

the increased tertiary/primary ratios observed with 2,3-dimethylbutane suggest that steric hindrance may reduce the reactivity of tertiary hydrogens toward highly substituted alkoxy radicals.

In summary, there appears to be no major differences in reactivity of alkoxy radicals of differing structure, either in their selectivity toward different C-H bonds, or in the competition between addition and hydrogen abstraction, strongly suggesting that, in the same system, their reactions with a substrate occur at comparable rates. On the other hand, there are enormous differences in the rates at which they undergo β scission; loss of a benzylic or tertiary radical from a tertiary alkoxy radical proceeds over 10^5 times as rapidly as loss of a primary radical from a primary alkoxy radical. These differences must be highly significant in a number of technical reactions in which alkoxy radicals play an important role, e.g., hydrocarbon autoxidation and the oxidative degradation of polymers, and need to be taken into account in interpreting the large changes in rate and reaction course which occur with change of structure in such systems.

Experimental Section

Materials were commercial reagents when available or were prepared by standard procedures (except as noted), purified by conventional means as necessary and purity checked by glc analysis. **Hypochlorites** were prepared from the corresponding alcohols, NaOCl solution, and acetic acid, essentially as in previous work.⁴ Except for *tert*-butyl hypochlorite, they were not isolated but prepared in the appropriate solvent (usually CCl_4), washed, and dried, and concentrations were determined by iodometric titration. β -Chloro ethers needed for reference ("Markovnikov" products) were prepared by a BF_3 catalyzed reaction of *tert*-butyl hypochlorite and a large excess of the appropriate alcohol with the appropriate olefin as described elsewhere.¹⁷ "Anti-Markovnikov" ethers were isolated from reaction mixtures by preparative glc.

Reactions were carried out in sealed, degassed tubes as in previous papers, and analyzed by glc. In β -scission experiments, all reactions were 4 M or higher in trichloroethylene. Experiments with isobutyl and 3-methyl-2-butyl hypochlorites were carried out at 0, 30, and 60°, Arrhenius parameters were calculated from these data, and the results in Table I were obtained by interpolation and extrapolation. Data were analyzed as in previous papers, and all slopes of linear plots reported were obtained by least-squares fitting of the data.

(17) C. Walling and R. T. Clark, *J. Org. Chem.*, **39**, 1962 (1974).

Reaction of Alkenes with Hydrogen Bromide in Acetic Acid. Polar Addition *via* the Ad3 Mechanism¹

Robert C. Fahey,* C. Allen McPherson, and Robert A. Smith

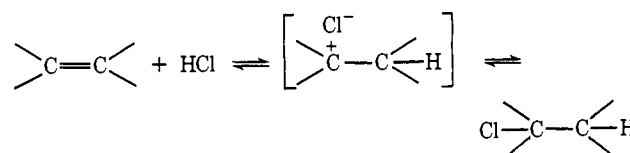
Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92037. Received January 31, 1973

Abstract: The rates and products for the polar reaction of cyclohexene and 1-hexene with HBr in acetic acid have been measured at 25°. The results are consistent with an Ad3 mechanism involving bromide ion catalysis for HBr addition and with an Ad3 mechanism involving HBr catalysis for HOAc addition. Studies with cyclohexene-1,3,3-*d*₃ show that HOAc and HBr add with a strong preference for anti addition between 15 and 60°. Factors influencing ion pairing in the Ad3 transition state and the relationships between Ad3 and E2 reactions are discussed.

Prompted by a report by Smirnov-Zamkov and Piskovitina² that DBr addition to cyclohexene in DOAc yields a mixture of syn and anti adduct in which the syn:anti ratio increases from ~ 0.3 to ~ 3 between 10 and 60°, we undertook, some years ago, a study of HBr addition to cyclohexene-1,3,3-*d*₃ in acetic acid in order to elaborate the origin of this interesting temperature effect. Our own results¹ differed from the earlier findings in that both HOAc and HBr adducts were observed, and both adducts resulted from predominant or exclusive anti addition in the temperature range 15–60°. Initial efforts to elaborate the kinetics of the reaction of cyclohexene with HBr in HOAc suggested a rather complex rate law and, fearing complications from competing homolytic reactions, we turned to a study of HCl addition.

In recent years we have reported a number of studies of the reaction of HCl with olefins and acetylenes which clarify the mechanism for polar addition of HCl to unsaturated hydrocarbons. For simple alkenes and

arenes two mechanisms are important. One involves reaction *via* a carbonium ion intermediate (Ade2 mechanism), formed as an ion pair in ion-pairing solvents, and is formally the reverse of the E1 elimination process.³



The second mechanism occurs *via* a transition state involving both C-H and C-Cl bond formation (Ade3 or Ad3 mechanism)⁴ and is formally the reverse of the E2 elimination process.^{5,6}

(3) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **91**, 3865 (1969).

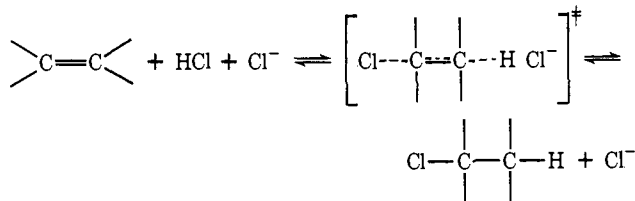
(4) We have previously used the designation Ade3 but now feel that the more general designation Ad3 is to be preferred until the detailed electronic structure of the transition state is elaborated.

(5) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *J. Amer. Chem. Soc.*, **92**, 2810 (1970); R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).

(6) R. C. Fahey and C. A. McPherson, *J. Amer. Chem. Soc.*, **93**, 2445 (1971).

(1) Reported in part in a preliminary communication: R. C. Fahey and R. A. Smith, *J. Amer. Chem. Soc.*, **86**, 5035 (1964).

(2) J. V. Smirnov-Zamkov and G. A. Piskovitina, *Ukr. Khim. Zh.*, **28**, 531 (1962).



The AdE2 mechanism dominates in the reaction of styrene and *tert*-butylethylene,³ but the two mechanisms are competitive in the reaction of cyclohexene⁵ and 1,2-dimethylcyclohexene.⁶ For the latter two olefins the Ad3 process involves stereospecific anti addition.

Having found that anti Ad3 addition of HCl to cyclohexene is a favorable process, it seemed reasonable that an analogous mechanism was responsible for the observed anti addition of HBr to cyclohexene and that the reaction involving HBr favors the Ad3 process to a greater extent than the reaction involving HCl. In order to verify this, we undertook further studies of the kinetics of HBr addition in acetic acid. In this paper we report the results of these studies along with the full details of the stereochemical studies of HBr addition to cyclohexene-1,3,3-*d*₃.

