8 g. (68% based on ketone not recovered) of the desired alcohol, b.p. 118–120° (11 mm.), $n^{25}{}_D$ 1.4860. The alcohol solidified upon standing.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.16; H, 12.85.

1-*t*-Butylcycloöctene.[42]—A solution of 3.2 g. of 1-*t*-butylcycloöctanol and 60 mg. of iodine in 25 ml. of toluene was heated under reflux for 17 hours. The water formed was removed with a Dean–Stark trap. The toluene was distilled and the residue was diluted with pentane. The pentane solution was washed with sodium thiosulfate solution followed by water. After drying the solution, the pentane was evaporated and the product was distilled; wt. 1.9 g. (66%), b.p. 88–89° (11 mm.), $n^{25}{}_D$ 1.4750.

Anal. Calcd. for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.39; H, 13.48.

N.m.r. spectra were obtained at 60 mc. in deuteriochloroform solvent with internal tetramethylsilane reference.

[CONTRIBUTION NO. 1038 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

The Mechanisms of Substitution of Propargylic Halides. 3-Bromo-3-methyl-1-butyne[1]

BY V. J. SHINER, JR.,[2] AND JOSEPH W. WILSON[3]

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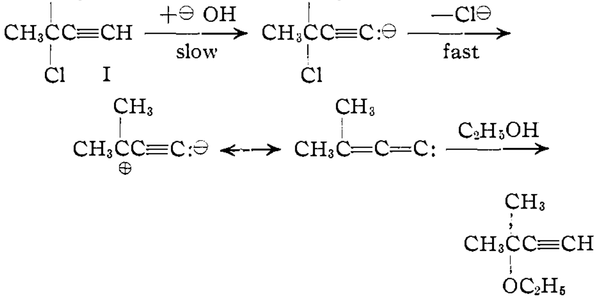
A study of the kinetics, salt effects, deuterium exchange with the solvent and product proportions shows that the base-promoted solvolysis of 3-bromo-3-methyl-1-butyne in 80% aqueous ethanol proceeds through at least three stages involving successively the conjugate base, the zwitterion-carbene, and the products, ethyl ether and carbinol. The initially neutral solvolysis involves the usual carbonium ion mechanism.

Introduction

A special mechanism involving an unusual zwitterion-carbene intermediate has been proposed by Hennion and Maloney[4,5] for the *second-order* reaction of a *tertiary* propargylic halide, 3-chloro-3-methyl-1-butyne (I) with sodium hydroxide in "80%" aqueous ethanol.



Two observations formed the original basis for this proposal: (1) a comparison of the kinetic behavior of this chloride with that of saturated analogs and (2) the nature of the products of the second-order reaction. The saturated analog, *t*-amyl chloride, was found to solvolyze in initially neutral "80%" aqueous ethanol at 25° *61 times faster* than the acetylenic chloride. Whereas the addition of sodium hydroxide at moderate concentration is known not to affect drastically the solvolysis rate of simple tertiary alkyl halides,[6] Hennion and Maloney noted that the propargylic halide I showed a fairly rapid second-order reaction with added base. The chief product of this process, isolated in 56.6% yield, was the ethyl ether of 2-methyl-3-butyne-2-ol.

Because the Hennion mechanism requires the presence of an unsubstituted ethynyl group (—C≡C—H), the report by Burawoy and Spinner[7] that the compound related to I by replacement of the acetylenic hydrogen with a methyl group (4-chloro-4-methyl-2-pentyne, II) showed "saturated behavior" (a fast first-order reaction that was unaffected by added base) in its replacement reaction was later cited by Hennion[5] as providing strong supporting evidence for his mechanism. Without commenting on Hennion's earlier proposal Burawoy and Spinner[7] had, however, suggested that "the alkaline hydrolysis of 3-chloro-3-methyl-1-butyne in 80% aqueous ethanol. . .occurs by a bimolecular (SN2) mechanism."

Indeed, although the arguments for the Hennion mechanism seemed most reasonable, they did not appear completely compelling and a case could be advanced for the belief that the SN2 mechanism obtained. First, the relationship between the nature of the products and the mechanism of their formation is ambiguous because of the equilibrium:

$$CH_3CH_2\text{-}O^- + H_2O \rightleftharpoons CH_3CH_2\text{-}OH + {}^-OH$$

It has been estimated that only about 60% of the stoichiometric base concentration in 80% ethanol is in the form of the hydroxide ion.[8,9] Since ethoxide may be a better nucleophile than hydroxide toward saturated carbon, as it is toward carbonyl carbon,[10] a direct displacement predominantly by ethoxide ion cannot be ruled out. Second, there is the possibility that the ethynyl group with its greater electronegativity and smaller size than an alkyl group could promote an SN2 attack. Several authors have argued that electron-withdrawing substituents

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[1] (a) Taken from the thesis submitted by Joseph W. Wilson to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. (b) Presented in part before the Division of Organic Chemistry at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 3, 1961. (c) Supported in part by Grant G 5062 from the National Science Foundation, Washington, D. C.

[2] Alfred P. Sloan Research Fellow.

[3] Dow Fellow, 1960–1961.

[4] G. F. Hennion and D. E. Maloney, *J. Am. Chem. Soc.*, **73**, 4735 (1951).

[5] G. F. Hennion and K. W. Nelson, *ibid.*, **79**, 2142 (1957).

[6] C. A. Bunton and B. Nayak, *J. Chem. Soc.*, 3854 (1959).

