Halide assisted addition of hydrogen halides to alkenes

Hilton M. Weiss* and Kim M. Touchette

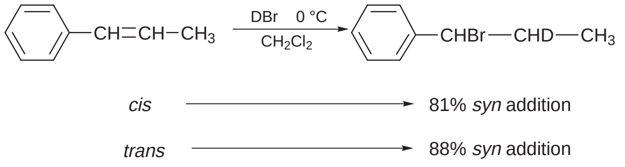
Department of Chemistry, Bard College, Annandale-on-Hudson, New York 12504, USA

The addition of 0.1 M quaternary ammonium halide to a solution of 20% trifluoroacetic acid in methylene chloride causes a large rate increase in the reaction of simple alkenes leading to a mixture of alkyl halides and trifluoroacetates. The mechanism is proposed to involve a halide assisted protonation of the alkene which produces a carbocation intermediate sandwiched between the attacking halide ion and the trifluoroacetate ion. At higher concentrations of halide ion, the proton donating ability of the solution decreases, slowing the reaction and increasing the efficiency of cation capture by the halide ion. This leads to a greater proportion of unrearranged halide product. At the highest concentration of halide ion, cation rearrangement is virtually eliminated.

Introduction

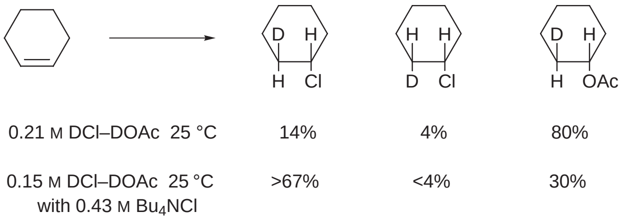
The electrophilic addition of hydrogen halides to alkenes is a versatile synthetic reaction which has promulgated a wide range of mechanistic possibilities.[1] Perhaps the best known mechanism is the Ad_E2 path in which slow proton transfer to the alkene generates a carbocation and halide anion. In polar solvents, alkenes capable of forming stable, usually conjugated, carbocations undergo this Ad_E2 mechanism and show little or no stereoselectivity in their addition products.

In less polar solvents, these conjugated alkenes are less reactive. When proton transfer to the alkene does occur, the carbocation, being less well solvated, maintains a strong attraction for the halide anion and this ion pair is likely to collapse rapidly to the addition product. In such cases, a *syn* addition product often predominates (Scheme 1).[2]



Scheme 1

With simple alkenes which form less stable (secondary) carbocations, stereorandom addition is rare. In fairly nucleophilic solvents such as acetic acid, proton transfer is slow and is assisted by the nucleophilic solvation of the developing carbocationic center during the proton transfer. In acetic acid, solvent incorporation is common and the alkyl acetate products usually show *anti* stereochemistry[3] indicative of 'backside' solvation followed by rapid collapse to the alkyl acetate (Scheme 2). In these reactions, the hydrogen halide adducts also show a preference for *anti* stereochemistry presumably arising from an analogous 'backside' participation by the halide ion during the proton transfer step.[4] This Ad_E3 mechanism (additionally dependent upon the halide ion concentration) often competes with the solvent assisted Ad_E2 mechanism and the alkyl halide products usually show increased *anti* stereoselectivity as the concentration of halide ion is increased. This mechanism is generally postulated to involve a nucleophilic attack by the halide ion upon a π-complex or encounter complex formed between the alkene and the hydrogen halide molecule 'bypassing a discrete carbocation'.[5] Both of these mechanistic possibilities have been called 'concerted Ad_E3' and we shall continue that somewhat misleading tradition.



Scheme 2

Since the stereochemical integrity and the lack of rearrangement inherent in such a mechanism could be synthetically useful, we decided to study this type of reaction further. To minimize the complications of a concomitant Ad_E2 reaction occurring, we used methylene chloride as solvent since it is less capable than acetic acid at solvating the potential carbocation. We also chose to utilize trifluoroacetic acid as the sole proton source to control and to limit the acidity of the reaction mixture while using different halide ions. This allowed us to add the elements of HBr without the presence of molecular HBr which is known to cause unwanted radical addition and isomerization.[6] By avoiding the hydrogen halides as proton donors, we also avoided the production of *syn*-generated ion pairs. Trifluoroacetic acid is also advantageous because of its low nucleophilicity[7] and its availability in deuterated form.