Experimental Section

Materials. 1-Hexene, cyclohexene (chromatoquality), 2-bromohexane, 1-bromohexane, 2-hexanol, cyclohexanone, pentane (chromatoquality), bromocyclohexane, and acetic anhydride were purchased from Matheson Coleman and Bell. Glacial acetic acid was titrated for water by the Karl Fisher method; slightly more than 1 equiv of acetic anhydride was added and the mixture either refluxed or allowed to stand until reaction was complete. Tetrabutylammonium bromide TBAB (J. T. Baker) was dried at 130° under vacuum before use. 2-Hexyl acetate was prepared from 2-hexanol and acetyl chloride (J. T. Baker). Cyclohexanone-2,2,6,6-*d*₄ was prepared by repeated (seven times) exchange of cyclohexanone (25 ml) with D₂O (10 ml) in the presence of K₂CO₃ (35 mg) for 12–20 hr at 60° followed by distillation (bp 90–92° (100 mm)); nmr analysis showed <2% α hydrogen. Cyclohexene-1,3,3-*d*₃ was prepared from cyclohexanone-2,2,6,6-*d*₄ as described previously.⁶

Addition to Cyclohexene-1,3,3-*d*₃. In a typical experiment, cyclohexene-1,3,3-*d*₃ (2.1 g) and 2,6-di-*tert*-butyl-*p*-cresol (10 mg) were dissolved in 100 ml of an 0.5 *M* stock solution of HBr in HOAc. The solution was sealed in an ampule and placed in a thermostated bath for 1–4 hr. The reaction mixture was quenched in water and extracted with pentane. The pentane fraction was washed with aqueous NaHCO₃, dried over anhydrous Na₂CO₃, and evaporated to give 75–95% yields of crude product. The product was analyzed by glpc (Aerograph Model 202 chromatograph with thermal conductivity detectors) using a 10 ft × 1/8 in. column packed with 30% DEGS on Chromosorb P operated at 70°; preparative separations were accomplished using a 10 ft × 3/8 in. column of the same type.

The pmr spectra of the glpc purified products were recorded on a Varian HR-60 spectrometer equipped with an NMR Specialties, Inc. Model SD-60 heteronuclear spin decoupler. Broad low-field resonances at 4.67 and 4.13 ppm were observed for the deuterated cyclohexyl acetate and bromide, respectively; these resonances sharpened to doublets (Figure 1) when deuterium decoupling was employed.

When the addition to cyclohexene was carried out at 25° in the presence of an equal amount of 1-hexene, the product of addition to 1-hexene was 2-bromohexane, <2% of 1-bromohexane being present at complete reaction. In other experiments it was found that cyclohexyl acetate is only slowly (<4% in 6 hr) converted to cyclohexyl bromide in 0.5 *M* HBr in HOAc at 40° and that cyclohexyl bromide is stable to these conditions.

The sample of isomerized deuterated cyclohexyl bromide was prepared by adding a 1.5-g sample in 30 ml of ether to 0.24 g of Mg in 100 ml of ether containing a trace of iodine and stirring for 6 hr at 50–60°. The mixture was cooled in ice and 1.5 g of bromine in 10 ml of pentane added. After stirring for 30 min, additional pentane was added and the pentane fraction washed with aqueous NaHCO₃, dilute HCl, and water. The pentane fraction was dried

over anhydrous Na₂CO₃ and evaporated to give a 74% crude recovery. After glpc purification the pmr spectrum was recorded (Figure 1D).

Kinetic and Product Studies. Solutions of hydrogen bromide in glacial acetic acid were prepared by weight and the concentrations determined by the addition of an excess amount of lithium acetate in acetic acid followed by potentiometric titration of the excess lithium acetate against standard *p*-toluenesulfonic acid in acetic acid.

The reaction solutions were prepared by mixing a stock solution of the acid with the olefin, internal standard, and diluent (if any) in a 50 ml volumetric flask and were transferred to a constant temperature bath (25.0 ± 0.1°) after rapid mixing of the solution. Aliquots (10 ml) were withdrawn at intervals and mixed with pentane (10 ml) and 10% aqueous sodium chloride solution (30 ml). The organic layer was separated and the water layer washed with two 10-ml portions of pentane. The combined organic layers were washed with a dilute solution of sodium bicarbonate, dried over anhydrous sodium carbonate, and concentrated on a rotary evaporator.

The concentrated samples obtained from reactions of 1-hexene were analyzed by glpc (Aerograph Hy-FI III Model 1200 chromatograph equipped with a flame ionization detector) on a 150 ft by 0.01 in. Carbowax 400 column at 50° with a nitrogen flow rate of 2.5 ml/min. Retention times (min) as measured from the injection point were: 1-hexene, 3.0; 2-bromohexane, 5.8; 1-bromohexane, 8.0; 2-acetoxylhexane, 9.6; mesitylene (internal standard), 13. Reaction mixture compositions were calculated from the peak area ratios which were calibrated with mixtures of known composition.

Analysis of a reaction mixture (0.0915 *M* 1-hexene and 0.435 *M* hydrogen bromide) after 26 hr of reaction showed the product concentrations to be 0.075 *M* 2-bromohexane, 0.016 *M* 2-hexylacetate, and 0.001 *M* 1-bromohexane. Control runs at 0.5 *M* HBr–0.18 *M* TBAB and at 0.1 *M* HBr–0.9 *M* TBAB for a reaction time of 1 day established that neither 2-bromohexane, 2-acetoxylhexane, nor 1-bromohexane undergo any appreciable reaction (<1%) under the conditions of the kinetic runs (reaction time ≤ 1 day at 25°).

The reaction of cyclohexene with hydrogen bromide in acetic acid was studied in a manner similar to the reaction of 1-hexene. The concentrated samples from the reaction of cyclohexene were analyzed by glpc on the 150 ft by 0.01 in. Carbowax 400 column at 45° with a flow rate of 2 ml/min. Retention times (min) as measured from the injection point were: cyclohexene, 3.5; cyclohexyl bromide, 10; cyclohexyl acetate, 15; durenene (internal standard), 17.

Reaction of a solution of 0.3 *M* *tert*-butylethylene and 0.5 *M* HBr in HOAc for 1 day at room temperature was followed by work-up as described above and analysis by pmr. The same experiment was repeated with the addition of 0.5 *M* TBAB to the solution. Pmr peak assignments (δ, ppm; *J*, Hz) were as follows: 3-bromo-2,2-dimethylbutane, 1.05 (9 H, singlet), 1.7 (3 H, doublet, *J* = 7), 4.1 (1 H, quartet, *J* = 7); 2-bromo-2,3-dimethylbutane, 1.05 (6 H, doublet, *J* = 7), 1.8 (6 H, singlet), 1.9 (1 H, multiplet); 3-acetoxy-2,2-dimethylbutane, 0.92 (9 H, singlet), 1.1 (3 H, doublet, *J* = 6), 2.0 (3 H, singlet), 4.7 (1 H, quartet, *J* = 6). Product compositions were calculated from the observed peak areas.

Results

Stereochemistry. The stereochemistry of HBr addition to cyclohexene-1,3,3-*d*₃ was studied following a procedure analogous to that described earlier for HCl addition.⁵ The three possible 1,2 adducts of HBr with cyclohexene-1,3,3-*d*₃ can be distinguished using pmr since BC, the bromide resulting from proton attack at C-2, exhibits no low-field resonance while SBC and ABC, the syn and anti adducts produced by proton attack at C-1, each exhibit low-field doublets for the CHBr group. Neglecting small secondary isotope effects, proton attack occurs with equal probability at C-1 and C-2 of cyclohexene-1,3,3-*d*₃ and the stereochemistry can be established from the low-field doublet splitting of the product derived from attack at C-2. Thus, the pmr spectrum of SBC is expected to show a larger splitting (axial–axial coupling in the more stable equatorial conformation) for the low-field doublet than the corresponding splitting in CBA (axial–equatorial coupling).