[7] A. Burawoy and E. Spinner, *ibid.*, 3752 (1954).

[8] E. F. Caldin and G. Long, *ibid.*, 3737 (1954).

[9] R. G. Burns and B. D. England, *Tetrahedron Letters*, **24**, 1 (1960).

[10] M. L. Bender and W. A. Glasson, *J. Am. Chem. Soc.*, **81**, 1590 (1959).

facilitate this mechanism.[11] Finally, the lack of a second-order reaction between II and base could be rationalized on the basis that the first-order reaction is so rapid (half-life of 0.375 hr. as compared to 770 hr. for I) that competition by a slower SN2 reaction (half-life of I for the second-order reaction with 0.05 *M* base is 14 hr.) is not observed.

Nevertheless, a detailed comparison of the rates of known SN2 processes in saturated primary halides with those in primary propargylic halides shows the second-order reaction of I to be unusually fast for an SN2 process. Also, Hartzler[12] obtained evidence for the existence of the allene-carbene intermediate by showing that it could be trapped by olefins, under non-solvolytic conditions, to yield alkenylidene cyclopropanes. A more detailed investigation of this reaction was therefore undertaken.

Results and Discussion

Deuterium Exchange.—In a typical experiment the acetylenic halide was mixed with a partial equivalent of sodium metal previously dissolved in "80%" ethanol-*d*-deuterium oxide mixture. After the base was consumed the acetylenic ether product and the unreacted halide were isolated by a combination of reduced pressure distillation and gas chromatography and analyzed for deuterium. In each of the several experiments of this type performed, on both acetylenic chloride and bromide with base quantities as low as $^1/_{16}$ equivalent, complete exchange of the acetylenic proton with solvent deuterium was observed.

TABLE I

BASE-CATALYZED DEUTERIUM EXCHANGE BY 3-CHLORO- AND 3-BROMO-3-METHYL-1-BUTYNE

Halide	"Equivalents" of base	% D[a]	
		Halide	Ether
RCl	$^1/_4$	90	93
RCl	$^1/_8$	91	97
RCl	$^1/_8$[b]	84	[c]
RBr	$^1/_8$	81[d]	89
RBr	$^1/_{16}$	87	[c]
RCl	0	2	
RBr	0	1	2

[a] Atoms of D × 100 per molecule. [b] Neutralized after 8 min. [c] Unavoidably lost. [d] Impure sample (64% RBr); analysis corrected for impurity.

As shown in Table I the heavy isotopic contents in the active position of the recovered halide and ether were uniformly between 85 and 95% of that in the active positions in the starting solvent. This slight deviation should be ascribed not to incomplete exchange but to several other sources, including hydrogen introduced by the organic halide itself, spurious pickup of moisture, a possible isotope effect on the exchange equilibrium, some small loss of deuterium in the chromatographic separation and some error in deuterium analyses. Thus, the base-catalyzed exchange of the acetylenic protons of both 3-chloro- and 3-bromo-3-methyl-1-butyne with mixed ethanol-*d* and deuterium oxide is appreciably faster than the base-promoted solvolysis. Although the rate of exchange was not measured, a lower limit of about sixteen times the solvolysis rate was established. If the Hennion mechanism applies, this result requires reformulation to involve a rapid equilibrium, rather than rate-determining, formation of the conjugate base. The rate-determing step must come later. This evidence does not, of course, rule out an SN2 process as the exchange might conceivably be just a side reaction. It does require that if the Hennion mechanism applies, it must be specific base catalyzed[13] under these conditions.

Salt Effects.—Perhaps the most compelling and classic evidence for the SN1 mechanism has been the observation of the "mass-law" effects of added common-ion salts.[14] Since the Hennion mechanism, modified to include equilibrium formation of the conjugate base, is simply an SN1 ionization of the conjugate base, the observation of a mass-law effect would be a conclusive proof of its validity. In Table II are summarized the salt effect data obtained in this investigation. In the presence of 0.22 *M* sodium bromide, the initial rate of the second-order reaction of 3-bromo-3-methyl-1-butyne is depressed by about 40% below the rate in the absence of added salt. That this is not a normal salt effect is shown by the observation that the same concentration of either sodium perchlorate or sodium nitrate depresses the rate only about 18%. The expected normal salt effect is a depression of rate because the transition state will have a more diffuse charge than the hydroxide ion of the initial state.[14]

TABLE II

SALT EFFECTS ON RATE OF REACTION OF 3-BROMO-3-METHYL-1-BUTYNE[a] WITH SODIUM HYDROXIDE IN "80%" ETHANOL AT 25°

Added salt	Concn., *M*	Rate coefficient[b]
None	. .	11.5, 11.6, 11.7
$NaNO_3$	0.22	9.5, 9.5
$NaClO_4$	.22	9.4
$NaClO_4$	.50	8.4
NaCl	.22	8.4
NaBr	.22	7.0
NaBr	.50	5.0

[a] Initial concentration about 0.05 *M*. [b] Integrated second-order rate coefficients extrapolated to initial value; units are 10^{-3} liter/mole/sec. The several values in some lines represent independent experiments and indicate the reproducibility obtained.