Results

Although monosubstituted alkenes are fairly reactive toward neat trifluoroacetic acid[7] ($t_{1/2} \approx 1$ h), we found that the half-life of a monosubstituted alkene in 20% TFA–methylene chloride at room temperature is approximately 95 h. The inclusion of a 0.1 M tetra-*n*-butylammonium halide ion in this reaction mixture produces alkyl chloride, bromide or iodide in reactions with half-lives of 6.6, 0.5 and 0.2 h respectively.

Although kinetic analyses of these reactions are difficult, it seems clear that the alkene, acid and salts are involved in the rate determining step. Furthermore, with the tremendous rate acceleration caused by the added halide ion, it is safe to assume that *virtually all of the products arise from the halide assisted reaction.*

Effect of bromide concentration on rates

We studied these reactions on a small scale using approximately 10^{-4} mol of alkene in a large excess of acid and bromide ion. Under these conditions, the reaction is first order in alkene for 60% of the reaction. For the product studies, samples were removed for chromatographic analysis and corrected for the

Table 1 Half-lives, relative product yields and relative acidities for the reaction of oct-1-ene with 20% TFA in CH_2Cl_2 with added tetrabutylammonium bromide

$[Br^-]$ used/M	$t_{1/2}$/min	RBr/ RTFAc	log [In]/ $[HIn^+]$
0.00	5730	—	0.08
0.01	69	4.5	
0.02	44	7.6	
0.04	32	8.7	
0.06	26	12.9	
0.08	24	10.0	
0.10	29	8.2	−1.61
0.20	45	9.3	−1.93
0.40	71	15.2	−2.01
0.60	185	18.2	−1.52
0.80	1300	32.6	−0.78
1.00	7500	135	0.40
0.10 (Cl^-)	396	3.5 (Cl^-)	
0.10 (Br^-)	29	8.2 (Br^-)	
0.10 (I^-)	12	20.3 (I^-)	
0.10 ($Bu_4N \pm O_2CCF_3$)	4800	—	
0.10 ($Bu_4N \pm Br$), 0.012 ($Bu_4N \pm O_2CCF_3$)	50	9.2	
0.10 ($Bu_4N \pm Br$), 0.071 ($Bu_4N \pm O_2CCF_3$), 0.89 ($Bu_4N \pm BF_4$)	15 800	5.5	

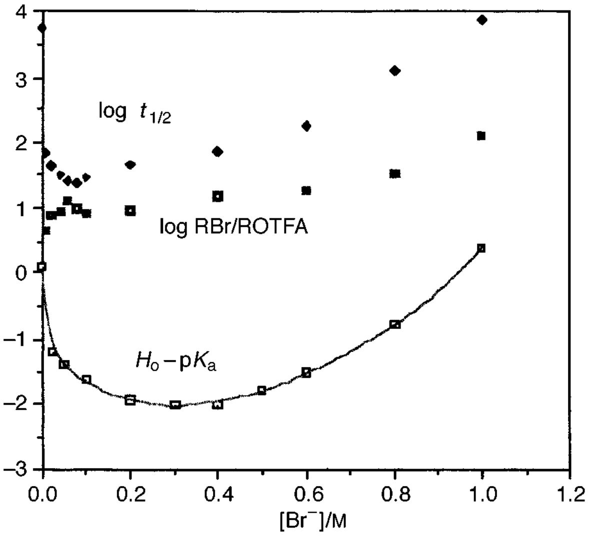


Fig. 1 Logarithmic graph of $t_{1/2}$, product ratios and relative acidity of reaction solution as functions of the bromide concentration in the oct-1-ene reaction solutions

Table 2 Product composition (%) from oct-1-ene at 34 ± 4% reaction in 20% TFA–CH_2Cl_2

$[Br^-]$/M	2-RBr	3-RBr	4-RBr	2-RTFAc	3-RTFAc	4-RTFAc
0.01	75.8	6.0	0	18.2	0	0
0.1	80.5	6.5	1.0	9.9	1.7	0.4
1.0	99.3	0.1	0	0.6	0	0
0.1	45	55	(from *trans*-oct-2-ene)			
0.1		51	49	(from *trans*-oct-3-ene)		

differential detector responses of reactants and products. In later kinetic studies, alkene disappearance was referenced to an internal standard. The resulting rate data parallel the rates found during the product studies but are 50 to 90% larger. All kinetic data are treated as pseudo first order reactions converting percent reaction to half-lives for convenience of comparison.