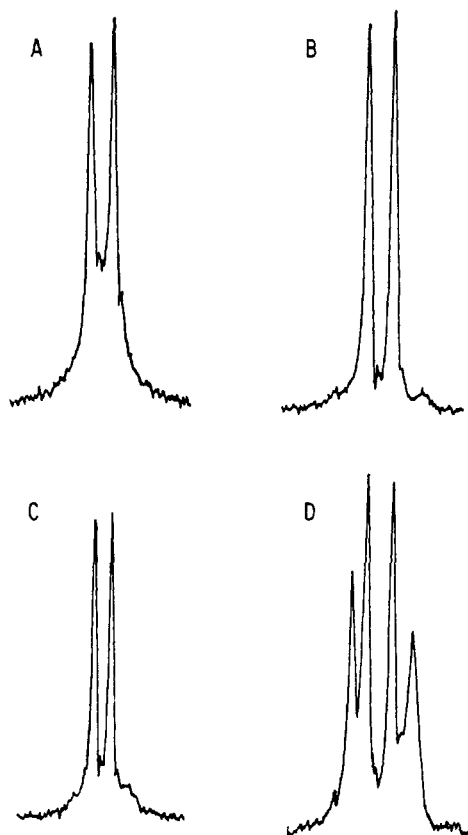
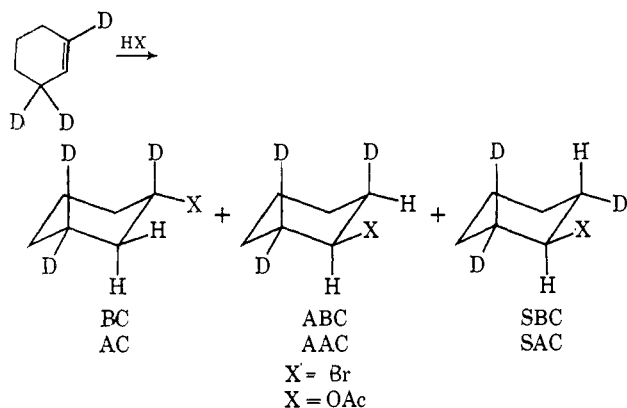


Figure 1. Low-field pmr signals, measured with deuterium decoupling, for the addition products obtained from reaction of cyclohexene-1,3,3- d_3 (0.25 M) in acetic acid at 0.5 M HBr: (A) HOAc adduct from reaction at 25°, $J = 3.3$ Hz; (B) HBr adduct from reaction at 25°, $J = 3.5$ Hz; (C) HBr adduct from reaction at 60°, $J = 3.5$ Hz; (D) isomerized HBr adduct, $J = 8.7$ and 3.5 Hz.



The corresponding HOAc adducts (AC, AAC, and SAC) can be distinguished on the same basis.

Additions were carried out with a twofold excess over olefin of 0.5 M HBr in HOAc containing a small amount of 2,6-di-*tert*-butyl-*p*-cresol. That the addition occurs predominantly *via* a polar mechanism was indicated by the observation that, under these conditions, 1-hexene added HBr to yield 2-bromohexane as the dominant product. In control experiments it was established that both cyclohexyl bromide and cyclohexyl acetate are stable to the reaction conditions. Additions were carried out at a number of temperatures and the ratio of bromide to acetate was established using glpc and pmr. The low-field resonances of the HBr and HOAc adducts were observed under condi-

tions of deuterium decoupling and found to have 3.5 and 3.3 Hz splittings, respectively. Representative spectra are shown in Figure 1. The magnitude of this splitting is that expected for the anti adducts and is much lower than would be expected for the syn adducts.

This conclusion was confirmed by examining an isomerized sample of the HBr adduct. A sample of the bromide was purified by glpc and then converted to the Grignard reagent which isomerizes rapidly at room temperature. The latter was converted back to the bromide by reaction with bromine and the product purified by glpc. The low-field resonance (Figure 1D) of this material showed a new 8.7-Hz doublet superimposed on the original 3.5-Hz doublet. The new peaks appear to be somewhat broader than the central lines, possibly as the result of long-range coupling or second-order splitting. Even considering the difference in line width, the outer lines appear to have lower integrated intensity than the inner pair, indicating that the bromide was not quantitatively converted to the Grignard reagent. The 8.7-Hz doublet also appears to be very slightly shifted to higher field relative to the 3.5-Hz doublet, possibly as the result of slightly different isotope effects on the chemical shift in the two isomers. The observed splittings are in good agreement with the corresponding splittings of 3.5 and 8.9 Hz reported previously⁵ for the respective anti and syn adducts of HCl with cyclohexene-1,3,3- d_3 , and the stereochemical assignment is thus firmly established. Couplings of a similar magnitude occur for the two HOAc adducts,³ and the adduct actually formed must therefore be the anti adduct, AAC.

No peaks clearly assignable to the syn adduct were found in the spectra of either the HBr or the HOAc adduct, so that only a lower limit could be obtained for the anti:syn product ratio. From this limit, and the observed ratio of bromide to acetate, the product composition data given in Table I were calculated.

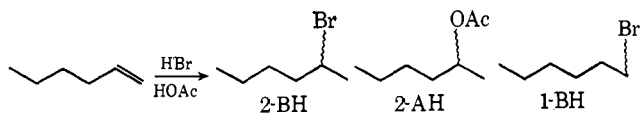
Table I. Product Composition and Stereochemistry for the Reaction of HBr (0.5 M) with Cyclohexene-1,3,3- d_3 in HOAc

T , °C	% adduct formed			
	<i>syn</i> -HOAc	<i>anti</i> -HOAc	<i>syn</i> -HBr	<i>anti</i> -HBr
15	<i>a</i>	<i>a</i>	≤3	90
25	<0.5	12	≤3	88
40	≤2	15	≤4	85
60	≤3	24	≤4	76

^a Anti:syn ratio not measured.

These results differ markedly from those reported by Smirnov-Zamkov and Piskovitina,² but since no details concerning procedure and reagent concentrations appeared in their original communication, and since a full paper on the work has not appeared, it is difficult to elaborate reasons for the discrepancy at the present time.

Rate and Product Studies. For the purpose of kinetic studies we chose to focus our attention on the addition to 1-hexene, rather than cyclohexene, since the polar addition products from 1-hexene, 2-bromohexane (2-BH), and 2-hexyl acetate (2-AH) could be readily distinguished from the free radical adduct, 1-bromohexane (1-BH), whereas with cyclohexene the



polar and free radical HBr adducts are identical. The reaction of 1-hexene was followed at 25° by removing aliquots from the reaction mixture, extracting, and analyzing the organic fraction by glpc. An internal standard was employed and the glpc procedure calibrated with standard mixtures. It was established in control experiments that no fractionation occurs in the work-up procedure, that 2-BH, 2-AH, and 1-BH are stable to the reaction conditions, and that no reaction of 1-hexene occurs in the absence of HBr. When the reaction was allowed to proceed to completion, $\geq 95\%$ of the starting 1-hexene was accounted for as 2-BH and 2-AH. Product concentrations were measured at $\leq 10\%$ conversion of the limiting reagent and initial rates, $R = ([2\text{-BH}] + [2\text{-AH}])/t$, calculated. The results, obtained at various concentrations of HBr and of TBAB (tetrabutylammonium bromide), are given in Table II.