These results present a pattern quite similar to that observed by Hine and co-workers for the basic hydrolysis of chloroform[15,16] and the analogy between the two reactions is remarkably close. In the chloroform reaction, sodium nitrate, perchlorate and fluoride caused identical rate depressions, but sodium chloride caused an even larger one. In addition, bromide and iodide salts depressed the initial rate of destruction of base to an extent which was correlated with their relative nucleophilicities. In the present study it is similarly found that sodium chloride causes an initial rate depression

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[11] This question has been reviewed by A. Streitwieser, Jr., *Chem. Rev.*, **56**, 571 (1956); see pp. 586–587.

[12] H. D. Hartzler, *J. Am. Chem. Soc.*, **81**, 2024 (1959); **83**, 4990 (1961).

[13] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, Chapt. 8.

[14] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 360 ff.

[15] J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950).

[16] J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

between that of sodium bromide and the non-nucleophilic salts.

There exists the *a priori* possibility that the pattern of observed salt effects could be characteristic of an SN2 process influenced by the salts through their effect on the extent of ion pairing of the ethoxide ion. Since measurements of ion-pairing constants for the relevant salts in "80%" aqueous ethanol are not available, this explanation cannot be explored in detail but seems, on the basis of related measurements, highly unlikely. The dielectric constant of "80%" ethanol at 25°, 34.9,[17] is comparable to that of absolute methanol, 32.4, where ion pairing is important[18] and also to that of 50 wt. % aqueous dioxane, 35.85, where ion pairing is insignificant.[19] The relative ion-pair-forming abilities of nitrate, bromide and chloride ions, crucial to the specific salt effect argument, are rated in methanol differently in two different studies.[18,20] It would seem that the aqueous dioxane solvent would be more nearly similar in electrolytic solvent properties to the aqueous ethanol of similar dielectric constant than would absolute methanol. The similar effects of sodium nitrate and sodium perchlorate also argue against the explanation based on ion pairing and special salt effects.

TABLE III

INTEGRATED SECOND-ORDER RATE COEFFICIENTS FOR REACTION OF 3-BROMO-3-METHYL-1-BUTYNE (III)[a] WITH NaOH[a] IN "80%" ETHANOL AT 25°

Added salt	Concn., M	k_2 at various % reaction[b] 0%	50%	75%
None		11.6	10.8	10.1
$NaNO_3$	0.22	9.5	8.8	8.3
NaCl	.22	8.4	7.8	6.7
NaBr	.22	7.0	6.2	4.5
NaBr	.50	5.0	4.1	1.9

[a] Initial concentration about 0.05 M. [b] Integrated second-order rate constants; units of 10^{-3} liter/mole/sec.

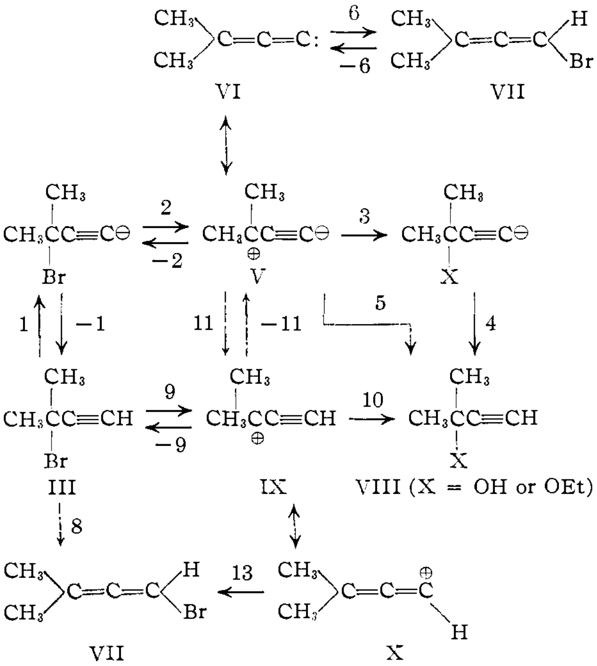

Fig. 1.

An important feature of these kinetic experiments, related to the salt effect problem, is their deviation from precisely second-order behavior. The simple integrated second-order rate constants fall off as the reaction progresses, as indicated in Table III. Three *a priori* reasonable explanations of this phenomenon are: (1) return to the acetylenic bromide III *via* routes −2, −1 of Fig. 1; (2) isomerization to the slowly reacting allenic bromide, VII *via* route 6 of Fig. 1; and (3) SN2′ attack yielding the isomeric allenic bromide VII *via* route 8. This latter effect, although it could not account for initial rate depression by added bromide ions, might account for the fall-off in the second-order rate coefficients. However, SN2′ attack should be independent of base concentration and would proceed at the same rate in both first- and second-order reactions. The fall-off observed in the first-order reaction is so slow that a similar process occurring along with the second-order reaction would have a negligible effect. The problem of distinguishing between common-ion return to acetylenic bromide and isomerization to allenic bromide would be solved most directly by either isolating the allenic bromide from the reaction mixture near the end of the solvolysis or establishing its absence. Young, Winstein and Goering[21] have successfully applied this technique in their study of the solvolysis and isomerization of α,α-dimethylallyl chloride (the allylic analog of our propargylic system). With the allylic compound rearrangement to the primary isomer was essentially complete after acetolysis had proceeded only to the extent of 30%. In the present example, even when the solvolysis was followed to greater than 90% completion, the instantaneous rates never decreased completely to the value known from independent experiments to be characteristic of the allenic bromide. The yield of allenic bromide at any time must only be about 5–10% at best. The extent of the fall-off in integrated second-order rate coefficients is too large to be explained alone in terms of return to the starting bromide. Thus, the increase in bromide ion concentration from the beginning of the solvolysis to the end is only about 0.05 M, yet the fall-off is most marked in the run with an initial added concentration of 0.5 M sodium bromide, somewhat less with 0.22 M initial sodium bromide, still less if no salt is added. Accordingly, application of an integrated rate law taking into account the mass-law effect and assuming the initial rate depression by added sodium bromide to be due to this alone also gave decreasing rate coefficients (see Table IV). An integrated rate law, assuming isomerization to the allene by external return, but neglecting the mass-law effect and the slower reaction of the allene bromide, over-corrected for the fall-off (see Table IV) and gave slightly rising rate coefficients

