained, yielding ρ values of 0.718, 0.766, and 0.825 at 35.3, 25.3, and 15.3°, respectively. The temperature dependence of ρ is given by eq 18,[10,30] in which the coefficients were obtained by a least-squares fit.[30]

$$\rho = -(0.823 \pm 0.095) + (475 \pm 28)/T \tag{18}$$

Furthermore, since log k varies either as σ *or* as $1/T$, it can be given rigorously by a concise four-parameter equation.[30]

$$\log k = -(0.829 \pm 1.012)\sigma - (1847 \pm 52)/T + (481 \pm 315)\sigma/T + 7.21 \pm 0.23 \tag{19}$$

Equation 19 was obtained by a computer fit of the data by a program which also gives the probable errors in the coefficients.[31] Although the fit of 13 k's may seem to be too accommodating, the differences between observed and calculated k's (not log k) are <3%, except for one k which is 8.5%.

Just as k_{obsd} is composite, we have the corresponding breakdown

$$\rho_{\mathrm{obsd}} = \rho_{\mathrm{a}} + \rho_{-\mathrm{a}} + \rho_{\mathrm{b}} \tag{20}$$

Our $\rho_{\mathrm{obsd}} = 0.77$ at 25.3° turns out to be quite similar to ρ values for related but simpler processes. The hydroxide-catalyzed detritiation of phenylacetylenes at 25° in methanol–water (1/4) has $\rho = 0.77$.[29] The debromination of phenylbromoacetylenes with ethanethiolate in methanol at 25.65° has $\rho = 1.15$[13] (if the ρ values for the pK's of the benzoic acid in water ($\rho = 1.0$) and in methanol ($\rho = 1.54$) are used to make an adjustment for solvent,[32] $\rho_{\mathrm{calcd}} \simeq 0.75$ for water). Since the ρ values of these "model" processes for the initial abstraction reaction from $\mathrm{ArC{\equiv}CX}$ indicate that $\rho_a \simeq 0.75$, it would seem that $\rho_{-a} + \rho_b \simeq 0$. From what is known about the pattern of ρ values, it is reasonable to suppose that ρ_{-a} and ρ_b have opposite signs.[32] Although one can devise arguments to show why $|\rho_{-a}|$ and $|\rho_b|$ should be nearly equal and perhaps small, these are still speculative. It does seem interesting that ρ_{obsd} for bromination is dominated by the contribution of a fast preequilibrium step not directly involved with hypobromite.

Medium Effects. Because the third-order rate law (eq 2) was unusual, we believed that it was essential to sort out medium effects, if any, on our rate data. We found that high salt concentrations increased the rate constants by affecting the activity coefficients of both the ions and the phenylacetylene.

Little or no medium effect up to ~1 *M* sodium hydroxide was observed in the chlorination of phenylacetylene. At higher concentrations of sodium hydroxide (Table II) or with added salts, *e.g.*, sodium chloride or sodium sulfate, the rate constants for eq 1 were markedly increased (Table V). Each of these compounds exerts a specific effect and gives rise to its own plot of k *vs.* ionic strength. As for the dependence on base, it is known that the acidity function $(h_-)^{-1}$ rises sharply at the higher concentrations of hydroxide ion.[33,34] In fact, k_ψ follows K_w/h_- somewhat better than [OH⁻], but neither really accounts for the whole enhancement in k_{obsd} (Figure 5).

From our limited studies, it is apparent that both sodium and its gegenions increase the rate constant. This conforms qualitatively to the classical Debye–Hückel effect, $\log k \propto z_A z_B \sqrt{\mu}$, which has so often been illustrated in fan-shaped Brønsted–LaMer plots.[35] In this context, we have the parallel example of a positive salt effect of alkali hydroxides on the decomposition of hypobromite ion in which the rate law has the form $v = k[\mathrm{OBr^-}]^2$.[17] We also have the example of a nega-

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[28] Reference 23, Chapter 7.

