Bromide assisted addition of hydrogen bromide to alkynes and allenes

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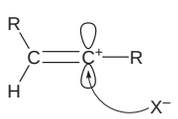
The addition of 0.1 M quaternary ammonium bromide to a solution of 20% trifluoroacetic acid in methylene chloride causes a large rate increase in the reaction of non-conjugated alkynes. The initial vinyl bromide product reacts further to provide a mixture of isomeric vinyl bromides and dibromides. At high salt concentrations however, the secondary reactions are prevented and only the initial vinyl bromide is found. In contrast to the corresponding addition to alkenes, the predominant mechanism is proposed to involve a one-step, concerted, nucleophilic attack by halide ion upon an acid–alkyne π-complex which produces the vinyl halide directly. A minor path involving *syn* addition is also seen. At all salt concentrations, allenes produce significant amounts of rearrangement products suggesting the significant involvement of a cationic mechanism.

Introduction

The addition of hydrogen halides to alkenes[1] and alkynes[2] has been postulated to occur by bimolecular and termolecular mechanisms depending upon whether or not the halide ion is specifically involved in the rate determining step of the reaction. The termolecular reactions had been thought to involve concerted bond formation to both elements of the hydrogen halide leading directly to *anti* addition products of the alkene and the alkyne. In a previous paper,[3] we showed that this is only true for alkenes under the most extreme reaction conditions that we could design. Under most conditions, the slow step involves a halide assisted protonation of the alkene leading to a secondary carbocation tightly sandwiched between the attacking halide anion and the anion derived from the proton-donating acid. This carbocation then undergoes the usual carbocationic reactions leading to unrearranged and rearranged halides, trifluoroacetates and alkene isomers. Only in the most concentrated halide solutions with weakened acidity,[3] do alkenes appear to undergo a concerted addition. The most persuasive evidence for the concerted mechanism with alkenes was the lack of rearrangement found in the addition of hydrogen iodide to 3,3-dimethylbut-1-ene.

The absence of rearrangement in the addition of hydrogen halides to alkynes is less significant since the rearrangement of vinyl cations is not facile. Solvent capture to form vinyl esters and ketones is a signature of a vinyl cation[4] but these reactions too may be minimal in a tight ion pair mechanism. The concerted addition of HCl to alkynes has been reported[2] to produce only the Markovnikov product with essentially 100% *anti* stereoselectivity and we believe that this is the best chemical evidence for a concerted addition to an alkyne. Since protonation of an internal alkyne would produce a vinyl cation with a steric preference for halide capture *syn* to the added proton, an *anti* adduct would be symptomatic of a



concerted addition. Although such results have been reported previously, we wished to analyze these reactions more carefully using our previously reported[3] reaction conditions. We therefore undertook this study to ascertain whether an intermediate carbocation is also involved in these reactions or whether the alkenes and alkynes react by different mechanisms.

Table 1 Half-lives (min) for the appearance of product at 20 °C

		20% TFA–CH_2Cl_2		
Compound	TFA (100%)	No added salt	0.1 M Br^-	1.0 M Br^-
Oct-1-yne	1600	62 000	360	5200
Oct-1-yne	1400	82 000	72	1100
Oct-1-yne	480	9000	60	1000
Octa-1,2-diene		2800	15	3400
Oct-1-ene	100	5730	29	7500
2-Bromooct-1-ene		89 000	80	400 000

Results and discussion

Effect of bromide ion† on rates

Non-conjugated alkynes have been found[4] to react with neat trifluoroacetic acid (TFA) at 60 °C to form a mixture of *cis* and *trans* trifluoroacetates, ketones and arene trimers. The mechanism is thought to involve an intermediate vinyl carbocation. The half-life reported[4] for the reaction of a terminal alkyne is 43 min at 60 °C [and we have found a half-life of 27 h for oct-1-yne at room temperature (20 °C)]. If a solution of 20% TFA in methylene chloride is used, the half-life for TFA addition increases to 1040 h producing a similar mixture of products. When we include 0.1 M tetra-*n*-butylammonium bromide in the latter reaction mixture, the half-life for the appearance of oct-1-yne products drops to 6 h and only HBr adducts are found. With the rate increasing by a factor of 170 and the exclusive formation of bromide products, it seems safe to assume that the bromide ion is involved in the rate determining step of all products. Similar results are found for internal alkynes and these results are shown in Table 1.