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[17] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," A.C.S. Monograph No. 137, 3rd. edition, Reinhold Publishing Corp., New York, N. Y., 1958, p. 161.

[18] E. C. Evers and A. G. Knox, *J. Am. Chem. Soc.*, **73**, 1739 (1951).

[19] C. A. Kraus, *J. Phys. Chem.*, **58**, 673 (1954).

[20] J. D. Reinheimer, W. F. Kieffer, S. W. Frey, J. C. Cochran and E. W. Barr, *J. Am. Chem. Soc.*, **80**, 164 (1958).

[21] W. G. Young, S. Winstein and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1958 (1951).

TABLE IV

INTEGRATED RATE COEFFICIENTS FOR REACTION OF 3-BROMO-3-METHYL-1-BUTYNE (III) WITH NaOH

Reacn., %	Second order	Mass law corrn. only	Isomzn. corrn. only
6.14	6.92	6.90	7.02
13.26	6.98	7.03	7.13
18.60	6.81	6.81	7.02
25.34	6.79	6.83	7.14
32.61	6.63	6.69	7.13
40.09	6.55	6.64	7.26
46.43	6.35	6.44	7.29
51.20	6.10	6.19	7.23
56.36	5.95	6.04	7.40
61.47	5.71	6.82	7.58
68.47	5.23	5.33	8.06

but a better over-all fit to the data. The rate expression allowing for mass-law effect, isomerization and reaction of the isomer proved too difficult to integrate. Application of the simpler rate laws indicates that most of the fall-off must be due to isomerization, but that some concurrent mass-law return cannot be ruled out.

Table III shows how the fall-off in integrated second-order rate coefficients depends on the nature and amount of added salt. The order obtained is: no salt $\sim$ 0.22 M $NaNO_3$ $<$ 0.22 M NaCl $<$ 0.22 M NaBr $<$ 0.50 M NaBr. Thus the fall-off increases with concentration and nucleophilicity of the added anion. This result opposes an explanation of the salt effects in terms of ion pairing referred to above. Such an explanation requires that the initial rate should be dependent on the nature of the added salt but the fall-off should not; the same salt, sodium bromide, is produced as the reaction proceeds, regardless of the nature of the initially added salt.

Product Formation.—Although Hennion[4] reported the isolation of the ethyl ether of 2-methyl-3-butyne-2-ol in 56.6% yield, no estimation of the total yield of this or any of the by-products was obtained. Using distillation and gas chromatography we have determined the relative proportions of the three main products, ether, carbinol and ene-yne (2-methyl-1-butene-3-yne), for both the neutral and basic solvolysis reactions. It was not determined precisely what total yield this represents, but no other major nonsolvent peaks appeared on the gas chromatograms. The results are given in Table V.

TABLE V

RELATIVE MOLAR PRODUCT PROPORTIONS FROM FIRST- AND SECOND-ORDER REACTIONS OF 3-BROMO-3-METHYL-1-BUTYNE IN "80%" ETHANOL AT 25°

Order	Ether	Carbinol	Olefin
Second	90	7	3
First	43	22	35

The large difference in product proportion obtained for the two reactions indicates that their product-forming steps must be different. Since we show below that the first-order reaction proceeds through a carbonium ion intermediate, the zwitterion-carbene intermediate produced in the second-order reaction must either give the products in a concerted step (Fig. 1, step 5) or add the nucleophilic fragment first (steps 3 and 4, Fig. 1). Protonation of this intermediate (step 11) would lead to a carbonium ion which should then yield products in the same proportion as in the neutral solvolysis. The difference in product proportions is apparently dictated by the greater difference in reactivity, and therefore selectivity, of the two intermediates, the carbonium ion and the zwitterion-carbene. The latter is more stable and more selective, because the allene-carbene resonance contributing form VI contains no formal charges and therefore contributes more importantly to the structure V $\leftrightarrow$ VI than the allene carbonium ion X does to the structure IX $\leftrightarrow$ X.

An attempt was made to trap the intermediate in the base-promoted reaction with azide ion. This species is too weakly basic to promote the Hennion mechanism effectively, but in the presence of hydroxide ion might act to trap the intermediate and produce a different product without altering the rate. If this behavior actually is characteristic, its observation was prevented by the incursion of a *second-order* reaction between azide and the propargyl bromide, as shown by the data in Table VI. It is important to note that this second-order reaction is not shown by acetate ion which has a basicity similar to that of azide, but is a much weaker nucleophile. Also, hydrazoic acid, which would reduce the pH of the azide solution, does not affect the rate of the reaction between azide and propargyl bromide. Since the Hennion mechanism must be specific base-catalyzed, the azide ion is acting in some other way, probably by an SN2 or SN2′ displacement. Several attempts at characterization of the product failed (see Experimental). Additional work on this and/or related reactions is planned.

