$$\mathrm{TMH} + \mathrm{I_2} \rightleftharpoons \mathrm{TMH \cdot I_2} \rightleftharpoons [\mathrm{TMH \cdot ^+ I_2 \cdot ^-}]_{solv} \longrightarrow [\mathrm{TMH \cdot ^+}]_{solv} + [\mathrm{I_2 \cdot ^-}]_{solv}$$

$$\uparrow\downarrow \mathrm{TMH} \qquad (7)$$

$$2\mathrm{TMH \cdot I_2}$$

$$[\mathrm{I_2 \cdot ^-}]_{solv} \longrightarrow [\mathrm{I^-}]_{solv} + \mathrm{I \cdot}$$

one proposed by Briegleb, *et al.*[4] (eq 1), except that in our case the last step is probably virtually irreversible. It is likely that mechanisms of this type are important in many biological oxidations.[26]

(26) *Cf.* A. Szent-Györgyi, *Discussions Faraday Soc.*, 27, 111 (1959).

Acknowledgment. We wish to thank Professor G. A. Gallup for helpful discussion in the early stage of this work. The computer program for the calculation of the esr spectra was written by Dr. Christopher Watts. D. R. was supported for part of the time by a research assistantship derived from a National Science Foundation Development Grant (NSF-GU2054) to the Department of Chemistry, University of Nebraska. Partial support from a grant from the Research Corporation, a foundation, is gratefully acknowledged.

The Mechanism of the Hydrochlorination of *t*-Butylethylene and Styrene in Acetic Acid[1]

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Abstract: The hydrochlorination of *t*-butylethylene in acetic acid yields 3-chloro-2,2-dimethylbutane (**SC**), 2-chloro-2,3-dimethylbutane (**TC**), and 3-acetoxy-2,2-dimethylbutane (**SA**) in the approximate ratio 2:2:1. Since **SC** and **SA** are stable to the reaction conditions, rearrangement is a kinetically controlled process; however, 2-acetoxy-2,3-dimethylbutane (**TA**) is rapidly converted to **TC** so that either **TA** or **TC** (or both) may be primary product(s). Although the rate of reaction varies significantly with chloride salt concentration (0–1.5 *M* $(CH_3)_4$NCl), water concentration (0–2.5 *M*), and temperature (25–125°), there is little accompanying change in the product composition. The hydrochlorination of styrene in acetic acid yields α-methylbenzyl chloride (**C**) and α-methylbenzyl acetate (**A**) in the approximate ratio 13:1 under conditions of kinetic control. The reaction is first order in [HCl] at low acid concentration (<0.1 *M*) and linear in effective acidity at high acid concentration. The ratio **C**/**A** varies little with [HCl] (0.006–0.5 *M*), with [$(CH_3)_4$NCl] (0–0.3 *M*), or with temperature (16.5–50°). From studies of the reactions in DCl–DOAc, kinetic isotope effects k_H/k_D = 1.2 and 1.4 were determined for addition to *t*-butyl ethylene and styrene, respectively. The results are discussed in terms of rate-limiting protonation of olefin by HCl to form a carbonium–chloride ion pair; collapse or rearrangement of the ion pair occurs at rates faster than or comparable to that of a diffusion-controlled process.

The addition of hydrogen halides to olefins has long been considered to occur *via* carbonium ions as intermediates.[3] The most compelling evidence for this view comes from studies like those of Whitmore and coworkers who showed that rearranged products are formed in the reaction of hydrogen halides with 3-methyl-1-butene[4] and *t*-butylethylene.[5]

The stereochemistry of hydrogen halide addition is very much dependent upon the structure of the olefin.[6] Arenes[7] and dienes[8] add hydrogen halides preferentially (but not exclusively) *cis* (*syn*)[9] in weakly dissociating solvents, an observation attributed to ion-pairing phenomenon. Norbornene derivatives[10] and other strained bicyclic olefins[11] also add hydrogen halides largely or entirely *cis* (*syn*) for reasons which are as yet not entirely clear—concerted reactions may be involved in at least some cases. However, nonconjugated olefins such as 1,2-dimethylcyclohexene,[12] 1,2-dimethylcyclopentene,[13] and cyclohexene[14] undergo very predominant *trans* (*anti*)[9] addition upon reaction with hydrogen halides. Such *trans* additions have been most often rationalized in terms of a protonium ion intermediate (**1**) but no definitive demonstration of the existence of this species as a discrete reaction inter-

(1) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P-42. Supported by the National Science Foundation under Grants GP-5852 and GP-8308.