Table 1 shows the kinetic results of varying the concentration of bromide ion† and these data are also seen graphically in Fig. 1. It is quite clear that small amounts of bromide cause a great increase in the rate of reaction, however, increasing the bromide concentration further has a marked inhibitory effect. This rate dependence upon bromide concentration suggests large salt effects in this non-polar medium. The inclusion of an inert anion (BF_4^-) in addition to 0.1 M bromide causes the same inhibition of the reaction seen with higher levels of bromide ion. To counter the effect of strongly acidic impurities in some quaternary ammonium salts, small amounts of trifluoroacetate ion were also added as a buffer to some reactions. Trifluoroacetate is found to have a small retarding effect on the hydrogen halide addition reactions and is assumed to cause the deviation from first order kinetics found late in the reactions.

Effect of bromide concentration on the acidity of the solution

The addition of tetrabutylammonium bromide to the 20% trifluoroacetic acid solution dilutes the acid somewhat but exerts its major influence on the activity coefficients of the solutes, especially the ionic solutes. To assess the effect of the added salt upon the acidity of these solutions, we determined its ability to protonate a neutral Hammett base. We spectrophotometrically[6,8] determined that 4-chloro-2-nitroaniline is 50% protonated in 20% TFA–methylene chloride. The addition of small amounts of the salt increases the protonated form of the Hammett base to 97% but additional salt eventually lowers the degree of protonation to 37% at 1.0 M salt. Although we have not determined the pK_a of 4-chloro-2-nitroaniline in our solvent system, we can evaluate the relative acidity of these solutions (Table 1) by determining the ratio of unprotonated to protonated indicator. Graphing these results (Fig. 1) suggests that the reaction rates parallel the acidity of the solutions.

Effect of bromide concentration on product composition

At the lower concentrations of bromide ion, a 10-fold increase in bromide ion leads to little change in the product compositions (Table 1). Higher bromide concentrations cause a significant increase in the alkyl bromides and the highest concentrations also generate a greater proportion of unrearranged products (Table 2). At all concentrations of bromide ion, the alkyl bromides are the primary products reinforcing the notion that the bromide ion is involved in the transition state. The proportion of bromide products also parallels the acidity of the reaction (Fig. 1) solutions except when the bromide ion concentration is extremely low.

Effect of halide nucleophilicity

Using 0.10 M halide ion, we have found half-lives for the reaction of chloride, bromide and iodide to be 396, 28 and 12 min, respectively. The ratio of alkyl halide products to alkyl trifluoroacetate increases with increasing halide nucleophilicity (Table 1). Unlike the chloride or bromide ion, the iodide ion is susceptible to air oxidation and the iodide reactions are best run under a nitrogen atmosphere. A number of oxyanions show behavior similar to the bromide ion and their reactions will be discussed in a later paper.

Effect of alkene structure on rates

The rates of the addition reactions were essentially identical for all monoalkyl and 1,2-dialkyl alkenes. In contrast, the rate of reaction of a 2,2-dialkyl alkene was significantly larger (see Table 3).

Stereochemistry

Because trifluoroacetic acid is the only proton donor in the

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† In this paper, we will not differentiate between associated and unassociated halide ions.