TABLE VI

RATE COEFFICIENTS FOR BROMIDE ION FORMATION FROM 3-BROMO-3-METHYL-1-BUTYNE IN "80%" ETHANOL

Added salt(s)	k_1, 10^{-6} sec.$^{-1}$	k_2, 10^{-3} l. m.$^{-1}$ sec.$^{-1}$
None	4.6	
0.05 M NaOH		11.5
.06 M NaOAc	5.0	
.047 M NaN_3	13.4[a]	0.27[a]
	3.9[b]	.17[b]
.10 M NaN_3	20.9[a]	.21[c]
.05 M NaN_3 .05 M HN_3 .05 M $NaClO_4$	13.9[a]	
.10 M $NaClO_4$	5.4	
.5 M $NaClO_4$	7.3	
.5 M NaBr	5.6[a]	

[a] Extrapolated initial rate coefficients from application of integrated rate equation; coefficients not constant. [b] Obtained by graphical separation into first- and second-order components. [c] Coefficient reasonably constant through first half-life.

The zwitterion-carbene can be classed as an ambident species which reacts, apparently first as an electrophile, to add a nucleophilic group at either the tertiary propargylic center or at the primary allenic center to give the conjugate base of the product. Our evidence indicates that the most reactive end of the ambident molecule is different for different nucleophiles. Bromide ion, as mentioned above, apparently reacts mainly to give the allene structure, whereas water and ethanol react mainly to give the propargylic product. Hartzler[22] observed that, under different reaction conditions, this intermediate reacts as the allene carbene in attacking styrene to give a cyclopropane derivative and remarks "... the reactions of the zwitterion-carbene with nucleophiles are unusual in that attack can occur at either the α- or γ-carbon. . .no satisfactory explanation for the differentiation in reaction paths is available at present. . .." This point is obviously worthy of further study.

The First-order Mechanism.—Three *a priori* possibilities suggest themselves: (1) a solvent-promoted mechanism involving the zwitterion intermediate, using either routes 1, 2 and 5 (Fig. 1) or 9, 11 and 5; (2) a bimolecular displacement by solvent (suggested by Burawoy and Spinner); and (3) an SN1 mechanism. The first possibility is rejected on the evidence that neither starting material nor product show incorporation of deuterium as the reaction proceeds in a deuterated ethanol–water mixture. The solvent SN2 mechanism can be rejected on the basis of the kinetic effects of added salts recorded in Table VI. These demonstrate a normal positive salt effect and a small mass-law effect and are consistent only with the SN1 mechanism. It is of interest to consider why the SN1 solvolysis in this example, which proceeds through a resonance-stabilized carbonium ion, goes about 60 times slower than the saturated analog. By application of the Taft[23] equation using the σ^* constant $+1.35$ for phenylethynyl[23] (in lieu of the one for ethynyl, which is not available) and the value for ρ^* -3.29 for solvolysis of *t*-alkyl halides,[24] it was estimated that the inductive effect slows the reaction by about $10^{4.5}$ and the resonance effect (and steric, if any) accelerates it by about $10^{2.9}$. This compares with a calculated inductive retardation of the solvolysis of α,α-dimethylallyl chloride by about $10^{1.4}$ and a resonance acceleration of about 10^4. Thus the resonance acceleration by an ethynyl group is about 10 times less than that of the vinyl group. This comparison corresponds qualitatively with the results of Kochi and Hammond[25] who proposed that ethynyl conjugates less than vinyl because the second pair of π-electrons shortens the bond and increases the overlap between the adjacent π-orbitals making overlap with any neighboring system less.

After this work was first reported[1b] the results of an investigation of the rates and equilibrium constants for proton abstraction from monosubstituted acetylenes came to the authors' attention.[26a] From this work the rate of proton abstraction from III can be estimated within a factor of about two or three to be 10^3 l. mole.$^{-1}$ sec.$^{-1}$.[26b] This is about 10^3 times faster than the minimum value determined in this work and supports the conclusion that carbanion formation from III is rapid in comparison to hydrolysis. The equilibrium constant for formation of the conjugate base from III and hydroxide ion is estimated[26b] to be about $10^{-6.5}$. From this and the present work, the first-order rate constant for solvolysis of the conjugate base of III is estimated to be about 10^3 sec.$^{-1}$, an acceleration of about 10^9 over the solvolysis rate of III itself. These figures also suggest that the solvolysis of the conjugate base does not proceed at an appreciable rate in acetate or azide buffer and are in accord with the lack of acceleration of the solvolysis by acetate.

Experimental

Gas Chromatography.—A Fisher–Gulf partitioner maintained at 50° was used. Two 7-foot 0.25″ o.d. stainless steel columns, one packed with Tide and one packed with Octoil-S supported on firebrick, were employed at a flow-rate of 50 ml. of helium per min. The machine was equipped with a mechanical integrator.

Materials. Solvent.—Two-liter batches of 80% (by volume) ethanol were prepared by weighing the appropriate amounts of conductivity ethanol and water on a large analytical balance to obtain a solvent composition of 75.90 weight-per cent. ethanol. A carbonate-free solution of sodium hydroxide in this solvent was prepared by the method of Hennion and Nelson.[5] Two grams of sodium hydroxide was dissolved in 13 ml. of 80% ethanol and filtered through a Gooch crucible. The filtrate was washed into a one-liter volumetric flask which was filled to the mark with 80% ethanol to obtain a solution approximately 0.05 *M* in sodium hydroxide.