(2) (a) Alfred P. Sloan Foundation Fellow, 1966–1968; (b) National Defense Education Act Predoctoral Fellow.

(3) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, Chapter 5.

(4) F. C. Whitmore and F. Johnston, *J. Am. Chem. Soc.*, 55, 5020 (1933).

(5) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *ibid.*, 72, 1511 (1950).

(6) R. C. Fahey in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968, p 237.

(7) M. J. S. Dewar and R. C. Fahey, *Angew. Chem. Intern. Ed. Engl.*, 3, 245 (1964).

(8) G. S. Hammond and J. Warkentin, *J. Am. Chem. Soc.*, 83, 2554 (1961).

(9) It has been pointed out by E. L. Eliel (*cf.* ref 6, p 238) that in describing the steric course of addition use of the terms "*syn*" in place of "*cis*" and "*anti*" in place of "*trans*" is desirable in order to avoid the confusion which arises when the reacting olefin or the addition product exhibits *cis–trans* isomerism. Since this usage is as yet not widespread, both designations are used in this paper.

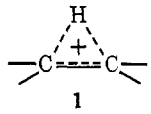
(10) H. Kwart and J. L. Nyce, *J. Am. Chem. Soc.*, 86, 2601 (1964); J. K. Stille, F. M. Sonnenberg, and T. H. Kinstle, *ibid.*, 88, 4922 (1966); H. C. Brown and K.-T. Liu, *ibid.*, 89, 3898, 3900 (1967); S. J. Cristol and R. Caple, *J. Org. Chem.*, 31, 2741 (1966).

(11) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *ibid.*, 32, 24 (1967); F. T. Bond, *J. Am. Chem. Soc.*, 90, 5326 (1968).

(12) G. S. Hammond and T. D. Nevitt, *ibid.*, 76, 4121 (1954).

(13) G. S. Hammond and C. H. Collins, *ibid.*, 82, 4323 (1960).

(14) R. C. Fahey and R. A. Smith, *ibid.*, 86, 5035 (1964).



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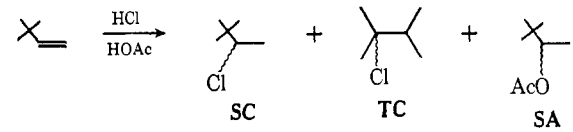
mediate has been given.[15] Preferential *trans* (*anti*) addition in these systems might alternatively be attributed to special conformational effects unique to these cyclic systems. Finally, a number of *trans* (*anti*) additions of hydrogen halides to α,β-unsaturated carboxylic acid derivatives have been reported;[16] these additions have been reasonably rationalized in terms of the formation of 1,4-addition intermediates which undergo stereoselective ketonization.[17]

This paper describes the first in a series of studies designed to elucidate the factors responsible for *trans* (*anti*) addition of hydrogen halides to olefins. After some preliminary studies, we decided to focus our attention on the hydrochlorination of olefins in acetic acid. There were several reasons for this choice: (1) the reaction is free from competing free radical addition; (2) the rates and kinetics of this reaction could be conveniently studied; (3) the reaction yields products resulting from addition of acetic acid as well as of hydrogen chloride so that the ratio of chloride to acetate could be studied. It seemed that a sufficiently wide variety of evidence might be obtained from studies of this reaction that a definitive description of the mechanism would result. The present studies parallel an analogous series on the hydrochlorination of acetylenes in acetic acid.[18]

In this first paper we report results on the hydrochlorination of *t*-butylethylene and styrene and show that these reactions occur *via* the well-recognized bimolecular mechanism involving a carbonium ion intermediate. In subsequent papers we will show that quite different results from those reported here obtain for the hydrochlorination of other olefins in acetic acid and that a different mechanism is involved in the *trans* (*anti*) addition of hydrogen halides to olefins.