Table 3 Half-lives of various alkenes in 0.1 M bromide ion, 20% trifluoroacetic acid in CH_2Cl_2

Alkene	$t_{1/2}$/min
Oct-1-ene	29
Oct-2-ene	30
Oct-3-ene	25
3,3-Dimethylbut-1-ene	18
2-Methylhept-1-ene	<0.1
2-Bromooct-1-ene	69

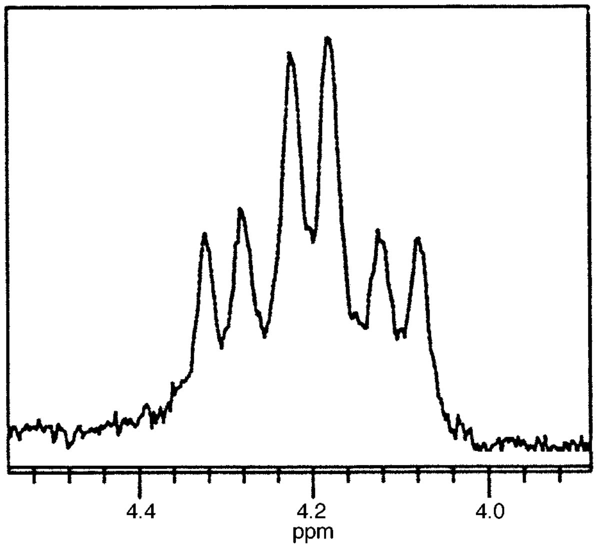


Fig. 2 NMR spectrum of the methine proton on 2-deuteriobromocyclohexane

reaction, it is reasonably easy and inexpensive to add DBr to alkenes. The addition to cyclohexene produces 2-deuteriobromocyclohexane with the deuterium-decoupled NMR spectrum shown in Fig. 2.

The proton on the brominated carbon is a triplet of doublets indicative of two *anti* protons (J = 8.9 Hz) and one *syn* proton (J = 4.0 Hz). Reported values[3d] are 8.7 and 3.5 Hz. The DBr addition therefore occurs primarily with *anti* stereochemistry. Deuterium NMR of this product produces a spectrum containing two peaks assigned to the equatorial (δ 2.38) and axial (δ 1.92) deuterium atoms. The relative areas of these peaks are 5.6 : 1 indicating that at least 85% of the reaction occurs in an *anti* manner. The 5 day reaction period in concentrated bromide may allow for some racemization.

Rearrangement

In order to probe the sensitivity of this reaction toward steric hindrance and rearrangement, the reaction was run using an equimolar mixture of oct-1-ene and 3,3-dimethylbut-1-ene. Analysis of the products after 20 ± 2% reaction gave the relative rates of reaction and the extent of rearrangement of the dimethylbutene. The results are shown in Table 4. It should be noted that the percentage of rearranged bromide increases with time as the rearranged (tertiary) trifluoroacetate is slowly converted to the halide. The percentage of total rearranged product, however, is independent of time.

Discussion

Fahey has reported that, under some conditions, alkenes may add the elements of HCl[3c] or HBr[3d] by a termolecular reaction. The rate of the (*anti*) addition of HCl to cyclohexene depends on the concentrations of the alkene, HCl and added chloride ion. He postulated that this product is formed by the nucleophilic attack of the chloride ion upon an alkene–HCl complex (Scheme 3).

Table 4 Half-lives and product ratios from the reaction of halide ion, 20% trifluoroacetic acid in CH_2Cl_2 and 3,3-dimethylbut-1-ene[a]

Halide	Conc./M	T/°C	$t_{1/2}$/min	% Rearrangement
None	0	20	5100	100 (as ester)
Br^-	0.1	20	18	77
Br^-	0.1	−15	192	77
Br^-	1.0	20	9000	31
I^-	0.1	20	8	66
I^-	0.1	−15	137	67
I^-	1.0	20	7000	7

[a] Uncorrected for detector response.