Salts.—Analyzed, reagent grade sodium chloride and potassium acid phthalate were dried and used without further purification. Reagent grade sodium bromide and sodium nitrate were recrystallized from water and dried at 140° *in vacuo*. Sodium perchlorate was recrystallized from a dioxane–water mixture (33 g. dissolved in 36 ml. of water and 200 ml. of dioxane) and dried *in vacuo* at 140° for 24 hours.[27]

Standard Solutions.—Aqueous, carbonate-free, 0.05 *M* sodium hydroxide was standardized with potassium acid phthalate in deionized water to the phenolphthalein end-point. The normality of the aqueous 0.05 *M* hydrochloric acid was obtained by titrating with standard sodium hydroxide several 10-ml. samples of the acid in 100 ml. of ice-cold acetone containing 2 drops of lacmoid indicator. It was found that this amount of water did not affect the sharp change, from red to blue, that is observed for this indicator in dry acetone. Because the analyses of samples from the kinetic experiments required acetone as a solvent, hydrochloric acid was standardized in that solvent. Because potassium acid phthalate is not soluble in acetone, water was the solvent used for the standardization of the base. Appropriate indicator blanks for the two titrations were determined; 10-ml. samples of the aqueous acid were titrated under both conditions and satisfactory agreement was obtained if corrections were made for the blanks.

Ethanol-*d* was prepared by the procedure of Shiner and Smith.[28]

2-Methyl-3-butyne-2-ol was kindly supplied by the Air Reduction Co. and by the Reilly Tar Co.

3-Chloro-3-methyl-1-butyne was prepared by the method of Hennion and Nelson.[5]

3-Bromo-3-methyl-1-butyne. A. Preparation.—A modification of the method of Moulin was used.[29] Phosphorus tribromide (72.0 g., 0.27 mole) was added dropwise over a period of 2 hours to 42.4 g. (0.50 mole) of 2-methyl-2-butyne-2-ol (b.p. 103–103.5°) stirred under an atmosphere of nitrogen. The temperature was maintained at 0–5°, during the addition and while the reaction was stirred for an hour afterward.

B. Purification.—The reaction mixture contained both the acetylenic bromide and the isomeric allenic bromide.

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[28] V. J. Shiner, Jr., and M. L. Smith, *ibid.*, **83**, 593 (1961).

[29] F. Moulin, *Helv. Chim. Acta*, **34**, 2416 (1951).

These were separated by a combination of distillation and vacuum line fractionation. Distillation at atmospheric pressure proved to be effective, because as the acetylenic bromide boiled up in the head of the fractionating column much of the allenic bromide decomposed in the pot. Because the acetylene is also thermally sensitive, the distillate contained some allenic bromide and the elimination product, 2-methyl-1-butene-3-yne.

The reaction mixture was decanted from the sirupy acid layer into a 100-ml. round-bottomed flask, and attached to the vacuum line. To remove hydrogen bromide the flask was maintained at $-63°$ (chloroform slush) and was opened first to the fore-pump alone (capable of maintaining a pressure of 0.2–0.3μ) for 2 hours. Subsequently, after cooling to $-78°$, it was connected to the diffusion pump (0.001μ) for 4 hours. The remaining volatile components were transferred out of this flask to another, which was then removed from the line.

Anhydrous potassium carbonate was added to the 50-ml. round-bottomed flask containing the bromide mixture and a magnetic stirring bar. The system was flushed with nitrogen prior to distillation of the bromide through a 15 × 500 mm. fractionating column packed with $^{3}/_{32}''$ glass helices. The bromide was collected at about 97° (reported[29] b.p. 88–89°), although the temperature was not quite constant due to the continual production of the low-boiling "ene-yne"; yield 17.75 g., 24%. The distillate was attached to the vacuum line, degassed and transferred to a fractionation train of four traps. To remove the less volatile allenic bromide, the mixture, excepting a 0.5-ml. residue enriched in allenic bromide, was transferred out of a trap at $-23°$ into a trap at $-196°$. To remove the more volatile "ene-yne," the mixture was pumped into a trap at $-63°$ designed to condense the acetylenic bromide. This trap was followed by one cooled to $-196°$ and designed to condense the "ene-yne." Two passages were necessary to reduce the allene concentration and four were necessary to remove the "ene-yne."

This method may represent the first preparation of a pure sample of 3-bromo-3-methyl-1-butyne. Its infrared spectrum corresponds closely to that of the known 3-chloro-3-methyl-1-butyne. In a large scale reaction with basic 80% ethanol, the main reaction product, the ethyl ether of 2-methyl-3 butyne-2-ol, was identified by its retention time (gas chromatography), boiling point, and infrared spectrum, all of which were identical with the same properties of an authentic sample.[4]

Anal. Calcd. for C_5H_7Br: Br, 54.35. Found: Br, 54.02.