[29] C. Eaborn, G. A. Skinner, and D. R. M. Walton, *J. Chem. Soc. B*, 922 (1966).

[30] (a) S. I. Miller, *J. Amer. Chem. Soc.*, **81**, 101 (1959); (b) G. S. Krishnamurthy and S. I. Miller, *ibid.*, **83**, 3961 (1961).

[31] G. Struble, "Non-linear Least Squares Curve Fitting Program," Statistical Laboratory and Computing Center, University of Oregon, Eugene, Oreg.; IBM 1620 Users Group Library.

[32] H. H. Jaffé, *Chem. Rev.*, **53**, 1911 (1953); P. R. Wells, *ibid.*, **63**, 171 (1963).

[33] C. H. Rochester, "Acidity Functions," Academic Press, New York, N. Y., 1970: (a) Chapter 7; (b) Chapter 3.

[34] J. R. Jones, *Progr. Phys. Org. Chem.*, **9**, 241 (1972).

[35] E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms," Academic Press, New York, N. Y., 1966, Chapter 1; K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, Chapter 5.

Table V. Salt Effects in the Reaction of Phenylacetylene with Chlorine and Sodium Hydroxide at 46.1 ± 0.1°

$10^5[C_6H_5C{\equiv}CH]$, *M*	[NaOH], *M*	$[CCl^-]$, *M*	[NaCl], *M*	$[Na_2SO_4]$, *M*	10^4k, M^{-2} min^{-1}
b	*b*	*b*			26
14	1.360	0.0470			38
12	1.672	0.0470			56
13	1.795	0.0245			53
14	1.672	0.0460			52
19	0.242	0.0473	0.625		40
19	0.242	0.0473	0.940		52
21	0.242	0.0473	1.041		54
11	0.282	0.0473	1.875		106
17	0.242	0.0468		0.625	53
14	0.282	0.0473		0.940	69
22	0.278	0.0468		1.000	77
12	0.282	0.0473		1.041	82

[a] Uncorrected for solvent expansion. [b] From Table III.

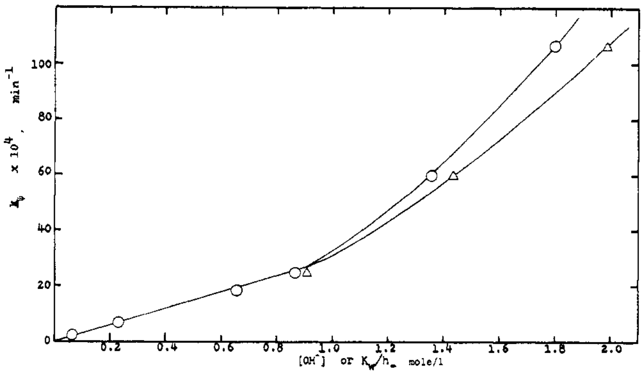

Figure 5. The reaction of phenylacetylene with sodium hypochlorite in aqueous sodium hydroxide at 25.3°: [OH⁻] (○); K$_w$/*h*$_-$ (△).

tive salt effect on the second-order reaction of hydroxide ion with acetone,[36] a model for eq 5, but not for eq 2. Evidently, our observed medium effects are in accord with the negative ion–negative ion process of eq 3.

The activity coefficient of phenylacetylene is also affected by the addition of salts to its aqueous solution. We studied this behavior by finding the solubility of phenylacetylene in sodium chloride solutions at 25° from measurements of the optical density at 244.5 nm. Over the range of our measurements, eq 21 held; *f* is

$$\log f_i/f_i^0 = \log s_i^0/s_i = k_S c_S \qquad (21)$$

the molar activity coefficient, *s* is the solubility of the phenylacetylene, $k_S = 0.196$ is the salting out parameter, and c_S is the molar concentration of salt.[33b] In 1 *M* sodium chloride, $f_i \simeq 1.5$ times the value of $f_i^0 = 1.0$ where $c_S = 0$. Since the activity coefficient of phenylacetylene enters the expression for the rate constant, *i.e.*

$$\log k_{\text{obsd}} = \log k_0 + \log f_A f_B f_C / f_{\ddagger} \qquad (22)$$

this is another component of the positive salt effect. However, a more detailed study than ours is needed to fit together all the medium effect contributions to the rate at $\mu > 1$.