Table II. The Rate and Product Composition for the Reaction of 1-Hexene and Cyclohexene with HBr in HOAc at 25°

[HBr], M	[TBAB], ^a M	$10^6 R$, ^b M sec ⁻¹	% 2-BH/ % 2-AH ^c	% 1-BH ^d
1-Hexene (0.091 M)				
0.0163		6.2	1.1	1
0.0326		13.8	1.4	8
0.0488		27 ^e	1.4	1
0.0814		56	1.7	1
0.116 ^e		65	1.9	46
0.116		60 ^e	1.8	39
0.163		172	2.7	1
0.435		751	4.1	10
0.727		1330	4.6	18
0.0814	0.186	110 ^e	4.3	1
0.076	0.0213	39 ^e	2.2	1
0.116	0.0213	76 ^e	2.2	2
0.116	0.053	91 ^e	2.8	1
0.116	0.107	94	3.2	1
0.116	0.270	112	4.4	1
0.116	0.51	144 ^e	6.6	1
0.116	0.87	124 ^e	8.1	1
Cyclohexene (0.099 M)				
0.081		81	2.3 ^f	
0.41			8 ^f	
0.081	0.183	300	11.5 ^f	

^a Tetrabutylammonium bromide. ^b Average deviation $\leq 5\%$ except as noted. ^c Average deviation $\leq 10\%$. ^d At $\sim 10\%$ conversion. ^e With 0.0127 M 2,6-di-*tert*-butyl-*p*-cresol. ^f Per cent cyclohexyl bromide:per cent cyclohexyl acetate.

Although little or no free radical adduct (1-BH) was detected when the reaction was allowed to proceed to completion, significant formation of 1-BH was found at low conversion in about one-third of the runs. In these reactions, 1-BH was found to be a major product at $< 1\%$ conversion but to remain at nearly constant concentration in the reaction mixture while the concentrations of 2-BH and 2-AH increased throughout the run. Thus, 1-BH appears to be formed in a rapid reaction which occurs during or shortly after mixing of the reactants and which then terminates. The presence of 2,6-di-*tert*-butyl-*p*-cresol, a free radical inhibitor, in the reaction mixture had no effect in sup-

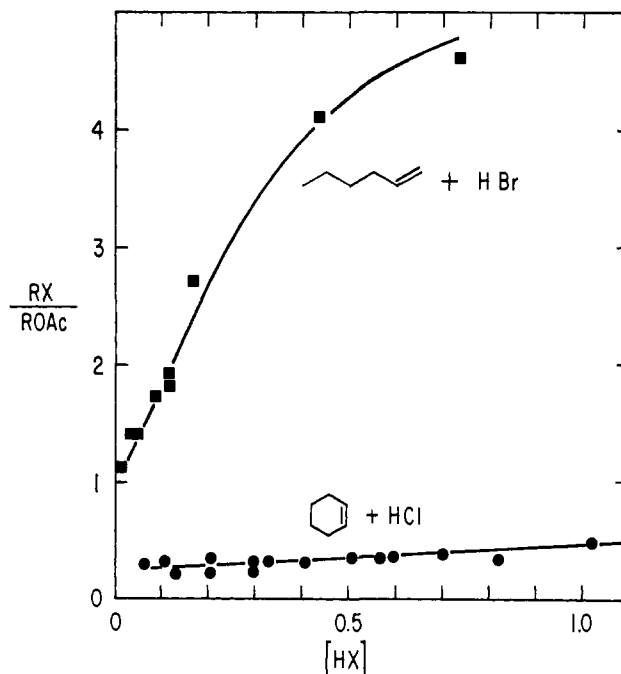


Figure 2. Variation in the ratio of alkyl halide to alkyl acetate product ratio with HX concentration for reaction in HOAc at 25°. Data for reaction of cyclohexene with HCl from ref 5.

pressing this reaction and there seems to be no consistent pattern in the conditions under which 1-BH is formed in substantial amount. Pasto and coworkers^{7,8} have examined the free radical isomerization of linear alkenes by HBr and find the radical addition to be kinetically unfavorable. It seems probable that homolytic addition competes in our experiments only under the conditions of mixing when high local concentrations of olefin provide favorable conditions for the radical chain process. It seems improbable that the reaction leading to 1-BH significantly influences the reactions leading to 2-BH and 2-AH, and, assuming this to be the case, we will treat the latter processes as being independent of the former.

A primary purpose of these studies was to ascertain to what extent the reaction of alkenes with HBr resembles the corresponding reaction with HCl and it is therefore useful to examine the results obtained with 1-hexene and HBr relative to those reported earlier for cyclohexene and HCl.⁶ Inherent in the comparison is the assumption that cyclohexene and 1-hexene exhibit similar behavior. Table II includes data from three runs obtained with cyclohexene and HBr. It is seen that the variation in product composition with HBr concentration, and the effect of bromide salt upon the product composition and upon the reaction rate, follow the same trends found with 1-hexene, lending credence to the assumption that these olefins behave similarly under these reaction conditions.

Considering first the variation in the halide to acetate product ratio, we note in Figure 2 that for HBr the ratio is higher at low acid concentration and increases more markedly with acid concentration than in the

(7) D. J. Pasto, G. R. Meyer, and S.-Z. Kang, *J. Amer. Chem. Soc.*, **91**, 2163 (1969).

(8) D. J. Pasto, G. R. Meyer, and B. Lepeska, *J. Amer. Chem. Soc.*, **96**, 1858 (1974).

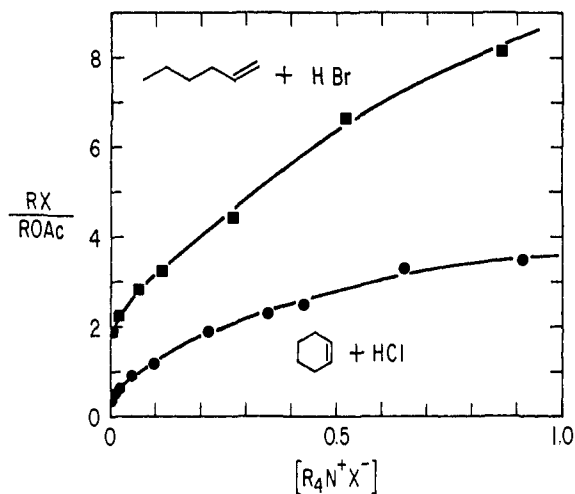


Figure 3. Variation in the ratio of alkyl halide to alkyl acetate product ratio with tetraalkylammonium halide concentration for reaction in HOAc at 25°: (■) 1-hexene (0.091 M), 0.116 M HBr, $R_4NX = TBAB$; (●) cyclohexene (0.587 M), 0.57 M HCl, $R_4NX = Me_4NCl$, from ref 5.

reaction with HCl. The effect of halide salt (Figure 3) upon the product ratio is generally more similar for HCl and HBr, but we see by comparing Figures 2 and 3 that whereas bromide salt is very roughly comparable to HBr in its effect upon the product ratio, chloride salt has a far greater effect than does HCl.