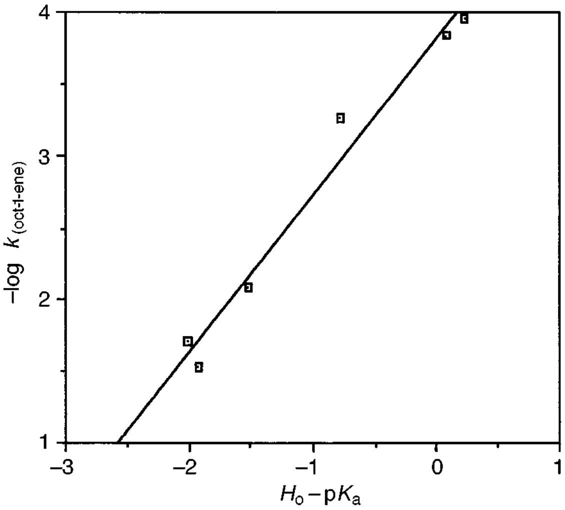
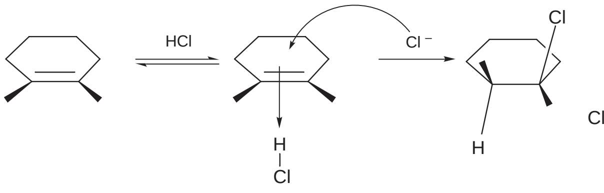


Fig. 3 Logarithm of pseudo first order rate constants against $H_o - pK_a$ of reaction solution



Scheme 3

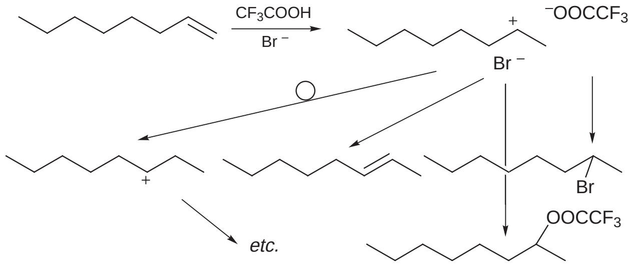
Noting the rate accelerating effects of the added chloride, Fahey stated that 'Since chloride salts produce no reaction in the absence of HCl, both the C–H and C–Cl bonds must be formed in the transition state and an Ad_E3 *anti* addition mechanism must be involved.'[5] We believe that this conclusion is exaggerated.

We found similar behavior under the conditions of our reaction. As did Fahey,[3d] we find a positive deuterium isotope effect (k_H/k_D = 2.2) indicating proton transfer in the transition state. The lack of reactivity in the absence of halide ion, coupled with the high proportion of halide product, suggests that these anions are involved in the transition states leading to virtually all of the products. The accelerating effect of the halide ion, however, merely indicates that it is involved in the slow step but not necessarily in covalent bond formation. Indeed, the variety of products formed strongly suggests the intermediacy of a carbocation resulting from a proton transfer from the trifluoroacetic acid molecule.

Somewhat more accurate kinetic data for the disappearance of oct-1-ene were obtained by referencing it to an internal decane standard. Plotting the negative logarithm of these pseudo first order rate constants against the negative acidities ($H_o - pK_a$) of the solutions gives a reasonably straight line with a slope of 1.1 (Fig. 3). The corresponding data for oct-4-ene produce a line with a slope of 1.2. The independence of this relationship to bromide concentration suggests that the bromide ion only affects the solution's ability to protonate the alkene. This kinetic dependence upon H_o and alkene supports the Ad_E2 mechanism leading to the formation of a cationic intermediate. Other anions affect the rate similarly.

We therefore believe that the role of the halide anion in this transition state is to 'solvate' the developing carbocationic center antiperiplanar to the protonation site. The insensitivity of the product ratios to the concentration of added bromide ion militates against a free carbocation. Thus, the intermediate is a short-lived carbocation sandwiched between an incoming halide ion and the newly formed conjugate base, trifluoroacetate. This form of 'ion sandwich' has been described previously[9] in nucleophilic substitutions and as an 'encumbered ion' in additions of trifluoroacetic acid to alkenes.[7] In the addition of DBr to cyclohexene, rapid collapse of this unsymmetrical cation sandwich can produce the *anti* addition product but we believe that the stereoselectivity of this reaction derives, in part, from the inflexibility of the cyclic system.