Isotope Effect. Rate constants for the deuterioxide-catalyzed chlorination and bromination of phenylacetylene in deuterium oxide were determined by methods identical with those used in water solutions. The results are included in Table III.

To discuss the isotope effect, we begin with eq 13 and make explicit the origin of K_a in terms of the dissociation constants of water (K_W) and of phenylacetylene (K_A) in hydrogen and deuterium oxide (eq 16 and 17).

$$k^H/k^D = (K_W{}^D/K_W{}^H)(K_{CH}{}^H/K_{CD}{}^D)(k_b{}^H/k_b{}^D) \qquad (23)$$

The term, $K_W{}^H/K_W{}^D$, is known to be 7.1–7.4.[37] From the available pK_a data, which have been reported mainly for p*K*'s < pK_W in water, it is difficult to guess which one of the possibilities $K_{CH}{}^H/K_{CD}{}^D \lesseqgtr K_W{}^H/K_W{}^D$ is appropriate.[5a,38] A not implausible view of this system is the simple one, namely, that there is no isotope effect on either K_a or k_b in eq 13, that is, $K_{CH}{}^H/K_{CD}{}^D \simeq K_W{}^D/K_W{}^H = 7.1–7.4$ and $k_b{}^H/k_b{}^D \simeq 1.0$ in eq 23. If this view of the over-all process is correct, it would be a strong argument against having water (or —OH species) involved in bond making or breaking in the transition state associated with k_b.

Despite the absence of close precedents,[37] we are inclined to the opinion that there are, in fact, appreciable isotope effects, as between light and heavy water, on K_a and k_b of eq 13. As possible sources for K_a, consider the published rate constants for deprotonation of 9-methoxyfluorene (p$K \simeq 21$)[34] or 1,3,5-triphenyl-2,4-diaza-1,3-pentadiene and protonation of their anions in methanol.[39a,b] If complications are absent, one can derive $K_{CH}{}^H/K_{CD}{}^D = 1/2.4$ for the former and $\gtrsim 2.5$ for the latter. The first value is not the ratio we would have predicted on the basis of apparently related data on the protonation of perylene dianion in which $k_{-a}{}^H/k_{-a}{}^D$ is *ca.* 10 for water and *ca.* 7 for methanol.[39c] For all of these weak acids, the possibility of specific ion aggregation and solvent effects makes uncertain any straightforward interpretation of the isotope effect.[39] With respect to the second step, $C^- + OX^-$, effects on nucleophilic substitution, *e.g.*, $H_2O + RX$ or $HO^- + R_3S^+$, fall in the range $k^H/k^D = 1.3$ to 1.3^{-1},[37] so that a similar effect on k_b might be anticipated. Then there are solvent isotope effects for two-step processes: the hydroxide-promoted formation of ring oxides from 1,2- and 1,4-chloro alcohols in water has $k^H/k^D \simeq 0.65$;[40] the E1cb reaction in water of 9-fluorenylmeth-

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(36) J. R. Jones and S. C. S. Rao, *Trans. Faraday Soc.*, **63**, 120 (1967).

(37) R. L. Schowen, *Progr. Phys. Org. Chem.*, **9**, 275 (1972).

(38) E. Hogfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, **82**, 15 (1960).

(39) R. D. Guthrie, A. T. Young, and G. W. Pendygraft, *ibid.*, **93**, 4947 (1971); (b) G. Levin, C. Sutphen, and M. Szwarc, *ibid.*, **94**, 2652 (1972); (c) D. H. Hunter and S. K. Sim, *Can. J. Chem.*, **50**, 678 (1972).