Results

The Hydrochlorination of *t*-Butylethylene. The reaction of *t*-butylethylene (3,3-dimethyl-1-butene) with hydrogen chloride in acetic acid proceeds slowly at 25° to yield a mixture of 3-chloro-2,2-dimethylbutane (**SC**), 2-chloro-2,3-dimethylbutane (**TC**), and 3-acetoxy-2,2-dimethylbutane (pinacolyl acetate) (**SA**). The reaction products were separated into two fractions by distillation. The low-boiling fraction, which gave a precipitate with alcoholic silver nitrate, was found to consist of two components which could be only partially

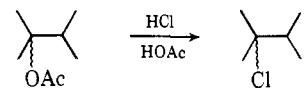


SC TC SA

resolved by glpc on a 25 ft × 1/8 in. XF-1150 column but could be almost completely separated on a 300-ft capillary column. The nmr spectra and glpc retention times of the two components were found to be identical with a mixture of authentically prepared 3-chloro-2,2-dimethylbutane and 2-chloro-2,3-dimethylbutane. The higher boiling fraction was found to have an nmr spectrum and glpc retention time identical with authentic 3-acetoxy-2,2-dimethylbutane.

Quantitative studies of the reaction were conducted using an internal standard. Aliquots of the reaction mixture were removed at intervals, quenched in pentane–water, and then extracted with pentane. The organic fraction was then concentrated and the product concentration determined by glpc. Authentic mixtures of known composition were used to correct peak area ratios to mole ratios and to show that no fractionation occurs in the work-up procedure. Control runs with authentic samples established that 3-chloro-2,2-dimethylbutane, 2-chloro-2,3-dimethylbutane, and 3-acetoxy-2,2-dimethylbutane are stable to the reaction conditions and that in the absence of hydrogen chloride no reaction occurs between 3,3-dimethyl-1-butene and acetic acid. Analysis at a high percentage reaction demonstrated that the three addition products comprise $\geq 90\%$ of the total product. Initial rates $R = -\mathrm{d[olefin]}/\mathrm{d}t = \Delta[\text{products}]/\Delta t$ were determined at $\leq 5\%$ reaction.

Since 2-acetoxy-2,3-dimethylbutane (**TA**) might also be formed under these reaction conditions it was necessary to test its stability to the reaction conditions. It was found that under comparable conditions 2-acetoxy-2,3-dimethylbutane is converted to 2-chloro-2,3-dimethylbutane at greater than 10^3 times the rate which 3,3-dimethyl-1-butene adds hydrogen chloride.



TA TC

Thus part or all of the 2-chloro-2,3-dimethylbutane may arise *via* 2-acetoxy-2,3-dimethylbutane as an intermediate. It is clear, however, that rearrangement is kinetically controlled since both 3-chloro-2,2-dimethylbutane and 3-acetoxy-2,2-dimethylbutane are stable to the reaction conditions.

The rates and product composition of the reaction were determined as a function of temperature and as a function of added tetramethylammonium chloride (TMAC). The results (Table I) show that, although the reaction rate increases by a factor of 2700 between 25 and 125°, the product composition shows only minor variations with temperature. Similarly, in the presence of TMAC, the rate of addition to 3,3-dimethyl-1-butene is accelerated but there is no significant change in the product composition. At low TMAC concentrations the rate increases approximately linearly with salt concentration but reaches a maximum and constant value at about 0.7 *M* TMAC.

(15) Taft and coworkers proposed in the 1950's that **1** is a reversibly formed intermediate in olefin hydration but the validity of the interpretation given their results has become suspect in recent years (*cf.* ref 3, pp 32–34). Although this mechanism has not been disproven for the specific cases studied by Taft and students, W. M. Schubert, B. Lamm, and J. R. Keeffe [*J. Am. Chem. Soc.*, 86, 4727 (1964)] have ruled it out in the hydration of *p*-methoxy-α-methylstyrene by showing that the reaction is subject to general acid catalysis.

(16) J. Wilicenus and H. P. Talbot, *Ann. Chem.*, **313**, 228 (1900); W. G. Young, R. T. Dillon, and H. J. Lucas, *J. Am. Chem. Soc.*, **51**, 2528 (1929); W. R. Vaughan and K. M. Milton, *ibid.*, **74**, 5623 (1952); W. R. Vaughan, R. L. Craven, R. Q. Little, and A. C. Schoenthaler, *ibid.*, 77, 1594 (1955); W. R. Vaughan and R. Caple, *ibid.*, 86, 4928 (1964); W. R. Vaughan, R. Caple, J. Csapilla, and P. Scheiner, *ibid.*, 87, 2204 (1965).

(17) R. Caple and W. R. Vaughan, *Tetrahedron Letters*, 4067 (1966).