The similar reactivities of oct-1-, -2- and -4-ene support the slow formation of a secondary carbocation in all cases. The 2-methylhept-1-ene rapidly forms a more stable tertiary carbocation (Scheme 4). While rapid collapse of the 2-octyl cation sandwich can produce the octyl bromide, many other routes are also available to it. Bonding to the trifluoroacetate produces the ester while proton loss, primarily to the more basic trifluoroacetate ion, produces *cis*- or *trans*-oct-2-ene. Rearrangement to the 3-octyl cation produces the corresponding 3-substituted derivatives as well as oct-2-enes and oct-3-enes. That virtually all of these products derive from a tight ion sandwich can be seen from the insensitivity of the product composition to the concentration of bromide ion in the bulk of the solution.



Scheme 4

The relative importance of these different pathways was evaluated further by using deuterated trifluoroacetic acid and analyzing the deuterium content of each compound as it passed through the GC–MS. (We chose to examine the reaction of oct-1-ene with 0.1 M bromide looking at the products formed when the reaction was 75% complete so that we could identify the alkene products which eventually add DBr.) In the mass spectrometer, the 2-bromooctane fragments by the loss of bromine and the resulting 2-octyl cation is detected as singly and doubly deuterated ions. The former results from the simple addition of DBr to the oct-1-ene whereas the doubly deuterated ion comes from an initial isomerization to monodeuteriooct-2-ene which adds DBr. After correcting for natural deuterium abundance, 95% of the 2-bromooctane is calculated to result from the direct addition process while 5% goes through the oct-2-ene.

Similarly, the 3-bromooctane gives singly, doubly and triply deuterated octyl cations in the mass spectrometer. The singly deuterated product derives from rearrangement of the initial 2-octyl cation followed by bromide capture. The doubly deuterated octyl fragment requires isomerization of the oct-1-ene to monodeuteriooct-2-ene which adds DBr. The triply deuterated octyl bromide comes from two deuteration/de-protonation steps forming doubly deuterated oct-2- and -3-enes which subsequently add DBr. Our results indicate that 22% of the 3-bromooctane is formed by the cationic rearrangement while 75% is formed through an initial isomerization to the monodeuteriooct-2-ene which adds DBr. Only 3% of the 3-bromooctane formation occurs through two octene isomerizations. The small amount of 4-bromooctane found in these reactions contains similar amounts of singly, doubly and triply deuterated octyl cations suggesting similar competitive pathways.

Approximately 80% of the 2-octyl trifluoroacetate appears to come from the simple addition of CF_3COOD with the remaining ester going through an alkene isomerization. The latter path also accounts for the majority of the 3-octyl trifluoroacetate. The predominance of this pathway has been described elsewhere.[7] Assuming trifluoroacetate to be the base which deprotonates the sandwiched cation, it deprotonates the cation nine times as often as it collapses to ester. At this 75% completion point in the reaction, the oct-2-ene is found to be 98% monodeuterated while the oct-3-ene is 30% monodeuterated, 68% dideuterated and 2% trideuterated.

An alternative way of grouping these results is to look at the percentage of products which derives from initial anion capture, proton loss or cationic rearrangement of the 2-octyl cation. This analysis indicates that the initial cation sandwich captures an anion 65% of the time (95% of this time the anion is bromide). It loses a proton 32% of the time and only 3% of the 2-octyl cation undergoes a hydride shift. Although less accurately calculated because of the smaller amounts of these products, the partitioning of the 3-octyl cation appears very similar.

When the concentration of bromide ion in these reactions approaches 1 M, we find a sharp decrease in the rate, coupled with a marked increase in the proportion of unrearranged Markovnikov bromide product. Both ‡ of these effects parallel the decreasing acidity § of the solution (Fig. 1). We believe that the high salt concentration makes protonation of the Hammett indicator more difficult and has a parallel effect on the protonation of the alkenes. The effect of this is to require a more developed participation of the halide ion in the transition state, a tighter ion sandwich and a greater yield of the Markovnikov addition product.