In each case, the inclusion of 0.1 M bromide increases the rate by two orders of magnitude indicating significant participation of the bromide ion. It should also be noted that the higher concentration of bromide slows the reaction of the alkyne by an order of magnitude but slows the subsequent reaction of the vinyl bromide product by over three orders of magnitude. Thus, the initial products of the reaction are stable to the concentrated bromide conditions and can easily be isolated using these conditions.

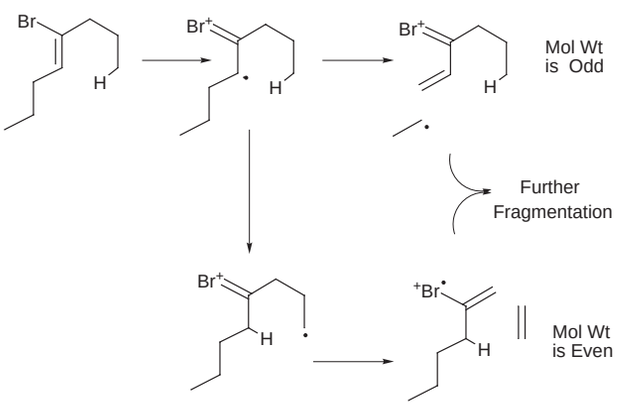
Because our parallel study with alkenes showed similar evi-

† In this paper, we use the term 'bromide ion' to include all ion pairs and free bromide ions.

dence for bromide ion participation in the transition state, we conducted a more detailed kinetic analysis of alkyne disappearance relative to an internal decane standard. These results parallel those obtained during the product studies but the half-lives are 30 to 50% shorter.

Identification of products by GC–MS

Over a dozen different reaction products were detected and analyzed by GC–MS. All peaks above 1% of total were identified and many peaks below that level could also be identified. Their identification was achieved by a combination of GC retention times and mass spectral analyses. In general, vinyl bromides have large molecular ion peaks whereas allyl bromides show no peaks containing bromine. Fragmentation of vinyl bromides appears to pass through an intermediate with radical character on the β-carbon. This intermediate undergoes a radical fragmentation where possible or an internal hydrogen abstraction followed by an alkene cleavage (Scheme 1). The two routes are



Scheme 1

rarely possible in the same molecule. For example, 2-bromooct-2-ene only loses the butyl radical generating a cation with molecular weights of 133 and 135. The 3-bromooct-2-ene preferentially abstracts a hydrogen atom and loses butene generating a cation with molecular weights 134 and 136. The corresponding trifluoroacetates appear to follow the same fragmentation paths. Because the (*Z*)-2-bromooct-2-ene and the (*Z*)-3-bromooct-2-ene have very similar retention times, a clear separation of these isomers was only feasible where similar amounts of each isomer were present. The area ratios of mass peaks 134 to 133 were calculated from these and used to calculate the isomer ratios in other mixtures. All pairs of (*E*)- and (*Z*)-isomers give virtually identical mass spectra. The (*Z*)-vinyl bromides are the predominant isomers and have shorter retention times than the (*E*)-isomers. In some cases, the (*Z*)-isomers were isolated and identified by NMR spectroscopy.

The allyl bromide retention times and mass spectra were reproduced by the reaction of oct-1-ene with *N*-bromosuccinimide. The stereochemistry of the 1-bromooct-2-enes was assigned solely on the basis of retention time and relative yields.

Identification of products by NMR spectroscopy

The addition of HBr to oct-1-yne produces 2-bromooct-1-ene with two olefinic resonances. The hydrogen *syn* to the bromine is a doublet of triplets centered at 5.37 ppm. The hydrogen *anti* to the bromine is an overlapping doublet of triplets centered at 5.54 ppm. The addition of DBr to oct-1-yne produces (*E*)-2-bromo-1-deuteriooct-1-ene with a single proton peak at 5.36 ppm and a deuterium absorbance at 5.52 ppm. These peaks are shown in Fig. 1.