(18) (a) R. C. Fahey and D.-J. Lee, *J. Am. Chem. Soc.*, 88, 5555 (1966); (b) *ibid.*, 90, 2124 (1968).

Table I. The Hydrochlorination of *t*-Butylethylene in Acetic Acid

Temp, °C	$[C_6H_{12}]$, *M*	[HCl], *M*	[TMAC], *M*	Product Composition, %[a] SC	TC	SA	$10^9 \times R$, *M* sec^{-1}
25	0.135	0.134		37	44	19	1.48 ± 0.04
50	0.135	0.134		35	48	17	18.0 ± 0.8
125	0.135	0.134		39	47	14	4020 ± 200
25	0.139	0.149		37	43	20[b]	1.58 ± 0.06
25	0.139	0.149	0.049	37	44	19	2.11 ± 0.02
25	0.139	0.149	0.099	36	43	20	2.52 ± 0.10
25	0.139	0.149	0.198	37	44	19	3.24 ± 0.03
25	0.135	0.134	0.286	36	45	19[b]	3.07 ± 0.06
25	0.135	0.134	0.572	35	45	20	3.58 ± 0.10
25	0.135	0.134	0.858	39	43	18	3.66 ± 0.16
25	0.135	0.134	1.53	42	41	17	3.63 ± 0.08
25	0.482	0.492		40	39	20	19.5 ± 0.7
25	0.486	0.492	0.372	39	42	19[b]	40.9 ± 1.0
25	0.485	0.496[c]		37	44	18[b]	17.0 ± 0.9
25	0.484	0.496[c]	0.371	35	46	19[b]	33.5 ± 1.2

[a] Average deviation of three or more analyses ≤1 except where noted. [b] Average deviation of three or more analyses ≤2. [c] DCl in DOAc.

The reaction was also studied in DCl–DOAc (Table I). From the results, kinetic isotope effects, k_H/k_D, were determined to be 1.15 ± 0.07 and 1.22 ± 0.05 in the absence and in the presence of 0.37 *M* TMAC, respectively.

Water in the reaction mixture has an effect on the reaction rate but only a small effect on the product composition (Table II). The rate increases to a maximum at about 0.6 *M* water and then decreases.

Table II. The Effect of Water on the Hydrochlorination of *t*-Butylethylene at 25°; $[C_6H_{12}]$ = 0.14 *M* and [HCl] = 0.13 *M*

$[H_2O]$, *M*	Product Composition, %[a] SC	TC	SA	$10^9 \times R$, *M* sec^{-1}
0	35	45	20[b]	1.21 ± 0.05
0.210	36	45	19	1.40 ± 0.01
0.402	34	45	20[b]	1.56 ± 0.06
0.602	34	49	16[b]	1.62 ± 0.02
1.00	29	48	23	1.56 ± 0.12
1.81	28	49	23	0.92 ± 0.01
2.01	29	50	21	0.79 ± 0.01
2.52	28	50	22	0.61 ± 0.04

[a] Average deviation of three or more analyses ≤2 except where noted. [b] Average deviation of three or more analyses ≤4.

The Hydrochlorination of Styrene. The reaction of styrene with hydrogen chloride in acetic acid at 25° yields a product mixture consisting of 93% (1-chloroethyl)benzene (**C**) and 7% α-methylbenzyl acetate (**A**).

$$C_6H_5CH{=}CH_2 \xrightarrow[HOAc]{HCl} \underset{\mathbf{C}}{C_6H_5CHClCH_3} + \underset{\mathbf{A}}{C_6H_5CH(OAc)CH_3}$$

The reaction products, (1-chloroethyl)benzene and α-methylbenzyl acetate, were separated by preparative glpc and found to be identical in glpc retention time and nmr spectrum with authentically prepared samples.

Quantitative studies were carried out in a fashion identical with that described above for addition to *t*-butylethylene. Control runs with authentic samples showed that (1-chloroethyl)benzene is stable to the reaction conditions at 25° and that no significant reaction occurs between styrene and acetic acid in the absence of hydrogen chloride. Analysis at a high percentage reaction shows that (1-chloroethyl)benzene and α-methylbenzyl acetate comprise greater than 95% of the total product.

The results are summarized in Table III and show that at 25° the product composition is independent of HCl over nearly a 100-fold variation in acid concentration. This clearly demonstrates that the observed product composition is the kinetically controlled composition and not an equilibrium mixture. At 50° and high hydrogen chloride concentration equilibration does occur during the latter stages of the reaction to give an equilibrium mixture. However, as shown in Table III, the initial product composition is essentially invariant to hydrogen chloride concentration and must therefore be kinetically controlled.