Fahey found[10] that 3,3-dimethylbut-1-ene undergoes significant rearrangement under the conditions of his cyclohexene study and he suggested that a cation is being formed in this particular case because steric hindrance prevents chloride attack on the acid–alkene complex. In our study, oct-1-ene, which would be expected to show no such hindrance, also appears to react *via* a carbocation. Furthermore, our study of 3,3-dimethylbut-1-ene shows a rate acceleration by 0.1 M bromide ion similar to that seen with the oct-1-ene. This indicates that nucleophilic involvement is not prevented by the *tert*-butyl group of the dimethylbutene. However, as in Fahey's study, the major product in this reaction is the rearranged bromide indicating a cationic intermediate. The rearrangement of the alkene is not diminished by lowering the temperature, indicating similar activation parameters for the pathways leading to both rearranged and unrearranged product. The more nucleophilic iodide ion reacts faster than the bromide ion but produces the corresponding 'ion sandwich' which suffers the same fate as in the bromide reaction. The great accelerating effects of the halide ions guarantee that these anions are stabilizing the transition state for proton transfer while the extensive rearrangement guarantees the intermediacy of a carbocationic intermediate.

As with the octenes, an increased concentration of bromide ion slows the reaction and produces a greater proportion of

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‡ The lowest concentrations of bromide lead to a lower yield of alkyl bromide and a significant deviation from the parallel behavior.

§ We are defining our relative acidities as $H_o - pK_a = \log [In]/[HIn]$ and measuring the absorbance of the Hammett indicator, 2-chloro-4-nitroaniline (see ref. 8). We have not determined the pK_a of this indicator in our solvent system.

unrearranged bromide. At the highest bromide concentration, the disappearance of the dimethylbutene is slower than the disappearance of the dimethylbutene in the absence of added salts and the unrearranged alkyl bromide represents approximately 70% of the product. Using 1.0 M iodide ion, greater than 90% of the addition product is unrearranged.¶ No esters are seen in either of these cases. The energy barrier for the methyl shift in the 2,3,3-trimethyl-2-butyl cation has been experimentally determined[11] to be 3.5 ± 0.1 kcal mol^{-1}. This translates into a rate constant of 10^{10} s^{-1} for a methyl shift at room temperature. Our methyl shift to a secondary carbocation would be expected to be faster. A 90% yield of unrearranged product would make the iodide capture an order of magnitude faster than the methyl shift. Using 1.5 M iodide ion, we could detect no rearranged product. These considerations put the rate constant for ion pair collapse to product in the range of 10^{12} s^{-1} indicating that the iodide ion must be present when the carbocation is formed. Rate constants of this magnitude are considered[12] to be borderline between a preassociation mechanism and a concerted mechanism.

While most workers in this area have described the electrophilic addition of hydrogen halides to alkenes as a competition between bimolecular and termolecular mechanisms, it appears that the halide ions are not covalently involved in the transition states leading to ion pair intermediates. We have considered the possibility of a competition between an Ad_E2 cation sandwich mechanism and an Ad_E3 unsymmetrical concerted mechanism but the kinetic independence of bromide ion makes the latter unlikely. The efficient trapping of a 3,3-dimethyl-2-butyl cation is remarkable and supports the case for concertedness only in the most extreme situations.

We believe that our results are best explained by the slow protonation of the alkene assisted by variable halide participation. In a non-polar solvent, low concentrations of anions will assist the protonation of neutral bases (*e.g.* nitroanilines) and, similarly, assist the proton transfer to an alkene. The resulting ion pair undergoes the reactions expected from cations. Higher concentrations of salts make protonation of both species more difficult. The weaker proton donating solution inhibits the protonation thus requiring greater halide ion participation, more efficient trapping of the intermediate cation and, perhaps, eventually cause a concerted reaction. This will lead to increasing proportions of unrearranged alkyl halide product. This mechanism, with variable nucleophilic participation, is reminiscent of the suggestions[13] for a nucleophilic substitution mechanism intermediate between the S_N1 and S_N2 limiting cases.

Since we have skewed the reaction conditions much further toward non-ionic reaction conditions than any other similar reaction that we can find, we expect that truly concerted termolecular additions of hydrogen halides to alkenes are extremely rare. Furthermore, since the iodide ion is an optimal nucleophile in strongly acidic solutions, it seems unlikely that there are many cases of acid catalyzed additions to alkenes which do not involve a carbocationic intermediate. We believe that the partial stereoselectivity found in additions of hydrogen halides to alkenes derives from the ion sandwich mechanism rather than from a true concerted addition. The inability of most reaction conditions to prevent the rearrangement of the dimethylbutyl cation supports this view.