(40) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Amer. Chem. Soc.*, **87**, 1553 (1965); C. G. Swain, A. D. Ketley, and R. F. W. Bader, *ibid.*, **81**, 2353 (1959); P. Ballinger and F. A. Long, *ibid.*, **81**, 2347 (1959).

anol has $k^H/k^D = 0.91$.[41] Note that these systems resemble ours in that there is a preequilibrium; they differ in that the rate-determining step is unimolecular rather than bimolecular, and that the activated complex is singly rather than doubly charged. On this basis, it would seem that our $k^H/k^D \simeq 1.0$ is the result of fortuitous cancellation rather than the absence of isotope rate effects. Unfortunately, we have no good models and/or reliable fractionation factors[37] to estimate all of the individual contributions. This means that the choice among mechanistic alternatives, which we shall make later for step b of eq 13, cannot be guided or limited by the measured isotope effect.

Halogenation Mechanism. Since the mechanism of the first step of process 3 seems to be firmly established, we turn to the subsequent steps which appear to be initiated by rate-determining attack of hypohalite ion on phenylacetylide ion. Several alternative paths to the final products are available, *e.g.*, eq 24–26. In these,

$$\begin{gathered}\mathrm{ArC{\equiv}C^- + XO^- \overset{a}{\rightleftharpoons} ArC{\equiv}CX + O^{2-}} \\ \mathrm{O^{2-} + H_2O \overset{b}{\rightleftharpoons} 2OH^-} \\ \mathrm{ArC{\equiv}C^- + XO^- + H_2O \overset{c}{\rightleftharpoons} ArC{\equiv}CX + 2OH^-}\end{gathered} \tag{24}$$

$$\begin{gathered}\mathrm{ArC{\equiv}C^- + XO^- \overset{a}{\rightleftharpoons} ArC{\equiv}CXO^{2-}} \\ \mathrm{ArC{\equiv}CXO^{2-} + H_2O \overset{b}{\rightleftharpoons} ArC{\equiv}CXOH^- + OH^-} \\ \mathrm{ArC{\equiv}CXOH^- \overset{c}{\rightleftharpoons} ArC{\equiv}CX + OH^-} \\ \mathrm{ArC{\equiv}CXO^{2-} + H_2O \overset{d}{\rightleftharpoons} ArC{\equiv}CX + 2OH^-}\end{gathered} \tag{25}$$

$$\begin{gathered}\mathrm{OX^- + H_2O \overset{a}{\rightleftharpoons} X(OH)_2^-} \\ \mathrm{ArC{\equiv}C^- + X(OH)_2^- \overset{b}{\rightleftharpoons} ArC{\equiv}CXOH^- + OH^-} \\ \mathrm{ArC{\equiv}C^- + X(OH)_2^- \overset{c}{\rightleftharpoons} ArC{\equiv}CX + 2OH^-}\end{gathered} \tag{26}$$

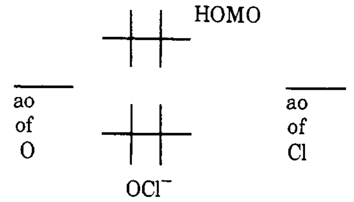
we make all steps reversible both because we shall consider these specifically and because we wish to point to the generality of such forward and reverse processes.

In evaluating these mechanisms we have tentatively rejected steps which appear to be implausible in at least one direction. Because of its high energy, we considered the formation of O^{2-} in (24a) improbable.[42] Since eq 24c and the reverse of eq 24c, 25d, and 26c are termolecular, we regard these as far less probable than alternative stepwise processes.