Table III. The Hydrochlorination of Styrene in Acetic Acid

Temp, °C	$[C_8H_8]$, *M*	[HCl], *M*	C/A	$10^8 \times R$, *M* sec^{-1}
25	0.099	0.0063	11.5 ± 1.4	1.34 ± 0.06
25	0.099	0.0315	13.7 ± 1.4	7.89 ± 0.39
25	0.099	0.0945	13.1 ± 0.6	20.8 ± 0.8
25	0.097	0.099	11.8 ± 0.7	25.7 ± 0.8
25	0.110	0.102	12.1 ± 1.1	25.1 ± 1.1
25	0.094	0.217	13.1 ± 1.4	65.6 ± 2.1
25	0.099	0.25	12.1 ± 0.4	89.5 ± 3.7
25	0.100	0.25	15.1 ± 0.6	89.1 ± 3.6
25	0.099	0.315	12.7 ± 0.6	118 ± 12
25	0.098	0.40	12.9 ± 1.0	180 ± 9
25	0.091	0.49	16.5 ± 2.1	248 ± 18
25	0.095	0.25[a]	10.9 ± 0.6	158 ± 2
16.5	0.097	0.099	11.5 ± 1.0	10.3 ± 0.6
50	0.108	0.0197	8.6 ± 0.6	38.0 ± 3.0
50	0.097	0.099	9.4 ± 1.2	200 ± 10
50	0.108	0.197	11.0 ± 0.7	497 ± 21
25	0.093	0.217[b]	14.6 ± 0.9	46.3 ± 1.5

[a] With 0.304 *M* TMAC. [b] DCl in DOAc.

Although the product composition is independent of the HCl concentration, the rate of reaction is not. Below 0.1 *M* HCl, the reaction is first order in acid but above 0.1 *M* the rate increases faster than the stoichiometric HCl concentration. The acidity of HCl–HOAc solutions has been measured at 18° by Satchell[19] using aniline bases. From his results an effective acidity, log *A* (analogous to $-H_0$), can be calculated.[18b] A plot of log $(R/[C_8H_8])$ *vs.* log *A* for the hydrochlorination of styrene at 25° is linear with slope 1.23.

Table III includes one experiment on the effect of TMAC on the hydrochlorination of styrene. As was the case with *t*-butylethylene, the salt accelerates the reaction but does not affect the product distribution.

From the rate measured in 0.217 *M* DCl in DOAc (Table III) the isotope effect k_H/k_D = 1.40 ± 0.09 was determined.

Comparison of the data in Tables I and III shows that styrene reacts roughly 300-fold faster than *t*-butylethylene under comparable conditions.

Discussion

The fact that *t*-butylethylene reacts with hydrogen chloride in acetic acid to give rearranged product

(19) D. P. N. Satchell, *J. Chem. Soc.*, 1916 (1958).

under conditions of kinetic control clearly demonstrates that a discrete carbonium ion intermediate must be involved in the reaction. Ecke, Cook, and Whitmore[5] have previously demonstrated the formation of rearranged product in the hydrochlorination of neat *t*-butylethylene, but whether the rearranged product derived from a primary or secondary reaction is not entirely clear from their results. In view of the present findings, it now seems likely that they were indeed observing kinetically controlled formation of rearranged product.

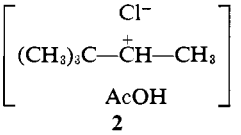
The results further show that the carbonium ion intermediate is formed by attack of hydrogen chloride (molecular or ionized but undissociated) on the olefin. It is known[20] that hydrogen chloride is partially ionized but very little dissociated in acetic acid. The hydro-

$$HCl \rightleftharpoons [H^+Cl^-] \rightleftharpoons H^+ + Cl^-$$

chlorination of styrene is essentially first order in hydrogen chloride and this rules out attack by dissociated H^+ which would depend upon the square root of the hydrogen chloride concentration. Simultaneous attack by dissociated H^+ and Cl^- to form chloride and by dissociated H^+ and acetic acid to form acetate is ruled out by the fact that the ratio of chloride to acetate does not depend upon the concentration of hydrogen chloride. Molecular or ionized hydrogen chloride must be the effective electrophile.