The addition of DBr to the following alkynes gives deuterium decoupled NMR spectra with single proton peaks at the following frequencies: hex-1-yne 5.38 ppm (*syn* to bromine);

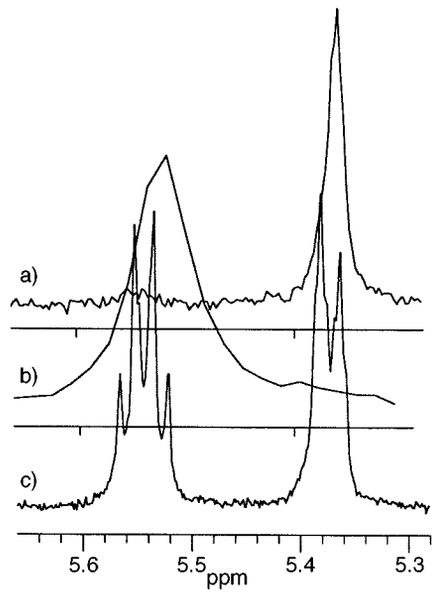
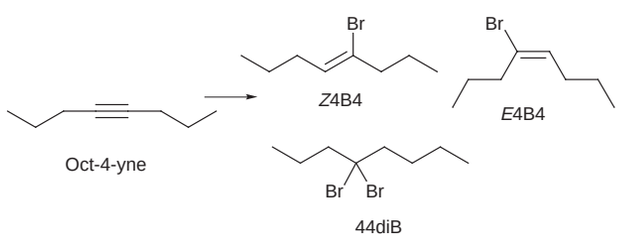


Fig. 1 NMR spectra of the vinyl region. (a) ^{1}H of (*E*)-2-bromo-1-deuteriooct-1-ene, (b) ^{2}H of (*E*)-2-bromo-1-deuteriooct-1-ene, (c) ^{1}H of 2-bromooct-1-ene.

3,3-dimethylbut-1-yne 5.37 ppm (*syn* to bromine). The addition of HBr to oct-4-yne affords the (*Z*)-4-bromooct-4-ene with a single proton resonance at 5.61 ppm (*anti* to bromine). The addition of HI to dec-1-yne gives 2-iododec-1-ene with peaks at 5.99 ppm (*anti* to iodine) and 5.66 ppm (*syn* to iodine).

Product distributions

Using 1.0 M bromide, we found that oct-4-yne produces only one product, 4-bromooct-4-ene (Scheme 2) and that greater

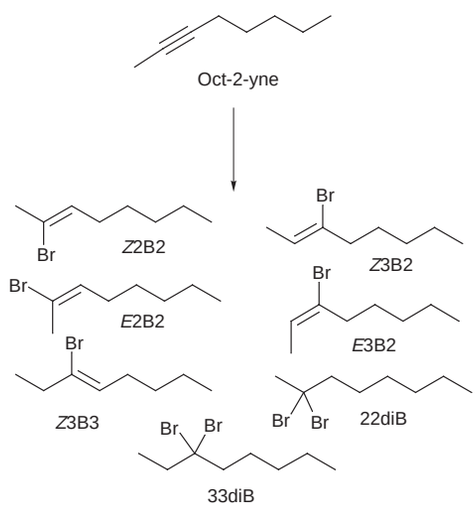


Reaction with 20% TFA–CH_2Cl_2 and 0.1 M $Bu_4N^+ Br^-$. Product distribution from oct-4-yne					Reaction with 20% TFA–CH_2Cl_2 and 1.0 M $Bu_4N^+ Br^-$. Product distribution from oct-4-yne		
t/h	%Rxn	*Z*4B4	*E*4B4	44diB	*t*/h	%Rxn	*Z*4B4
0.58	45	96.3	3.7	—	3	17	100
1.0	58	95.6	3.6	0.8	25.4	72	100
1.75	72	95.9	3.2	0.9	144	100	100
23.5	100	84.9	3.4	11.9			

Scheme 2

than 99.9% of this product is the (*Z*)-isomer (*Z*4B4). No other products can be detected after 10 half-lives. When 0.1 M bromide is used, 4-bromooct-4-ene remains the initial product but it contains a few percent of the (*E*)-isomer (*E*4B4). The ratio of (*Z*)- to (*E*)-isomer remains constant throughout 90% of the reaction suggesting that both isomers are formed directly from the alkyne. No ketone or trifluoroacetate esters could ever be detected and we have shown that such compounds are stable and detectable under the conditions of the reaction.