We are left with the mechanistic sequences (25a,b) *or* (26a,b), followed by (25c). Both of these involve doubly coordinated positive halogen ions, *e.g.*, $X(OH)_2^-$, $ArC{\equiv}CXOH^-$, and $ArC{\equiv}CXO^{2-}$. The first of these is obviously related to trihalide or analogous ions such as X_2OH^- and $XYOH^-$ which have in fact been proposed as intermediates in reactions of hypohalites.[17,26,43] Acetylide (like cyanide) may be regarded as a pseudo halide and, therefore, is included in the group. One can also point to stable haloacetylene–base complexes, $RC{\equiv}C{-}X\cdots B$, *e.g.*, phenyliodoacetylene with aniline or morpholine,[44] as models for the species we postulate. At this stage, we can find no compelling reasons to reject any of the species or steps involved either in path 25a–25b–25c, or in 26a–26b–25c.

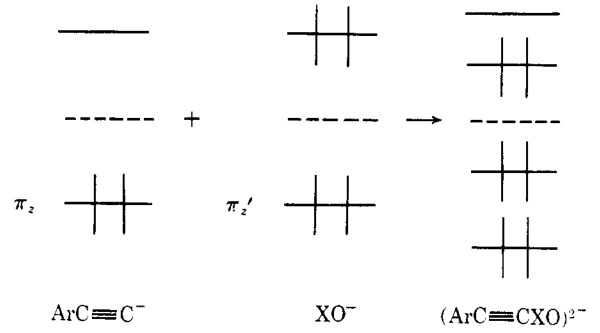
The doubly charged transition state leading to $ArC{\equiv}CXO^{2-}$ in 25a deserves comment. Although Rappe considered and dismissed a negative ion–negative ion transition state in the reactions of enolate ions with hypohalite,[45] such a species seems to be required by the observed kinetics.[5,6] There is no difficulty in finding precedents for reactions of similarly charged ions, *e.g.*, Br_3^- + enolates,[29] $XO^- + XO^-$,[16,17] $S_2O_3^{2-} + ClCH_2COO^-$,[28] $BrO^- + C_2O_4^{2-}$,[46] etc.

A second factor which bears on the existence of $ArC{\equiv}CXO^{2-}$ may be the so-called α effect.[47] Hypohalite is a reactive species, a "superphile," by virtue of the lone pairs of electrons on the atom adjacent to the attacking center.[47] In the ground state, the filled p atomic orbitals are thought to form two molecular orbitals, *e.g.*



Thus, the HOMO is relatively high and XO^- relatively reactive.[47] Such α effects have precedent in the reactions of hydroperoxide, hypohalite, etc., with 4-nitrophenylacetate.[47] Thirdly, both reacting ions, $ArC{\equiv}C^-$ and XO^- have no π stabilization energy on the simple Hückel MO model, but the intermediate, $ArC{\equiv}CXO^{2-}$, formed from them has twice the Hückel stabilization energy of butadiene (see Scheme I). In this diagram, we show only the π_z orbitals of $ArC{\equiv}C^-$, and π_z' for XO^-. We assume that the π_z and π_z' energy levels are very close; this would not change appreciably for a more exact treatment. Using a butadiene model for our intermediate, we find 1.24 β stabilization energy for π_z orbitals. This figure should be doubled, if all of the π electrons are considered. Therefore, the transition state ($ArC{\equiv}CXO^{2-}$) may not be unreasonable.

Scheme I



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[41] R. A. More O'Ferrall and S. Slae, *J. Chem. Soc. B*, 260 (1970).

[42] C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, London, 1966, p 502, give $\Delta H_f°(O^{2-}) = 217$ kcal/mol for reaction 24b in the vapor phase; $\Delta H \simeq -224$ kcal/mol for eq 24b.

[43] M. Anbar, S. Guttmann, and R. Rein, *J. Amer. Chem. Soc.*, **81**, 1816 (1959).