Turning now to the effect of HBr concentration upon the rate of reaction, we find that a somewhat better correlation is obtained between $\log R$ and $\log [HBr]$ than between $\log R$ and $-H_0$ for HBr-HOAc solutions.⁸ The slope of the $\log R$ - $\log [HBr]$ correlation is 1.46. For reasons to be elaborated under Discussion, it is of interest to examine the dependence of the individual partial rates for formation of 2-BH and 2-AH. From Figure 4 we see that the apparent order in HBr for formation of 2-BH is 1.58 while that of 2-AH is 1.18, the maximum uncertainties in these apparent orders being ± 0.05 and ± 0.1 , respectively, after allowing for the uncertainties in the rate and product distribution measurements.

The effects of halide salts upon the partial rates of reaction are significantly different for the HBr and HCl reactions. Thus, while tetramethylammonium chloride at $\sim 0.5 M$ concentration produces a roughly 15-fold increase in the rate of HCl addition and a ~ 2 -fold increase in the rate of HOAc addition to cyclohexene, a comparable concentration of TBAB causes only a two-fold increase in the rate of HBr addition and leads to an $\sim 20\%$ decrease in the rate of HOAc addition to 1-hexene at a fixed acid concentration.

Finally, we report results of a preliminary experiment designed to ascertain whether *tert*-butylethylene might react with HBr in a fashion similar to that observed for reaction with HCl,³ specifically without halide salts influencing the product composition. Product compositions were estimated from the pmr spectrum of the crude reaction mixture and the results are summarized below. We note only that TBAB does have a significant influence on the product composition, increasing the amount of HBr 1,2 adduct at the expense of the Wagner-Meerwein rearranged product.

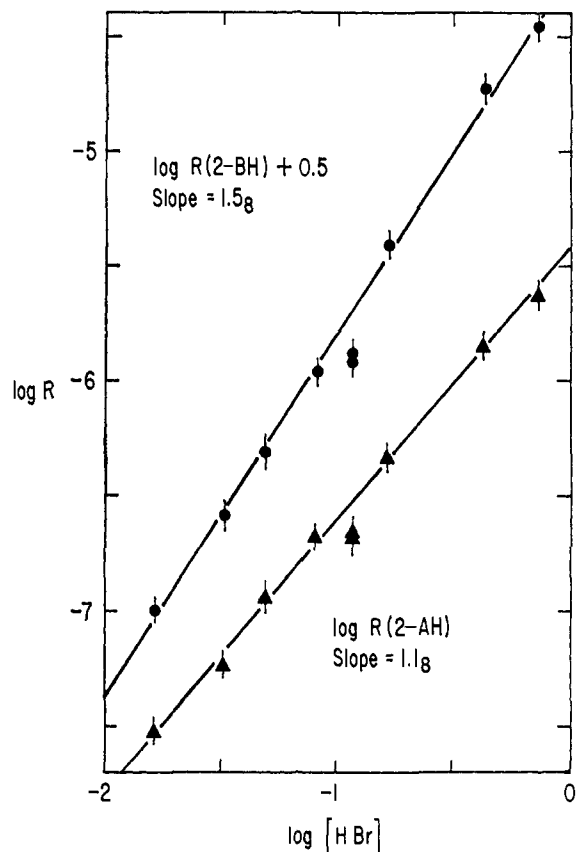
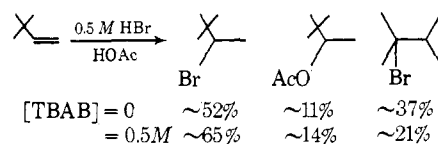
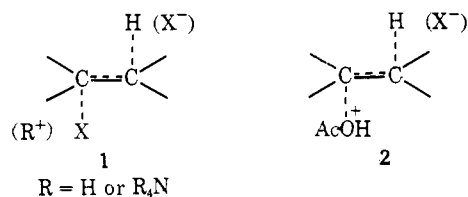


Figure 4. Log-log plot of the partial initial rate for formation of 2-bromohexane and 2-hexyl acetate vs. HBr concentration for reaction of 1-hexene (0.091 M) in HOAc at 25°. The two points $[HBr] = 0.116 M$ were not included in the calculation of the slope.



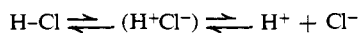
Discussion

General Considerations. The results obtained with HBr are generally similar to those found earlier⁵ for the reaction of cyclohexene with HCl in acetic acid. In both reactions, addition of HX and also of HOAc to cyclohexene-1,3,3-*d*₃ occurs with a strong preference for anti addition. In both reactions, the ratio of halide to acetate product is low at low-halide concentration and increases with halide ion concentration. The more extensive results with the HCl system⁵ implicate an anti Ad3 mechanism for the formation of alkyl chloride and an analogous mechanism leading to alkyl acetate; the results of the present more limited studies are consistent with the same mechanisms for the reaction of 1-hexene and cyclohexene with HBr in acetic acid. The transition states for these reactions are viewed as resembling 1 and 2, where we denote in

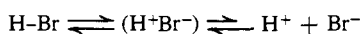


parentheses the possible counterions which may be present if the attacking species is of a molecular or ion pair nature.

The differences between the HCl and HBr reactions can be understood on the basis of the differences in the ground state. While HCl is largely molecular in acetic acid and is little dissociated ($K_d = 2.9 \times 10^{-9} M$)⁹



HBr is significantly ionized and is dissociated ($K_d = 10^{-5}$ to $10^{-6} M$) to an extent comparable to halide salts.⁹



Because it is more ionized and more dissociated than HCl, HBr serves as a better halide ion source, explaining why the ratio of alkyl halide to alkyl acetate product is larger at a given HX concentration for the HBr reaction than for the HCl reaction. Moreover, on this basis HBr and $R_4\text{NBr}$ should have similar effects upon the alkyl bromide to alkyl acetate ratio while $R_4\text{NCl}$ should have a much greater effect than HCl upon the alkyl chloride to alkyl acetate ratio, and this is in accord with the observations (Figures 2 and 3).

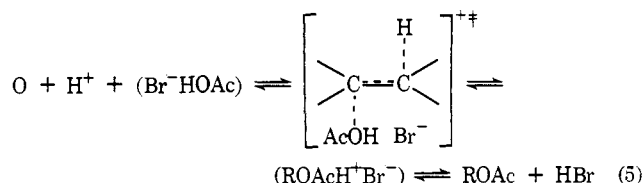
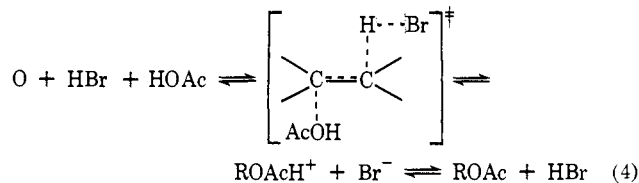
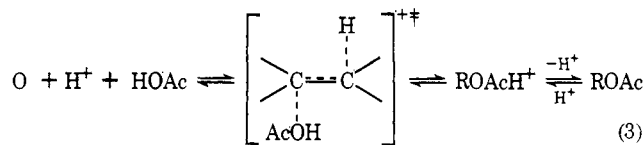
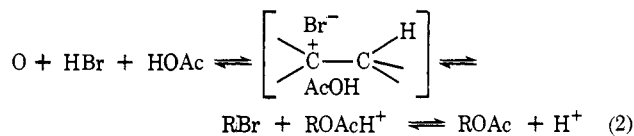
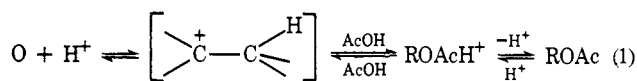
From the foregoing considerations, it follows that in acetic acid Ad3 addition of HX is favored (relative to AdE2 addition *via* a carbonium ion) to a greater extent for HBr than for HCl. The same conclusion can be drawn from the observation that added bromide salt reduces formation of rearranged product in the reaction of HBr with *tert*-butylethylene whereas, in the analogous reaction with HCl,³ chloride salt has no significant effect upon the extent of rearrangement. The fact that Wagner-Meerwein rearrangement does accompany HBr addition to *tert*-butylethylene does show, nevertheless, that the AdE2 mechanism is of importance for reaction of HBr with some alkenes in acetic acid. Presumably the *tert*-butyl group has a retarding effect on the Ad3 reaction which allows the AdE2 reaction to compete.