The reaction of oct-2-yne with 1.0 M bromide is quite similar, producing a mixture of (*Z*)-2-bromooct-2-ene (43%) (*Z*2B2)



Product distribution from oct-2-yne reaction with 20% TFA–CH_2Cl_2 and 0.1 M Bu_4N^+ Br^-

t/h	%Rxn	*Z*2B2	*Z*3B2	*E*2B2	*E*3B2	*Z*3B3	22diB	33diB
0.58	35	39.6	58.0	1.0	1.4	—	—	—
2.8	78	40.1	54.9	0.6	1.4	0.5	0.6	1.9
28.3	100	46.6	53.4	—	—	—	5.8	17.4

Product distribution from oct-2-yne reaction with 20% TFA–CH_2Cl_2 and 1.0 M Bu_4N^+ Br^-

t/h	%Rxn	*Z*2B2	*Z*3B2
26	87	43.4	56.3
336	100	41.7	58.3
720	100	42.7	57.3

Scheme 3

and (*Z*)-3-bromooct-2-ene (57%) (*Z*3B2) as the only products after all alkyne has reacted (Scheme 3). No (*E*)-isomers can be detected. Doubling the reaction time affords no further reaction. Trace amounts of a dibromooctene can be detected early in the reaction but it does not increase with time and it was found to derive from a small amount of bromine which is generated initially and quickly adds to the alkyne. The GC retention time and mass spectrum can be reproduced by adding bromine to oct-2-yne in carbon tetrachloride. When the HBr additions are performed in the dilute bromide solutions, the same mixture of (*Z*)-vinyl bromides is found early in the reaction along with a small amount of the (*E*)-isomers but these are subsequently converted to an increasing amount of 2,2- and 3,3-dibromides (22diB and 33diB).

The reaction of oct-1-yne is slightly more complicated. As expected, oct-1-yne reacts with the 1.0 M bromide solution to form 2-bromooct-1-ene quite cleanly, showing only trace amounts of the 2-bromooct-2-ene. This product can be isolated easily and subjected to analysis and further reaction. It is also possible, using deuterated trifluoroacetic acid, to add DBr to oct-1-yne and to show by NMR spectroscopy that the addition occurs with 97 ± 3% *anti* steroselectivity. In this experiment, we are unable to detect any deuterium exchange into the unreacted starting material. Unlike the internal alkenes, the 2-bromooct-1-ene undergoes some further reaction (isomerization and addition) before the alkyne disappears completely. These secondary reactions remain slow and account for less than 5% of the products.

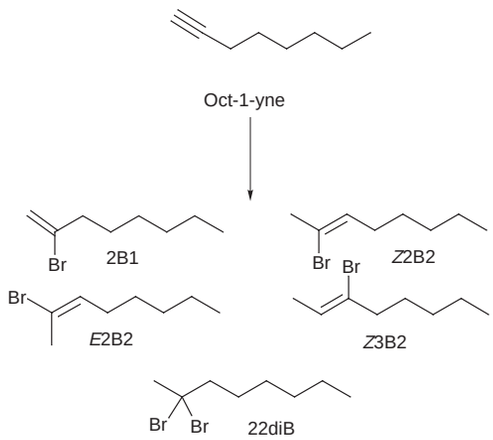
When 0.1 M bromide is used, these secondary reaction products are seen in the earliest stages of the reaction and become the principal products before the alkyne is half reacted. After approximately 5 h (45% reaction), the product mixture contains 2-bromooct-1-ene (28%) (2B1), and (*Z*)-2-bromooct-2-ene (*Z*2B2), (*E*)-2-bromooct-2-ene (*E*2B2) and 2,2-dibromooctane (22diB) in the ratio 2 : 1 : 4 (Scheme 4). When the 2-bromooct-1-ene is isolated and subjected to the 0.1 M bromide reaction conditions, a very similar mixture of dibromide and vinyl bromides is produced. Eventually, the dibromide becomes the major product.