[44] J. U. Nef, *Justus Liebigs Ann. Chem.*, **308**, 264 (1899); P. L. Southwick and J. R. Kirchner, *J. Org. Chem.*, **27**, 3305 (1962); R. H. Baughman, *ibid.*, **29**, 964 (1964).

[45] C. Rappe, *Acta Chem. Scand.*, **22**, 219 (1968).

[46] K. C. Grover and R. C. Mehrotra, *Z. Phys. Chem. (Frankfurt am Main)*, **69**, 308 (1970).

[47] G. Klopman, K. Tsuda, J. B. Louis, and R. E. Davis, *Tetrahedron*, **26**, 4549 (1970); J. D. Aubort and R. F. Hudson, *Chem. Commun.*, 937 (1970).

Kinetic Order of Halogenations. It is necessary to emphasize that second-order kinetics for the halogenation of weak carbon acids is generally accepted and is often valid. Why then do we have a third-order rate law? Our answer in general terms is that these two rate laws reflect numerous mechanistic variations in halogenation mechanisms as one passes from very low to very high pH values. As the pH changes, the number, kind, and reactivity of halogenating species change. Of course, the same applies to the weak carbon acid species. Unless this is taken into account, qualitative observations and even rate laws may seem confusing; *e.g.*, phenylbromoacetylene can be produced from both acidic[21] and basic solutions containing phenylacetylene and bromine.

If we confine ourselves to the basic range, then the second-order kinetics can usually be associated with the fast reactions of the carbon acid anion with X_3^-, X_2, or XOH. Certain factors, however, may contribute to the incursion of the third-order rate law (eq 2). First, the weaker the carbon acid, the closer to the encounter rate will be the reaction of the carbanion (C^-) with water (k_{-a}). Therefore, competition from the halogenating step is less effective. Second, at high pH, $[XO^-] \gg [X_2]$, and the fast reaction of X_2 with C^- is negligible; thus the conditions for second-order kinetics are unfavorable. Third, chlorine is "slow," judging from the large gap in our hypobromite and hypochlorite rates; it is conceivable that in reactions with iodine, bromine, or chlorine at high pH, a given carbon acid may follow either a second- or third-order rate law, or perhaps both.

An exact balance between second- and third-order kinetics, or "equipartition" as we have called it,[6] occurs when the two terms in the denominator of eq 4 are equal, that is

$$[OX^-]_{ec} = [H_2O]k_{-a}/k_b \qquad (27)$$

Alternatively, the equipartition condition (ec) applies to that concentration of hypohalite ion above which second-order, and below which third-order, kinetics dominate. In the case of phenylacetylene at pH >11 and 25°, it can be shown that $[OCl^-]_{ec} = 3 \times 10^6$, $[OBr^-]_{ec} = 2 \times 10^2$, and $[OI^-]_{ec} = 9 \times 10\ M$.[6]

1-Dehalogenation of Positive Halogen. If process 1 is reversible and if the kinetics (eq 2) and the mechanisms we proposed are correct, then the simplest kinetics of the reverse process, *e.g.*

$$C_6H_5C{\equiv}CBr + 2OH^- \longrightarrow C_6H_5C{\equiv}CH + OBr^- + OH^- \qquad (28)$$

would be first order in haloalkyne and second order in hydroxide ion. For this reason, we thought that a study of 1-dehalogenation of haloalkynes could be instructive. Dehalogenations such as process 28 are well known in the chemistry of haloalkynes.[3,10,13,15,48] Indeed, abstractions of positive halogen by methoxide,[15] tributylphosphine,[48] or ethanethiolate[13] are first order in each reagent. What is special about process 28 is the requirement for third-order kinetics. An analogy for this unusual situation is found in the deiodination of iodomalonate esters, in which the contribution of the term $v' = k[I^-]^2\,[ICH(COOR)_2]$ to the total rate is important.[27a]