With these overall considerations as background we turn now to a more careful and detailed analysis of the results in terms of possible mechanisms.

Addition of HOAc. We first consider the plausible mechanisms which might produce alkyl acetate product, excluding those involving acetate ion on the ground that in the highly acidic solutions employed the acetate ion concentration is prohibitively small and excluding cyclic mechanisms which would require exclusive *syn* addition. This leaves two mechanisms of the AdE2 type (eq 1 and 2) and three of the Ad3 type (eq 3-5). In these equations, HBr is taken to include the molecular and ion pair, (H^+Br^-) , forms, the two being kinetically indistinguishable. To be acceptable we will require that the mechanism be compatible with the kinetic results obtained with 1-hexene and also with the anti addition found with cyclohexene-1,3,3-*d*₃. We will further require that the mechanism accommodate the inverse deuterium isotope effects observed by Pasto and coworkers⁸ for the anti additions HBr ($k_H/k_D \sim 0.5$) and HOAc ($k_H/k_D \sim 0.6$) to cyclopentene under similar conditions.

Mechanisms 1 and 3 can be eliminated on the basis that, depending upon dissociated H^+ concentration,

(9) I. M. Kolthoff and S. Bruckenstein, *J. Amer. Chem. Soc.*, **78**, 1 (1956).



they should exhibit a square-root dependence upon $[\text{HBr}]$ which is incompatible with the observed dependence of somewhat more than unity (Figure 4). Also, it is difficult to envision why mechanism 1, involving an open cation, should result in very predominant anti addition. Further, proton transfer from protonated acetic acid to carbon would be expected to involve a positive isotope effect, rather than the inverse effect found with cyclopentene.⁸ Mechanism 5 can also be excluded on the basis of incompatibility with an inverse isotope effect.

The remaining mechanisms involve rate laws which are first order in HBr and are thus in reasonable accord with the kinetic data, but the mechanism of eq 2 appears inconsistent with the stereochemical results. Thus, while the bromide ion might well block the attack of acetic acid at the side of the carbonium ion which would give rise to *syn* HOAc adduct, and thereby cause alkyl acetate to be formed by dominant anti addition, collapse to bromide should occur with substantial formation of the *syn*-HBr adduct, but this is not observed. Moreover, collapse of the intermediate ion pair should give substantially more alkyl bromide than alkyl acetate, and the fact that nearly equal amounts of these products are formed at low HBr concentration is not in accord with this expectation.

This leaves the mechanism of eq 4. It might seem that this mechanism would also involve a positive deuterium isotope effect. However, Pasto, *et al.*,⁸ point out that an inverse isotope effect can be rationalized if it is assumed that the attacking species is molecular HBr. Thus, the HBr stretching frequency is lower than that for typical C-H bonds and the transition state may well have bending frequencies associated with H whereas HBr has none. The result could reasonably be a greater total of vibrational frequency associated with H for the transition state than for the ground state giving rise to an inverse isotope effect. Thus, the inverse isotope effect cannot be taken as evi-

dence against the mechanism of eq 4. We conclude that this mechanism is in best accord with all of the data.

Comparing the HBr and HCl promoted Ad3 addition of HOAc, we note that salts produce a small decrease in the rate of the former reaction but increase the rate of the latter.⁵ This difference can reasonably be accounted for on the basis of the differences in ground state. Since HBr in HOAc exists significantly in the ion pair form, the ground state has considerable ionic character while in the transition state part of the charge is likely to be distributed over several atoms. Thus there could easily be charge dispersal in the transition state relative to the ground state explaining the slightly negative effect of salt upon the reaction rate. Since HCl is largely molecular in the ground state, a positive salt effect is to be expected for the HCl promoted reaction.

A comparison of the rates for Ad3 addition of HOAc to cyclohexene shows that the HBr catalyzed reaction is about 190-fold faster than the HCl catalyzed reaction.¹⁰ This is a somewhat greater difference than expected from the difference in H_0 measured by Smith and Elliot.¹¹ At $5 \times 10^{-3} M$ HX the difference in H_0 is 1.73 compared with the log of the observed relative Ad3 reactivity which is 2.28.

These results show that the HBr and HCl catalyzed addition of acetic acid to cyclohexene occurs very predominantly *via* an anti Ad3 mechanism. In a future paper¹² we will present evidence that the reaction of cyclohexene with HClO_4 in acetic acid, which gives cyclohexyl acetate as the sole product, also occurs *via* an anti Ad3 mechanism. This conclusion conflicts with that drawn by Corriu and Guenzet¹³ from the results of studies of acid catalyzed addition of acetic acid to cyclohexene. They found that $\log k_{\text{obsd}}$ correlates with $-H_0$, that the reaction exhibits the characteristics of general acid catalysis, and that $k_{\text{H}}/k_{\text{D}} \sim 1.5$. From these observations they concluded that rate-limiting protonation leading to a cyclohexyl cation (AdE2 mechanism) is involved. However, the observations are also consistent with an Ad3 mechanism and the close relationship between the reactions studied by Corriu and Guenzet¹³ and those discussed here suggests that their reactions actually involve an Ad3 mechanism.

It is our view, based on the present and preceding studies, that both the Ad3 and the AdE2 mechanisms are of quite general importance in the strong acid catalyzed addition of weak acids to olefins. The problem of experimentally distinguishing these mechanisms is not an easy one and in many respects resembles the problem of distinguishing $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ mechanisms for solvolytic displacement reactions. The AdE2 and Ad3 mechanisms for this type of reaction will both exhibit general acid catalysis, will have similar kinetic behavior in the weak acid as solvent, and can have comparable kinetic isotope effects. To the extent that

(10) This rate factor is obtained by comparing the initial rates for HBr catalyzed addition of HOAc to 1-hexene with those for HCl catalyzed addition to cyclohexene⁶ at $[\text{HX}] = 0.1\text{--}0.7 M$ and then correcting for differences in olefin concentration and the relative reactivity of 1-hexene and cyclohexene.

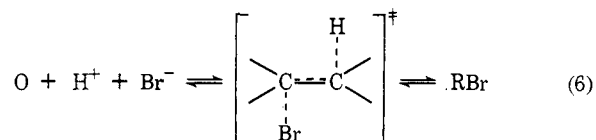
(11) T. L. Smith and J. H. Elliot, *J. Amer. Chem. Soc.*, **75**, 3566 (1953).