The absence of cation derived products (ketone, trifluoroacetates) coupled with the high proportion of *anti* addition products suggests that the addition to the alkyne proceeds by a concerted mechanism (*i.e.* both covalent bonds to the alkyne form simultaneously). The small amount of *anti* proton detected in the NMR spectrum of 2-bromo-1-deuteriooct-1-ene may be an artifact arising from protic impurities in the reaction mixture. Thus, the NMR analysis is less dependable than the GC results for assessing stereochemical purity.

An important difference, however, is seen in the reaction of the allene octa-1,2-diene (Scheme 5). Using 1.0 M bromide, the simple addition of HBr to the allene system can account for the 2-bromooct-1-ene (2B1), the (*E*)- and (*Z*)-2-bromooct-2-ene (*E*2B2 and *Z*2B2) and the 3-bromooct-1-ene (3B1). However, a significant amount of oct-2-yne is also detected early in the reaction. That the oct-2-yne concentration increased to approximately 7% of the products suggests that at least 7% of the reaction proceeds through a carbocation. The absence of 3-bromooct-2-ene in the product mixture suggests that oct-2-yne is not an intermediate on the route to other products and that the other products derive from a short lived cation sandwich which can also form the oct-2-yne.

In the more acidic[3] 0.1 M bromide solution, the presumed carbocation is less associated and produces a wider variety of products including oct-2-yne and its addition products, 3-bromooct-2-ene and a proportionate amount of the 2-bromooct-2-ene along with some trifluoroacetates. These products account for over 40% of the total products and support the intermediacy of a carbocation intermediate. The rate enhancement found with the bromide ion coupled with the paucity of trifluoroacetate products‡ (Tf) suggests that the ion sandwich mechanism, rather than a free carbocation, is the predominant path for the allene reaction. That the allene forms a vinyl cation while the alkynes do not form the same cation is presumably due to the greater instability of the allene as evidenced in the predominance of alkynes in the acid catalyzed isomerization[5] of allenes and alkynes.

‡ The allyl trifluoroacetates may well be converted to bromides under these reaction conditions. The vinyl trifluoroacetates, however, are stable to these reaction conditions.



Product distribution from oct-1-yne reaction with 20% TFA–CH_2Cl_2 and 0.1 M Bu_4N^+ Br^-

t/h	%Rxn	2B1	*Z*2B2	*Z*3B2	*E*2B2	22diB
0.58	6	75.3	8.9	—	6.2	9.6
1.2	25	57.8	14.1	—	9.5	18.6
4.9	56	28.0	19.9	3.0	10.7	38.4
28.3	94	4.7	24.4	2.7	11.1	57.5
75	100	3.0	15.9	0.6	7.0	73.5
Products from 2-bromooct-1-ene						
1.2	56	44	23.6	—	11.9	64.5

Product distribution from oct-1-yne reaction with 20% TFA–CH_2Cl_2 and 1.0 M Bu_4N^+ Br^-

t/h	%Rxn	2B1	*Z*2B2	*E*2B2	22diB
48	52	100	—	—	—
336	100	98.0	0.4	0.6	1.0
720	100	94.0	2.3	1.0	2.7

Scheme 4

Conclusions

This work was aimed at answering the question of whether, as suggested, hydrogen halides can add to alkynes by a concerted mechanism. Our previous work shows that such a mechanism is extremely rare for alkenes since skeletal rearrangements are pervasive in these reactions and the reaction rates were found to be independent of halide ion concentration. Using the same reaction conditions that we employed in our alkene study, we have found strong evidence for the concerted mechanism with alkynes. Persuasive evidence for this is the stereospecific addition of HBr to the internal alkynes which can be shown to occur with 95 to 99.9% *anti* stereospecificity. The NMR analyses of the DBr adducts to the terminal alkynes, hex-1-yne, oct-1-yne and 3,3-dimethylbut-1-yne are relatively less sensitive and more vulnerable to protic impurities in the reaction mixture as well as acid catalyzed isomerization of the vinyl halide products.

We realize that the 97 ± 2% stereoselective *anti* additions to oct-2- and -4-yne in the less concentrated bromide solutions could be interpreted as coming from a very tight ion pair with some leakage to produce the *syn* adduct. However, the stereospecific results obtained with the more concentrated bromide solutions generate an unreasonable rate requirement for the ion pair collapse and a concerted mechanism seems unavoidable. Although it might be argued that a tight ion pair might always collapse to the *anti* adduct, we can see no difference between this situation and an unsymmetrically bonded concerted mechanism. In either case, there is halide bonding to the developing cationic center and a single downhill path to one product.