To reverse process 1, we sought a scavenger which would react with hypohalite as it formed and would not otherwise alter the system. Accordingly, we examined phenylbromoacetylene and several scavengers looking for the disappearance of λ_{max} 253.5 nm and the appearance of λ_{max} 244.5 of phenylacetylene at 26°. Suffice it to say that phenylbromoacetylene (10^{-4}–10^{-5} *M*) either did not react with sodium hydroxide (*ca.* 2 *M*) in *ca.* 2–15 hr at 26° in the presence of reductant (<0.05 *M*), *e.g.*, NO_2^-, $C_2O_4^{2-}$, H_2O_2, or cyclohexene, or it appeared to react directly with the scavenger, *e.g.*, $C_6H_5O^-$, $S_2O_3^{2-}$, N_2H_4, or SO_3^{2-}, to give products other than phenylacetylene. Clearly one must change the haloalkyne or the reaction conditions to reverse process 1.

However, when arsenious oxide was used as a scavenger, the product detected spectrometrically was phenylacetylene. Therefore, the kinetics was investigated briefly. The kinetic data, given in Table VI, indicate a curious rate law in the concentration range examined, namely, first order with respect to arsenious oxide, first order with respect to phenylbromoacetylene, and second order with respect to hydroxide ion.

Table VI. Rate Data for the Reaction of Phenylbromoacetylene with Arsenious Oxide in Aqueous Sodium Hydroxide at 26.0°

$10^3[As_2O_3]$, *M*	[NaOH], *M*	10^4k_ψ, sec^{-1}	*k*, $M^{-3}\ sec^{-1}$
3.13	0.26	5.98	2.83
3.13	0.12	1.29	2.86
1.56	0.26	2.87	2.72
1.56	0.064	1.79	2.80
3.13	0.062	0.34	2.83
0.78	0.26	1.47	2.78
6.25	0.052	0.47	2.76
		Mean	2.80 ± 0.04

$$-d[ArC{\equiv}CBr]/dt = k_\psi[ArC{\equiv}CBr] = k[ArC{\equiv}CBr][As_2O_3][OH^-]^2 \qquad (29)$$

When the concentration of hydroxide ion was larger than 0.26 *M*, the product differed from that of pure phenylacetylene, and we did not investigate the reaction further. Since it has been reported that a relatively large amount of the arsenious oxide must be in alkaline solution in the form AsO_2^-,[49] one of several possible mechanisms might be

$$\begin{gathered}
As_2O_3 + 2OH^- \xrightleftharpoons{\text{fast}} 2AsO_2^- + H_2O \\
2AsO_2^- \xrightleftharpoons{\text{fast}} As_2O_4^{2-} \\
ArC{\equiv}CBr + As_2O_4^{2-} \xrightarrow{\text{slow}} ArC{\equiv}C^- + AsO_2Br + AsO_2^- \\
ArC{\equiv}C^- + H_2O \xrightleftharpoons{\text{fast}} ArC{\equiv}CH + OH^-
\end{gathered} \qquad (30)$$

This is yet another unanticipated mechanism for 1-debromination.

Conclusion

Rather than focus on *1-halogenation* or *1-dehalogenation*, we prefer to emphasize positive halogen here. It has been known for many years that 1-haloalkynes,

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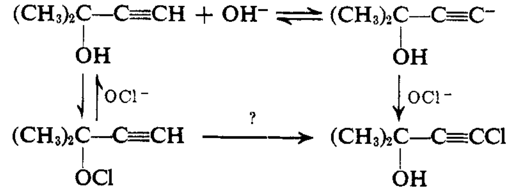
[48] J. I. Dickstein and S. I. Miller, *J. Org. Chem.*, **37**, 2168 (1972).

[49] B. A. Garrett, O. Holmes, and A. Laube, *J. Amer. Chem. Soc.*, **62**, 2024 (1940).