(12) R. C. Fahey and M. W. Monahan, unpublished results.

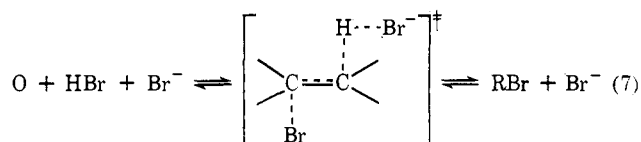
(13) R. Corriu and J. Guenzet, *Tetrahedron Lett.*, 671 (1970).

kinetically controlled Wagner–Meerwein or related rearrangement is observed in a given system, an AdE2 mechanism is clearly implicated. Similarly, observation of anti stereochemistry for addition in systems where Ad3–E2 reactions are known to have a strong preference for anti stereospecificity (*e.g.*, the cyclohexane system) can be taken as strong evidence for the Ad3 mechanism.

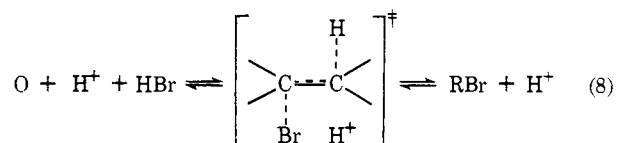
Addition of HBr. Plausible mechanisms for the addition of HBr must accommodate the anti stereochemistry of addition and the higher than first-order dependence upon HBr. AdE-2 type mechanisms involving an open cation (*e.g.*, eq 2) are excluded on the basis of the observed stereochemistry. The anti Ad3 mechanisms of eq 6–9 merit consideration. With each



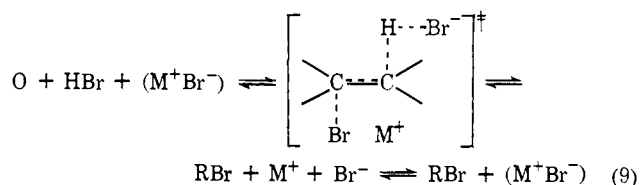
$$R = k[\text{O}][\text{H}^+][\text{Br}^-] = kK_{\text{d}}[\text{O}]C_{\text{HBr}}$$



$$R = k_3[\text{O}][\text{HBr}][\text{Br}^-] = k_3[\text{O}]C_{\text{HBr}}(K_{\text{d}}C_{\text{HBr}} + K_{\text{d}}'C_{\text{TBAB}})^{-1/2}$$



$$R = k[\text{O}][\text{H}^+][\text{HBr}] = kK_{\text{d}}[\text{O}]C_{\text{HBr}}^2(K_{\text{d}}C_{\text{HBr}} + K_{\text{d}}'C_{\text{TBAB}})^{-1/2}$$



$$\text{M} = \text{H or Bu}_4\text{N}$$

$$R = k[\text{O}][\text{HBr}][\text{M}^+\text{Br}^-] = k[\text{O}]C_{\text{HBr}}^2 + k_3[\text{O}]C_{\text{HBr}}C_{\text{TBAB}}$$

mechanism is given the expected rate expression, expressed in terms of the stoichiometric concentrations, C_{HBr} , and C_{TBAB} , and the respective dissociation constants, K_{d} and K_{d}' , of HBr and TBAB.

The mechanism of eq 6 should in principle exhibit first-order dependence upon HBr and be independent of TBAB. The observed 1.58 order dependence upon HBr and the increase in rate with added TBAB are not in accord with this mechanism. The deviation from expected dependence is not easily accommodated in terms of medium or salt effects upon the rate. We conclude that the mechanism of eq 6 is excluded by the results as the primary mode for HBr addition.

The mechanisms of eqs 7 and 8 involve $3/2$ -order dependence upon HBr in the absence of TBAB and are thus consistent with the observed kinetic order. The two mechanisms differ in their dependence upon TBAB, the mechanism of eq 7 requiring catalysis by TBAB and that of eq 8 requiring inhibition by TBAB. The observed increase in rate of alkyl bromide formation with TBAB is thus more in accord with the mech-

anism of eq 7 than eq 8. Moreover, the mechanism of eq 8 can be excluded on the basis that it should involve a positive deuterium isotope effect.

The mechanism of eq 7 is in general accord with the results. A quantitative test of the rate law of eq 7 is hampered by lack of accurate values for K_d and K_d' , but if we assume $K_d = K_d'$ than a value of $10^4 k_3 K_d^{1/2} = 1.7 \pm 0.3 M^{-1.5} \text{ sec}^{-1}$ is calculated from all of the data points of Table II for 1-hexene, excluding the two where the most radical product is formed. While the average deviation in this rate parameter is somewhat larger than the experimental errors, the fit of the rate law appears acceptable considering the wide range of reactant concentrations involved and the possible complications which can arise in the runs at the higher salt and HBr concentrations.

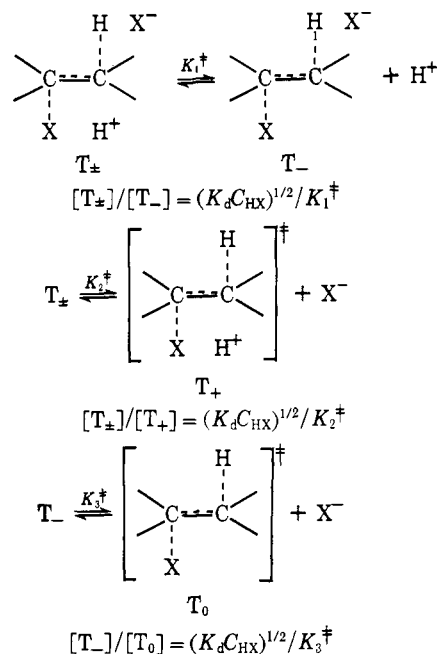
We consider last the mechanism of eq 9. The rate law for this mechanism predicts second-order dependence upon HBr and a first-order catalysis term involving TBAB. The required dependence upon both HBr and TBAB is clearly greater than observed. The difference might be rationalized in terms of a negative "medium" effect by HBr at higher HBr concentrations and a negative salt effect by TBAB. In view of the polar nature of the ground state and the charge destruction occurring in the transition state, this is certainly a plausible complication. But if this were the case we might expect to see the apparent order in HBr increase at lower HBr concentrations and this does not seem to occur.

On balance, the mechanism of eq 7 is in best agreement with the results. This is the same general mechanism that provided the best fit of the results for the Ad3 addition of HCl to cyclohexene⁵ and also to 1,2-dimethylcyclohexene,⁶ and it is of interest to compare the rates for the HBr and HCl additions. If the observed initial rates for alkyl halide formation (corrected for olefin concentration) for reaction of HBr with 1-hexene are compared to those for reaction of HCl with cyclohexene⁵ in the range 0.1–0.7 M HX, it is found that the HBr reaction is faster on average by a factor of about 1700. Correcting this by the reactivity of cyclohexene relative to 1-hexene at 0.081 M HBr, we find that Ad3 addition of HBr is on average some 2500-fold faster than that of HCl at a given HX concentration. The origin of this factor can be analyzed in terms of the values of k_3 .