The kinetic study of the reactions of oct-1- and -4-yne with a range of bromide ion concentrations shows behaviour similar to that seen with the alkenes. However, while the logarithms of the alkene rate constants are found[3] to be proportional to $H_o - pK_a$, this relationship is not linear with the alkynes. When the pseudo first order rate constants for the octynes are divided by the concentrations of bromide ion, the negative logarithms of these values are found to show a linear relationship to $H_o - pK_a$ with proportionality constants of 0.8 and 0.9 (Fig. 2).

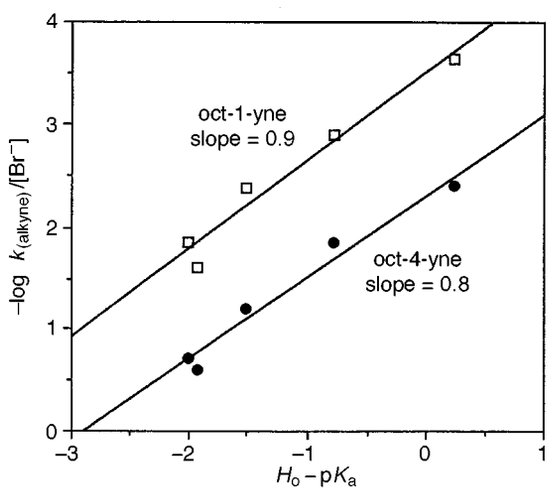
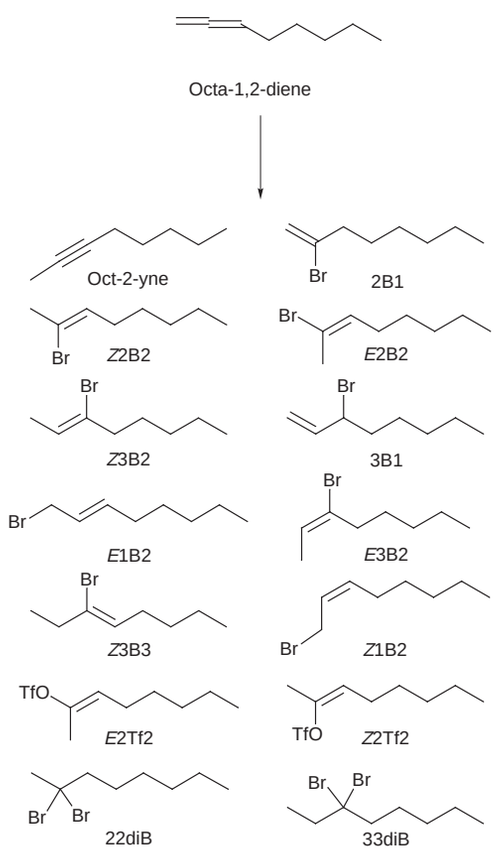


Fig. 2 Pseudo first order rate constants for oct-1-yne and oct-4-yne divided by bromide *versus* the acidity of the solutions ($H_o - pK_a$)

We also found that the rate constants for HBr addition to alkynes are not proportional to those found for the alkene additions. Dividing the rate constants for alkyne addition by the concentrations of bromide used produces values which are proportional to the alkene rate constants. These results are shown in Figs. 3 and 4.

This somewhat surprising result supports our thesis that, while the alkenes react by an Ad_E2 mechanism independent of bromide, the alkynes show termolecular kinetics with the additional dependence upon the tetrabutylammonium bromide. This provides additional support for the concerted reaction of alkynes and the cationic mechanism for alkenes. That the lines are straight and intersect the origin suggests that no other mechanisms are significantly involved at any bromide concentration. The surprising linear dependence of the rates upon the concentration of added tetrabutylammonium bromide suggests that either, 1) the effectiveness of the halide ion is independent