It should be noted that oct-1-ene, cyclohexene and 3,3-dimethylbut-1-ene all appear to react by the same termolecular cation sandwich mechanism at the lower bromide concentrations.

No anti-Markovnikov products and no radical induced isomerizations were found in any of these reactions although no efforts were made to exclude oxygen or peroxides. This result is rarely found[6] in HBr addition reactions and is taken as evidence that no HBr is formed during the reaction. It also underscores the value of this reagent for the addition of HBr and DBr to simple alkenes. The ability to add HI to 3,3-dimethylbut-1-ene with minimal rearrangement is extremely rare and suggests that this reagent may find use in similar situations.

Experimental

The oct-1-ene (99.5% purity) used in this experiment was obtained from Fluka Chemical Co. The other alkenes, trifluoroacetic acid and solvents (HPLC grade) were obtained from Aldrich Chemical Co. and were used without further purification. The quaternary ammonium salts were obtained from Fluka Chemical and/or 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 volumetric flasks by adding 1 or‖ 2 drops of the alkene** 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 purchased or synthesized and analyzed by NMR spectroscopy. Weight averaged detector responses for the octyl bromides relative to oct-1-ene were determined by synthesis of a bromide mixture, adding a known amount of oct-1-ene and analyzing the mixture by GC–MS. Detector responses for these secondary alkyl bromides were assumed to be equal. Relative detector responses for the secondary octyl trifluoroacetates were determined in a similar fashion. Relative detector responses for the diverse octyl halides were assumed to be proportional to the responses for the corresponding cyclohexyl halides which were analyzed in the usual manner. The secondary alkyl 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.

The additions of HI were accompanied by some iodide substitution into the methylene chloride solvent. When this interfered with purification of the product, 1,1,1-trichloroethane became the preferred reaction solvent. Flash chromatography was often useful in product purification.

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.

Tetra-*n*-butylammonium trifluoroacetate

A 25 ml sample of tetra-*n*-butylammonium hydroxide (Fluka Chemical) was neutralized with trifluoroacetic acid, then cooled and extracted with two 50 ml portions of methylene chloride which were rotary evaporated to a thick syrup. Application of a high vacuum for 24 h produced a thick mass which was broken up and dried by vacuum for another 24 h at 65 °C. The resulting white powder melted at 81–82 °C (Found: C,

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¶ Under these conditions, the addition of HI to 3-methylbut-1-ene also produces greater than 90% unrearranged product. This product ratio remains unchanged in the reaction for more than ten weeks. The 2,3-dimethyl-2-iodobutane appears to be somewhat less stable.

‖ Results from 1 or 2 drops of alkene (approximately 10^{-4} mol) are identical within our experimental uncertainty.

** In all kinetic studies, a preanalyzed mixture of alkene and decane was used.

†† At least 10^{-3} mol of bromide ion was used.

60.26; H, 10.27; N, 3.80. $C_{16}H_{36}NO_2F_3$ requires C, 60.81; H, 10.21; N, 3.94%).

2-Deuteriobromocyclohexane

A solution of tetra-*n*-butylammonium bromide (5.51 g, 17.1 mmol, 1.88 equiv.) in 20 ml of methylene chloride under a nitrogen atmosphere was treated with 4.0 ml (51.5 mmol, 5.6 equiv.) of deuteriotrifluoroacetic acid. After stirring the reaction mixture for 10 min, 0.75 g (9.1 mmol) of cyclohexene was added. The reaction mixture was protected from light with aluminum foil and allowed to react at room temperature for 5 days. The entire reaction mixture was transferred to a separatory funnel, washed with 2 × 50 ml water, 50 ml saturated $NaHCO_3$, 50 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 20 ml brine then dried over K_2CO_3, filtered and concentrated under reduced pressure. Distillation gave 0.93 g (63% yield) of a colorless liquid. ^1H NMR, IR, GC retention times and mass spectrum were consistent with authentic material (Aldrich Chemical).

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