Formation of a solvated carbonium–chloride ion pair must be the rate-limiting step. Since hydrogen chloride is the electrophilic species and acetic acid is a weakly dissociating solvent, an ion pair must be formed. That this ion pair is formed in the rate-limiting step is consistent with the small but positive observed isotope effects and with the observation that styrene, capable of forming a resonance-stabilized benzylic cation, reacts at about 300 times the rate of *t*-butylethylene. It has been shown numerous acid additions to olefins[21] that proton exchange in the starting olefin does not significantly compete with addition, as expected for a rate-limiting proton transfer.

Collapse and rearrangement of the intermediate ion pair must occur at rates comparable to or faster than those for diffusion-controlled processes. The fact that in the reaction of *t*-butylethylene rearrangement, formation of chloride and formation of acetate occur in the approximation ratio 2:2:1 shows that **2** is a highly unstable species which discriminates very little between



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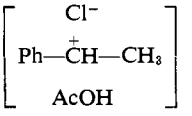
the three modes of decomposition. As would be expected, the more stable intermediate **3** formed from styrene is more selective, collapsing with chloride ion some 13 times faster than with acetic acid. In neither case, however, is the selectivity large, suggesting that



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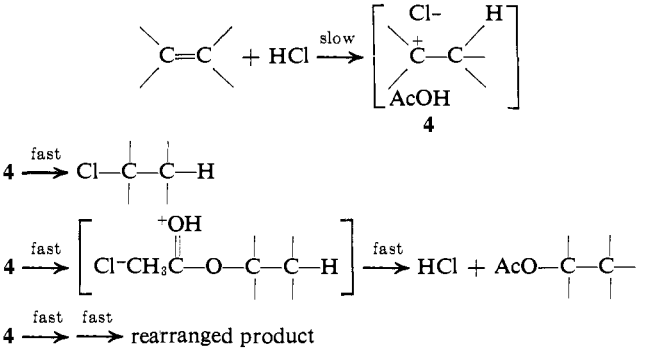
very fast reactions are involved. The fact that the product distributions are not significantly dependent upon the concentration of chloride ion shows that, once formed, neither **2** nor **3** is capable of being captured by external chloride ion. Thus, collapse of these ion pairs must occur before diffusion-controlled encounter with nucleophiles in the solvent.

The fact that the product distribution varies little with temperature is also consistent with this conclusion. If the reactions of these ion pairs occur with free energies of activation of $\leqslant 5$ kcal (diffusion-controlled value), then for these competing processes the maximum reasonable difference in the enthalpy of activation is 5 kcal and, in practice, much smaller differences ($\leqslant 2$ kcal) would be expected. In view of this, there should be little variation in the product distribution with changes in reaction temperature, and this is what is found. From the small observed variations in the product distribution with temperature the apparent differences in activation enthalpy, $\Delta\Delta H^{\ddagger}$, for product formation can be estimated. For the hydrochlorination of *t*-butylethylene $\Delta H_{SC}^{\ddagger} - \Delta H_{SA}^{\ddagger}$ and $\Delta H_{TC}^{\ddagger} - \Delta H_{SA}^{\ddagger}$ are both calculated to be 1.0 ± 0.5 kcal/mol. From the less accurate data obtained with styrene $\Delta H_A^{\ddagger} - \Delta H_C^{\ddagger} = 0$–2.5 kcal/mol.

Combining the above considerations and conclusions we arrive at an over-all view of the mechanism as outlined in Scheme I. This scheme is entirely con-

Scheme I



sistent with preferential *cis* (*syn*) addition of hydrogen halides in ion-pairing solvents but provides no basis for understanding *trans* (*anti*) additions. In subsequent papers, we will show, however, that such *trans* (*anti*) additions are associated with significantly different kinetic and product distribution behavior than that found here for *t*-butylethylene and styrene. The results presented here define the characteristics expected for a stepwise carbonium ion mechanism and are crucial to the interpretation of similar studies of the hydrochlorination of cyclohexene, already reported in preliminary form[22] and the subject of the next papers in this series.