Product distribution from octa-1,2-diene reaction with 20% TFA–CH_2Cl_2 and 0.2 M Bu_4N^+ Br^-

t/h	%Rxn	2B1	*Z*2B2	*Z*3B2	*E*2B2	*E*3B2	*Z*3B3	*Z*1B2	*E*1B2	3B1	*E*2Tf2	*Z*2Tf2	22diB	33diB	Oct-2-yne
3.5	99.5	0.8	46.8	20.0	22.0	0.7	—	0.9	1.0	1.7	0.7	1.3	1.0	0.4	2.7
48	100	0.6	42.7	16.3	17.6	0.6	1.7	0.7	1.8	—	0.5	1.2	10.1	5.4	—

Product distribution from octa-1,2-diene reaction with 20% TFA–CH_2Cl_2 and 1.0 M Bu_4N^+ Br^-

t/h	%Rxn	2B1	*Z*2B2	*Z*3B2	*E*2B2	*Z*1B2	*E*1B2	3B1	Oct-2-yne
1	4.8	15.5	30.0	—	32.0	—	—	16.2	6.0
3.5	7.3	13.0	34.8	—	29.3	—	—	15.7	7.2
28	38	10.9	29.1	4.2	30.0	3.7	3.6	16.8	1.7

Scheme 5

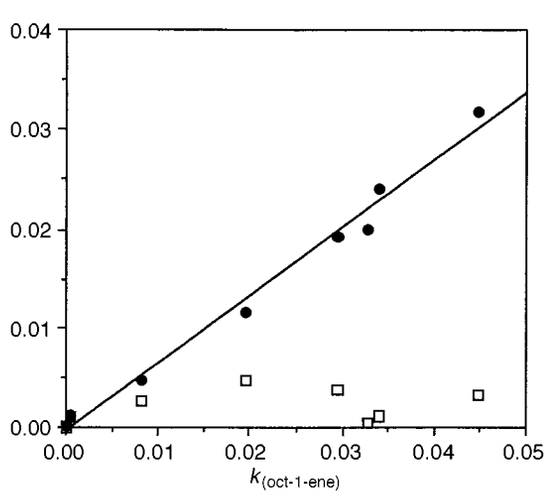


Fig. 3 Pseudo first order rate constants for oct-1-yne (□) and oct-1-yne divided by bromide concentrations (●) *versus* pseudo first order rate constants for oct-1-ene

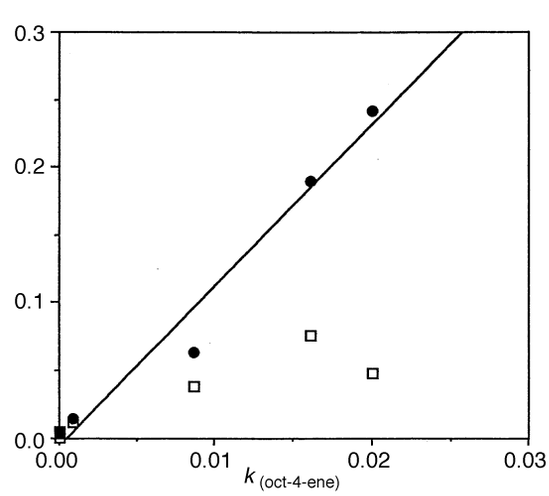


Fig. 4 Pseudo first order rate constants for oct-4-yne (□) and oct-4-yne divided by bromide concentrations (●) *versus* pseudo first order rate constants for oct-4-ene

of its degree of association in these solutions or, 2) the salt maintains the same degree of association throughout the range of salt concentrations which were studied. The latter possibility seems more likely with the salt existing as ion pairs in this solvent system.

This paper addresses the question of the factors which determine whether the electrophilic attack will generate a carbocation or directly produce the halide product. We believe that the greater instability of the vinyl cation formed from an alkyne requires a greater association of the nucleophile to the incipient cationic center before proton transfer to the alkyne can be completed. The proven ability of alkynes[6] to form π-complexes with strong acids may also facilitate the concerted mechanism. The five-fold greater reactivity of the internal alkynes over the terminal alkyne may derive from their greater π-donor potential. In contrast, the (less stable) terminal alkenes are found to be slightly more reactive than the internal alkenes supporting the idea of a slow formation of the cation.