1-Bromo-3-methyl-1,2-butadiene was prepared by the method of Jacobs and Brill.[30] 3-Bromo-3-methyl-1-butyne (5.7 g., 0.039 mole), 0.52 g. of cuprous bromide, 0.36 g. of ammonium bromide, 0.93 g. of 48% hydrobromic acid and 20 mg. of copper-bronze powder were mixed together and stored for about one week at 5° with occasional shaking. When the acetylenic bromide peak on a gas chromatogram of the mixture had nearly disappeared, the volatile products were introduced into the vacuum line. The major impurity, 2-methyl-1-butene-3-yne, was removed by the same purification procedure used to remove it from the acetylenic bromide. Seven such passages into a trap cooled to $-63°$ failed to remove small amounts of other low-boiling impurities. The infrared spectrum of the product had in common with the spectrum of its acetylenic isomer several strong peaks which are due to the *gem*-dimethyl groups[31] at 3.2 – 3.4, at 6.9 – 7.0, at 7.3 – 7.5 and at 8.6 μ. It did not possess either of the characteristic acetylenic bands at 3.0 and at 4.7μ but showed the very strong C=C=C stretching band at 5.1μ.[32]

Deuterium Exchange.—In a typical experiment 3-bromo-3-methyl-1-butyne (6.48 g. 0.044 mole) was added to a solution of 0.064 g. of sodium (0.0028 mole) in 35 ml. of 80% ethanol-*d*-D_2O. After standing several hours at room temperature, the reaction mixture was distilled at reduced pressure through a 10 × 390 mm. fractionating column packed with $^{1}/_{16}''$ glass helices and fitted with an ice-cooled condenser. The azeotropic mixture boiling between 16° and 24° at about 50 mm. pressure was extracted with water and dried. This mixture of acetylenic ether and bromide was separated by gas chromatography on the Octoil column. Although an analytical scale column was used, the separation of large samples (0.2 ml.) proved possible, because the peaks of the two compounds were widely separated. In U-tubes cooled to $-78°$, two fractions were collected from three such injections and were reinjected for further purification. The resulting fractions were analyzed by gas chromatography on the Tide column and by infrared spectroscopy and found to be pure (>95%) samples of ether and bromide. Combustion analysis of the bromide showed that it contained 0.87 atom of D per molecule. The absence of significant exchange on the chromatographic column was demonstrated by the observation that a sample of 3-chloro-3-methyl-1-butyne (0.90 atom of D per molecule) was repassed through the column and found to contain 0.88 atom of D per molecule.

The above isolation procedure was also used for exchange experiments in the absence of base. Halide and ether were recovered from neutral "80%" ethanol-*d* after about one-half of the halide had been converted to the ether. Both contained not more than 0.02 atom of deuterium per molecule by combustion analysis. Some isomerization of the bromide to the allenic bromide (1-bromo-3-methyl-1,2-butadiene) occurs during passage through the Octoil column as evidenced by a peak on the chromatogram which could not be removed on further purification. The appearance of the peak coincided with the appearance of a band at 5.1μ on the infrared spectrum (C=C=C stretching).[32] The presence of this isomer does not affect the results of the deuterium analysis. The previously described[33] method of combustion analysis for deuterium was employed.

Kinetic Procedure.—The dry salt was weighed in a 250-ml. volumetric flask (with a neck shortened to allow a 10-ml. pipet to reach the bottom). Solvent was added almost to the mark and the flask was reweighed. After the salt was dissolved by stirring, the density of the solution was determined by a single weighing in a Weld pycnometer. The normality of the basic solvent was determined by titrating in acetone two samples of standard hydrochloric acid; the basic, salt-containing solvent was delivered from the buret. As a check of the normalities of the three standard solutions (0.05 *M* HCl, 0.05 *M* aqueous NaOH and 0.05 *M* alcoholic base), two samples of the solvent were pipetted into cold acetone containing 10 ml. of 0.05 *M* hydrochloric acid and were titrated with aqueous sodium hydroxide to the lacmoid end-point. Finally the solvent volume was reduced to about 200 ml. and the flask was weighed again before being clamped in the constant temperature bath at 25.00° overnight. The volume of the solvent was calculated from its weight and density.

Some of the organic bromide was transferred out of the vacuum line where it was stored and was delivered from a 1-ml. pipet through a capillary funnel into a thin-walled glass bulb. The tared bulb was sealed, weighed and attached to a glass rod for crushing under the solvent. The flask was removed from the bath, the bulb was crushed at zero time, and the flask was quickly returned to the bath after vigorous shaking. The crushing rod was removed before the first sample was taken.

Calibrated pipets were used to withdraw samples, which were quenched in 100 ml. of ice-cold acetone containing 10 ml. of standard aqueous 0.05 *M* hydrochloric acid and were titrated according to the procedure described above for the acid standardization. The sample time was taken as the half-time of the delivery as determined by a stopwatch. The calculations were corrected for the indicator blank, which did not vary significantly with the amount of aqueous sodium hydroxide delivered from the buret. Over half the samples were taken during the first two half-lives.

The procedure for the first-order reaction was the same, except that the acid quenching procedure was unnecessary.

Rate of Production of Bromide Ions.—This technique was employed in several of the early runs before the acid-base titrations were used. The procedure for beginning a run was similar to that described above, except that the acetylenic bromide was weighed in and introduced from a syringe. The analytical method used was the potentiometric titration of bromide with silver nitrate described by Shiner and Smith.[34]

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(30) T. L. Jacobs and W. F. Brill, *J. Am. Chem. Soc.*, **75**, 1314 (1953).

(31) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1954, Chapt. 2.

(32) Reference 31, p. 49.

(33) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **74**, 5285 (1952).

(34) V. J. Shiner, Jr., and M. L. Smith, *Anal. Chem.*, **28**, 1043 (1956).