The effects of water and TMAC on the reaction rate, although not understood in detail, deserve some comment. We note that water at low concentrations increases the reaction rate by a small amount but that the rate reaches a maximum around 0.6 *M* water and

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

(21) E. L. Purlee and R. W. Taft, Jr., *ibid.*, 78, 5807 (1956); M. J. S. Dewar and R. C. Fahey, *ibid.*, 85, 2245, 3645 (1963); W. M. Schubert, B. Lamm, and J. R. Keeffe, *ibid.*, 86, 4727 (1964); Y. Pocker, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 22S; V. Gold and M. A. Kessick, *J. Chem. Soc.*, 6718 (1965); N. C. Deno, F. A. Kish, and H. J. Peterson, *J. Am. Chem. Soc.*, 87, 2157 (1965); W. M. Schubert and B. Lamm, *ibid.*, 88, 120 (1966).

(22) R. C. Fahey and M. W. Monahan, *Chem. Commun.*, 936 (1967).

then rapidly decreases at higher water concentrations. A similar effect has been reported by Peterson and Allen[23] for the reaction of 1-hexene with trifluoroacetic acid in the latter as solvent. Water should increase both the ionizing power and the basicity of acetic acid and these changes would have opposing effects on the rate of reaction. The observed effect can be rationalized by assuming that the effect on the ionizing power of the solvent dominates at low water concentrations and that the effect on the acidity of the medium dominates at high water content.

The origin of the effect of TMAC on the rate of reaction may be similar to that of water. At low salt concentrations a salt or medium effect enhances the reaction rate while at high salt concentrations the acidity of the medium is significantly reduced, offsetting the salt effect and leading to a leveling in the effect of salt concentration on reaction rate.

Experimental Section

An Aerograph Hy-Fi III Model 1200 chromatograph equipped with a flame ionization detector, linear temperature programmer, and capillary-splitter injector was employed with two 150 ft × 0.01 in. stainless steel columns, one packed with XF-1150 and the other with Carbowax 400. Analytical measurements were done using both columns in series (column A) or the 150 ft × 0.01 in. XF-1150 column separately (column B). An Aerograph Model 200 chromatograph equipped with thermal conductivity detectors and a linear temperature programmer was employed with an 18 ft × 0.25 in. column containing 20% XF-1150 on Chromosorb P-HMDS (column C) for preparative separations and an 8 ft × 1/8 in. 20% Apiezon L on Chromosorb P-HMDS (column D) for analytical measurements. Nmr spectra were measured on a Varian Associates HR-60 spectrometer and calibrated by the side-band technique. Chemical shifts of the samples, approximately 10% w/v solutions in carbon tetrachloride, are reported in parts per million (ppm) downfield from TMS as internal standard.

Materials. 3,3-Dimethyl-1-butene, 2,2-dimethyl-3-butanol, and 2,3-dimethyl-2-butanol were purchased from Columbia Organic Chemicals; (1-chloroethyl)benzene was purchased from Pflatz and Bauer; 2,2-dimethylbutane and styrene were obtained from Matheson Coleman and Bell. Styrene was distilled, bp 55° (26 mm), prior to its use. Glacial acetic acid (Allied Chemical) was titrated for water by the Karl Fisher method; slightly more than 1 equiv of acetic anhydride was added and the mixture allowed to stand until reaction with the water was complete. Tetramethylammonium chloride (Matheson Coleman and Bell) was recrystallized from water and dried at 150° in a vacuum oven prior to its use.

3-Chloro-2,2-dimethylbutane (SC). The procedure followed was a modification of that of Whitmore[24] and Walling.[25] Chlorine (2 g) was dissolved in carbon disulfide (60 ml), the solution cooled in a Dry Ice–acetone bath, and 2,2-dimethylbutane (6.5 g) added. The solution was irradiated with a GE sun lamp during which time the solution was allowed to warm to 0° and turned from yellow to colorless. Distillation yielded 1 g of products consisting of a mixture of 90% 3-chloro-2,2-dimethylbutane and 10% 1-chloro-2,2-dimethylbutane, bp 111°. Purification by glpc (column C at 100° with a helium flow rate of 40 cc/min) yielded **SC**, bp 109.5°. The nmr spectrum of **SC** showed peaks at 0.99 (9 H, singlet), 1.41 (3 H, doublet, J = 6.6 Hz), and 3.82 (1 H, quartet, J = 6.6 Hz); n^{24}D 1.4176 (lit.[24] n^{20}D 1.4181). The product gave a white precipitate with alcoholic silver nitrate.