In our previous paper,[3] we asserted that the ionic additions of all protic reagents to alkenes probably occur *via* cationic intermediates. In this work, we find that the addition of hydrogen halides to alkynes easily occurs by a concerted mechanism. We must point out, however, that there is ample evidence for cationic intermediates in the addition of other reagents to alkynes. The most direct evidence is the isomerization of alkynes by strong acids,[5] the rearranged products coming from the reaction of 3,3-dimethylbut-1-yne with liquid HCl[7] and the non-stereospecific addition of trifluoroacetic acid to hex-3-yne.[4] It should be noted that, in each of these cases, there were strong acids and weak nucleophiles present in the reaction. Thus, in contrast to the reaction of alkenes, most termolecular additions to an unconjugated alkyne are unlikely to proceed through cationic intermediates.

Finally, we would like to point out the synthetic potential of this reaction. Using the most concentrated salt solution, the reactions proceed in essentially 100% yield and formed only the Markovnikov products with *anti* stereospecificity. There was no evidence of the radical reactions seen[2a] in other HBr additions. A similar reagent has also been reported[8] for the addition of HBr to alkynes.

Experimental

The oct-1-yne (99.5% purity), oct-2-yne, oct-3-yne and oct-4-yne used in these experiments were obtained from Farchan Chemical Co. The 3,3-dimethylbut-1-yne, trifluoroacetic acid and solvents (HPLC grade) were obtained from Aldrich Chemical Co. and were used without further purification. The octa-1,2-diene was synthesized by the method previously[9] described. The quaternary ammonium salts were obtained from Fluka Chemical and from Aldrich Chemical Co. and were kept in a desiccator prior to use. The tetrabutylammonium bromide was dried under vacuum at regular intervals.

Reactions were performed in glass-stoppered flasks by adding 1 or§ 2 drops of the alkyne¶ to 5 to‖ 100 ml of the 20% trifluoroacetic acid in methylene chloride solution containing the quaternary ammonium salt. Aliquots (approximately 0.5 ml) were removed and quenched with 15 ml of water and 10 ml of hexanes. The hexanes layer was washed with another 10 ml of water and dried over anhydrous potassium carbonate prior to GC–MS analysis. Chromatographic peaks were identified by their mass spectrum as well as by retention time of compounds synthesized and analyzed by NMR spectroscopy. Detector responses for the vinyl bromides relative to oct-1-yne were determined by synthesis of a bromide mixture adding a known amount of oct-1-yne and analyzing the mixture by GC–MS. Detector responses for all the vinyl bromides were assumed to be equal. The vinyl trifluoroacetates and halides were shown to be stable under the reaction conditions. Unless otherwise noted, all reactions were run at room temperature (20 ± 2 °C) and showed no evidence of exothermicity. Decane was used as an internal standard in all kinetic studies designed to determine the overall rate of disappearance of alkyne.

NMR spectra were recorded on a JEOL FX90Q spectrometer. Proton spectra utilized a deuterium lock and TMS as internal reference. Deuterium spectra utilized a lithium lock and $CDCl_3$ (δ 7.24) as the internal reference. Mass spectra and chromatographic analyses were performed on a Hewlett-Packard 5890 Chromatograph with a 12 m HP-1 capillary column and a 5971A mass selective detector.

General method for preparative HBr (or DBr) additions

Tetra-*n*-butylammonium bromide (16.12 g, 50 mmol) was put into a 50 ml volumetric flask and dried overnight in a vacuum desiccator. The salt was dissolved in approximately 25 ml of methylene chloride followed by trifluoroacetic acid (10 g, 6.7 ml, 89 mmol). The appropriate alkyne (10 mmol) was added. The reaction mixture was protected from light and allowed to react at room temperature for 5 to 7 days (monitored by chromatography). The entire reaction mixture was transferred to a separating funnel, washed with 2 × 100 ml water, 1 × 100 ml saturated $NaHCO_3$, 1 × 100 ml water, then dried over K_2CO_3 and concentrated to give a colorless oil. The solution was diluted with 50 ml of pentane and washed with 2 × 50 ml water and 1 × 20 ml brine then dried over K_2CO_3, filtered and concentrated under reduced pressure. At this point, the products were sufficiently pure for GC and NMR analyses.

§ Results from 1 or 2 drops of alkyne (approximately 10^{-4} mol) were identical within our experimental method.

¶ In all rate studies, a mixture of alkyne and decane standard was used and analyzed after the standard workup.

‖ At least 10^{-3} mol of bromide ion were used in all rate studies.

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