A 10-ml. sample from the reaction mixture was delivered into a separatory funnel containing 100 ml. of ether and 15 ml. of 0.2 M acetic acid–sodium acetate buffer. The ether layer was extracted with 45 ml. of buffer in three portions, and the aqueous buffer layers were mixed with 4 ml. of Tergitol in an electrolytic beaker. Silver nitrate was added until the equivalence potential, approximately 173 mv., was reached.

To test the stability of the products to hydrobromic acid, a blank, 0.1 M in both hydrobromic acid and acetylenic carbinol, was prepared and analyzed for bromide ion. The bromide ion concentration was constant to 1% over the period of a month.

Rate of Production of Bromide Ions in the Presence of Azide Ions.—The presence of sodium azide in the reaction mixture necessitated a modification of the above procedure for the analysis of bromide ion, because azide obscured the previously clear maximum in the plot of Δe.m.f. *vs.* volume of silver nitrate. The sample was run into ether and was extracted with water instead of buffer solution. One milliliter of concentrated sulfuric acid was then added to the titration beaker containing the water extracts and Tergitol and the bromide was titrated by the conductometric procedure. Under these conditions the end-point potential was found to be 125 mv.

C. **Treatment of Data.**—First- and second-order integrated rate constants were calculated from the equations

$$\bar{k}_1 = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\bar{k}_2 = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

In these equations a is the initial concentration of sodium hydroxide in "80%" ethanol, b is the initial concentration of organic halide and x is the amount of hydroxide that has reacted (in moles per liter) at time t. The initial rate constant $\bar{k}_2^\circ$ was found from a plot of integrated rate constants *versus* percentage reaction, 100 (x/b).[35] A smooth curve drawn through the points was extrapolated to zero percentage reaction. The initial rate constants thus calculated were reproducible to within ±2%. The main limitation on the accuracy of $\bar{k}_2^\circ$ was the determination of b, the initial concentration of organic halide. Because of isomerization, it was not practical to wait until a steady infinity titer was reached. Thus, four variables were involved: the weight and density of the solvent, and the weight and purity of the solute. Of these the largest variation probably occurred in the last, although it was difficult to estimate purity from the flat chromatographic peaks of the impurities.

Product Composition.—3-Bromo-3-methyl-1-butyne (4.531 g., 0.0308 mole, 0.123 M) was added to a solution of 1.312 g. (0.0328 mole, 0.131 M) of sodium hydroxide in 250 ml. of "80%" ethanol. After standing for 2 days at room temperature and then for 11 days in a refrigerator, the mixture was distilled through a 10 × 390 mm. fractionating column packed with $^1/_{16}''$ glass helices. The condenser and receiver were cooled with ice-water to prevent escape of the low-boiling 2-methyl-1-butene-3-yne (b.p. 32°). Two fractions were collected: (1) 68–77.5° (740 mm.), containing "ene-yne" and the acetylenic ether–ethanol azeotrope and (2) 77.5–78.5°, containing ethanol and water. After most of the ethanol–water azeotrope was removed, the remaining liquid was transferred to a smaller flask and a third fraction (3) 78.5–99.5°, containing mainly an acetylenic carbinol–water azeotrope, was collected. Fractions 1 and 3 were combined and analyzed by gas chromatography; the integrator was used for determination of peak area. The area under each product peak was also estimated by multiplying its height by its width at half-height. The two sets of mole per cent. composition values were not different by more than 1 mole per cent. Quantitative analysis of a mixture of known amounts of ether and carbinol established the reliability of this procedure to an accuracy of about ±2 mole per cent.

A similar procedure was followed in a determination of the relative amounts of "ene-yne," ether and carbinol formed in the first-order solvolysis, except that 29 days elapsed before the distillation was begun.

In the chromatogram of the products of the second-order reaction, in addition to the major product peaks there were two very small peaks between the olefin peak and the ether peak. In the first-order chromatogram a single small peak appeared between olefin and ether and two small peaks appeared between ether and carbinol.

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[35] O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2488 (1952).

[CONTRIBUTION NO. 1042 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

The Effects of Deuterium Substitution on the Rates of Organic Reactions. VII. Secondary Effects on the Solvolysis of 3-Halo-3-methyl-1-butynes[1]

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The isotopic variant of 3-bromo-3-methyl-1-butyne (I) having all six hydrogens of the two methyl groups replaced by deuterium (II), undergoes the SN1, carbonium ion solvolysis reaction in "80%" ethanol at 25° 1.84 times slower than I itself. The second-order hydroxide ion-promoted solvolysis, which is an SN1 reaction of the conjugate base, is slowed, by this deuterium substitution, by only a factor of 1.31. This is apparently most reasonably explained in terms of differing demand for hyperconjugation in the two closely related transition states. Replacement of the acetylenic hydrogen by deuterium has very little if any influence on the solvolysis rate of the analogous chloro compound. This represents a "vinylog" of α-deuterium substitution and the absence of any isotope effect is consistent with the accepted steric origin of the α-deuterium isotope effect.

Introduction

Because of their close relationship to changes in molecular structure on activation, isotope rate effects provide an especially valuable tool in the investigation of reaction mechanism or transition state structure. The importance of carbonium ion reactions in the theory and practice of organic chemistry and the rather large observed effects have led to considerable interest in the rate retardations caused by β-deuterium substitution in carbonium ion forming processes. Although these β-deuterium secondary isotope rate effects are certainly largely due to differential changes in vibration frequencies on activation, between the

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