α-halocarbonyl compounds, polyhaloalkanes,[50] *N*-haloamines, *N*-haloamides, 1,2-dihalides,[51] etc., show positive halogen chemistry. To the extent that this information was qualitative (synthetic), each system could be regarded as novel and perhaps unique. Indeed, the recently discovered positive halogen chemistry of haloaromatics,[9] carbon tetrachloride,[52] *N*-chlorobenzotriazole,[53] etc., should be extremely useful. The time, however, is long overdue for a mechanistic–kinetic approach to all of these systems. Not only can we then expect consolidation of miscellaneous facts into a few patterns, but interesting areas for further exploration should be uncovered. We believe that the unconventional positive halogen mechanisms that we found or considered here for alkynes, ketones, and nitro compounds contribute to this unifying approach.[2,6,7]

Appendix

In the chlorination of MB, the rate data conformed to the pseudo-first-order behavior after *ca.* 15% reaction (Figure 6). The rate constant listed in Table III only applies to the well-behaved region. The overall process seems straightforward, since yields of chloroalkyne according to eq 1 exceed 90%[3b] and we find $OD_\infty = 0$ for hypochlorite after the reaction is over. The data can be rationalized if it is supposed that some hypochlorite was tied up fairly rapidly in an equilibrium. If the equilibrium on the left of eq 31 is rapidly established, the initial rate, based on hypochlorite, could appear to be high, but the later measurements would correspond to process 1. That hypochlorite could react faster with an alcohol (or alkoxide) than with a carbanion had been proposed for the halogenation of a ketone by hypohalite.[54] A closer model is the relatively rapid exchange of chlorine atom between *tert*-butoxide and hydroxide ions.[43]



$$\begin{array}{ccc} (CH_3)_2\underset{\displaystyle OH}{C}—C{\equiv}CH + OH^- & \rightleftharpoons & (CH_3)_2\underset{\displaystyle OH}{C}—C{\equiv}C^- \\ \downarrow\uparrow OCl^- & & \downarrow OCl^- \\ (CH_3)_2\underset{\displaystyle OCl}{C}—C{\equiv}CH & \xrightarrow{?} & (CH_3)_2\underset{\displaystyle OH}{C}—C{\equiv}CCl \end{array} \qquad (31)$$

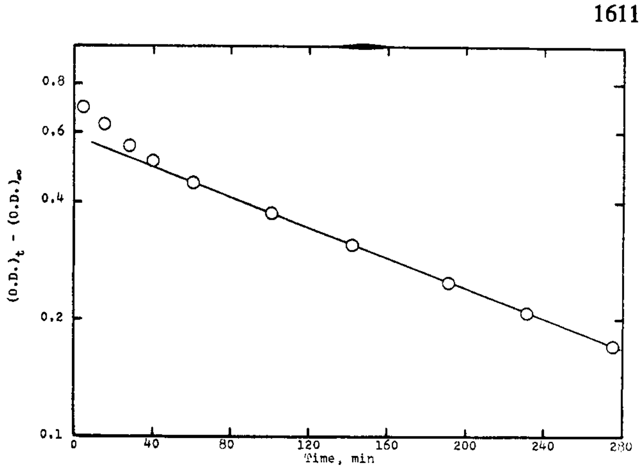


Figure 6. Pseudo-first-order plot for the reaction of 3-methylbut-1-yn-3-ol with sodium hypochlorite in water at 25.3°.

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(50) W. G. Kofron and C. R. Hauser, *J. Amer. Chem. Soc.*, **90**, 4126 (1968).

(51) W. K. Kwok and S. I. Miller, *J. Org. Chem.*, **35**, 4034 (1970), and citations herein.

(52) C. Y. Meyers, A. M. Malte, and W. S. Matthews, *J. Amer. Chem. Soc.*, **91**, 7510 (1969).

(53) C. W. Rees and R. C. Storr, *J. Chem. Soc. C*, 1475, 1478 (1969).

(54) F. Straus and R. Kühnel, *Chem. Ber.*, **66**, 1834 (1933).