In order to obtain k_3 for HBr it is necessary to know K_d for HBr, and this value has not been measured accurately. The best estimate is that of Koltoff and Bruckenstein⁹ who find $K_d \sim 10^{-5}$ – 10^{-6} M; taking $K_d = 3 \times 10^{-6}$ we obtain $k_3 = 0.10 M^{-2} \text{ sec}^{-1}$ for HBr with 1-hexene compared with $k_3 = 10^{-3} M^{-2} \text{ sec}^{-1}$ for HCl with cyclohexene. Correcting for the cyclohexene:1-hexene relative reactivity for HBr addition, $k_3^{\text{HBr}}/k_3^{\text{HCl}} \sim 150$ which can be compared to the ratio of 190 found for Ad3 addition of HOAc catalyzed by HX and the ratio of 54 predicted from the difference in $-H_0$ values (see preceding section). It thus appears that the increase in rate for Ad3 addition of HBr over that for HCl results primarily from the greater acidity and extent of dissociation of HBr than of HCl in acetic acid and that differences in nucleophilicity between bromide and chloride ion play a more minor role.

Ion Pairing Phenomenon and the Ad3 Transition

State. What features determine whether dissociated ions or ion pairs are more effective in promoting Ad3 addition? The factors bearing on the answer to this question are best discussed in terms of hypothetical equilibria¹⁴ between the various types of transition states in eq 6–9. The appropriate equations under ion-pairing conditions and in the absence of added salt are



where K_d and C_{HX} are the respective dissociation constant and stoichiometric concentration of HX.

It is evident from these expressions that high concentrations of HX will favor the more ion-paired transition states; this is simply a reflection of the fact that the ratio of dissociated to undissociated HX decreases with increasing HX concentration. At $C_{\text{HX}} = 1 M$ the conditions under which a given transition state is favored can be established from the above equations; we see that if the free energy to dissociate either H^+ or X^- from a given transition state is greater than half the free energy to dissociate HX, then the undissociated transition state will be favored at $C_{\text{HX}} = 1 M$. Since the kinetics implicate T_- as the preferred transition state, we can conclude that the halide counterion is bound more tightly in T_\pm than is the proton. For Ad3 addition of HBr the approximate requirements, taking $K_d \sim 10^{-6} M$ for HBr,⁹ are that $K_1^\ddagger > K_2^\ddagger$, $K_1^\ddagger > 10^{-3} M$, and $K_3^\ddagger < 10^{-3} M$.

A number of factors can influence which transition state will be favored. We have already noted that high HX concentration will tend to favor the more ion-paired transition states. For halide salt catalyzed Ad3 addition of HX, extension of the above treatment shows that the dissociation constant of the salt plays an important role in determining the favored transition state. Moreover, the electronic structure of the transition state may well vary with the structure of the unsaturated reactant resulting in changes in the values of K_1^\ddagger , K_2^\ddagger , and K_3^\ddagger . All of these considerations suggest that it is unwise to generalize that T_- will be the favored transition state in all cases and, in this connection, we note that the results for chloride salt catalyzed Ad3

(14) For a discussion of the theoretical basis of this type of approach, see J. L. Kurz, *J. Amer. Chem. Soc.*, **85**, 987 (1963).

addition of HCl to 3-hexyne proved most consistent with reaction *via* a transition state resembling T_{\pm} .¹⁵

The Relationship between Ad3 and E2 Reactions.

We have noted earlier that Ad3 reactions resemble the reverse of E2 eliminations but did not elaborate this relationship because the conditions for the usual base promoted E2 reactions and those for Ad3 reactions are so different. However, in recent years work by Winstein, Parker, and coworkers¹⁶⁻²⁴ and by Eck and Bunnett²⁵ has been published on elimination reactions promoted by halide ions and other weak proton bases which makes the relationship between Ad3 and E2 reactions far clearer.

They find that tetraalkylammonium halide salts promote elimination from alkyl halides and tosylates in acetone and other solvents, the second-order observed rate constants for elimination reflecting catalysis by halide ion.¹⁶⁻²⁴ In substituted cyclohexyl²⁴ and related¹⁹ systems the reaction occurs with a strong preference for anti elimination. They conclude, on the basis of the variation in rate with substituent, leaving group, base, and solvent that a spectrum of transition states is involved in E2 reactions and that halide promoted reactions occur *via* a "loose" transition state involving a well-developed double bond.

It is evident that the transition state composition and stereochemical requirements in these elimination reactions are identical with those for the Ad3 addition reactions described above. Although different solvents are involved in the addition and elimination

reactions, the chloride promoted elimination does not appear to be markedly influenced by solvent²⁴ and there is thus good reason to believe that the halide promoted E2 and Ad3 reactions do involve analogous reaction pathways. In this regard, it would be of interest to examine these addition and elimination processes in the same solvent, shifting the equilibrium in favor of addition or elimination by varying the activity of HX.

Comparison to Other Studies of HBr Addition. The available data on the kinetics and stereochemistry of HBr addition to alkenes are still very limited. The anti addition of HBr to 1,2-dimethylcyclohexene in HOAc observed by Hammond and Nevitt²⁶ is in accord with the view expressed here that polar addition of HBr to alkenes in HOAc tends to favor the Ad3 relative to AdE2 mechanism. Similarly, Pasto and Meyer⁸ find that DBr addition to cyclopentene in DOAc occurs with anti stereospecificity. These same authors find that the isomeric 2-butenes and 3-hexenes add DBr and DOAc in DBr-DOAc to yield anti and syn adducts in a ratio of ~5:1, the ratio being independent of HBr concentration. They interpret the results as arising from competing syn and anti Ad3 addition. If Ad3 and E2 reactions are related, this latter result is surprising since E2 reactions show a marked preference for anti elimination. Further elaboration of the stereochemical requirements and the detailed electronic structure of the transition state for Ad3 addition will have to await further results.

Acknowledgment. Support of this research by the National Science Foundation (Grants GP-5852 and GP-24562) is gratefully acknowledged. We thank Dr. Michael W. Monahan and Arthur Ayers for assistance with preliminary experiments and the John Simon Guggenheim Foundation for a fellowship to R. C. F., under the tenure of which most of the manuscript was prepared. Finally, we thank Professor Daniel J. Pasto for comments and information in advance of publication and Professor Charles L. Perrin for helpful discussions.

(15) R. C. Fahey and D.-J. Lee, *J. Amer. Chem. Soc.*, **90**, 2124 (1968).

(16) A. J. Parker, M. Ruane, G. Biale, and S. Winstein, *Tetrahedron Lett.*, 2113 (1968).

(17) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5183 (1968).

(18) D. Cook, A. J. Parker, and M. Ruane, *Tetrahedron Lett.*, 5715 (1968).

(19) G. Biale, A. J. Parker, S. G. Smith, I. D. R. Stevens, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 115 (1970).

(20) D. J. Lloyd and A. J. Parker, *Tetrahedron Lett.*, 5029 (1970).

(21) G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 4735 (1971).

(22) A. J. Parker, M. Ruane, D. A. Palmer, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2228 (1972).

(23) G. Biale, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2235 (1972).

(24) P. Beltrame, G. Biale, D. J. Lloyd, A. J. Parker, M. Ruane, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2240 (1972).

(25) J. F. Bunnett and D. L. Eck, *J. Amer. Chem. Soc.*, **95**, 1897, 1900 (1972).

(26) G. S. Hammond and T. D. Nevitt, *J. Amer. Chem. Soc.*, **76**, 4121 (1954).