2-Chloro-2,3-dimethylbutane (TC).[5] Hydrogen chloride was bubbled through a solution of 2,3-dimethyl-2-butene (3 g) in methylene chloride (30 ml) for 3 hr at room temperature. Distillation yielded 2 g of 2-chloro-2,3-dimethylbutane, bp 47° (80 mm). Nmr spectrum of **TC**: 1.00 (6 H, doublet, J = 6.3 Hz), 1.49 (6 H, singlet), multiplet centered at *ca.* 1.7 (1 H); n^{24}D 1.4181 (lit.[26] n^{25}D 1.4178). The product gave a white precipitate with alcoholic silver nitrate.

3-Acetoxy-2,2-dimethylbutane (SA) and 2-Acetoxy-2,3-dimethylbutane (TA). The procedure followed was that of Sarel and Newman.[27] Acetyl chloride addition to 2,2-dimethyl-3-butanol and 2,3-dimethyl-2-butanol yielded 3-acetoxy-2,2-dimethylbutane, bp 140°, and 2-acetoxy-2,3-dimethylbutane, bp 52.5° (21 mm), respectively. Nmr spectrum of **SA**: 0.90 (9 H, singlet), 1.08 (3 H, doublet, J = 6.3 Hz), 1.92 (3 H, singlet), 4.64 (1 H, quartet, J = 6.4 Hz); n^{24}D 1.4005 (lit.[27] n^{25}D 1.4002). Spectrum of **TA**: 0.88 (6 H, doublet, J = 6.6 Hz), 1.36 (6 H, singlet), 1.86 (3 H, singlet), multiplet centered at *ca.* 1.9 (1 H); n^{24}D 1.4059 (lit.[28] n^{25}D 1.4052).

α-Methylbenzyl Acetate (A). Styrene (10 g) was added to a solution (200 ml) of perchloric acid (0.02 M) in acetic acid and allowed to react at room temperature for 2 days. Distillation yielded 4 g of α-methylbenzyl acetate, bp 123° (20 mm). Nmr spectrum of **A**: 1.45 (3 H, doublet, J = 7.2 Hz), 1.93 (3 H, singlet), 5.81 (1 H, quartet, J = 7.2 Hz), and 7.22 (5 H, singlet).

Kinetic and Product Studies. Solutions of hydrogen chloride (Matheson Co.) 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 ± 0.01°) after rapid mixing of the solutions. Reactions at higher temperatures were run in sealed ampoules. 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 calcium carbonate, and concentrated on a rotary evaporator.

The concentrated reaction mixtures of 3,3-dimethyl-1-butene were analyzed by vpc on column A at 70° with a nitrogen flow rate of 1.9 cc/min. Retention times (min) as measured from the injection point were: 3,3-dimethyl-1-butene, 8.6; **SC**, 11.0; **TC**, 11.2; **SA**, 16.7; **TA**, 17.3; chlorobenzene (internal standard), 22.7. Reaction mixture compositions were calculated from the peak area ratios which were calibrated with mixtures of known composition.

Control experiments at 0.4 M hydrogen chloride and 25° showed that neither 3-chloro-2,2-dimethylbutane, 2-chloro-2,3-dimethylbutane, nor 3-acetoxy-2,2-dimethylbutane undergo any detectable reaction during a period of 3 weeks. At 0.4 M hydrogen chloride and 25° 2-acetoxy-2,3-dimethylbutane is completely converted to 2-chloro-2,3-dimethylbutane in 6 hr. Analysis of synthetic mixtures showed that 3-chloro-2,2-dimethylbutane, 2-chloro-2,3-dimethylbutane, 3-acetoxy-2,2-dimethylbutane, and 2-acetoxy-2,3-dimethylbutane are stable to the work-up procedure.

The concentrated reaction mixtures of styrene were analyzed by glpc on column B at 100° with a nitrogen flow rate of 2 cc/min, or column D at 100° with a helium flow rate of 50 cc/min. The retention times (min) as measured on column B were: styrene, 3.0; **C**, 5.9; **A**, 11.3; propiophenone (internal standard), 13.3. The retention times (min) as measured on column D were: styrene, 2.0; **C**, 6.0; **A**, 11.2; naphthalene (internal standard), 18.7. Reaction mixture compositions were calculated from the peak area ratios, this procedure having been checked with mixtures of known composition. At 1.97 × 10^{-2} M hydrogen chloride at 25° the rate of conversion of (1-chloroethyl)benzene to α-methylbenzyl acetate is found to be 100 times slower than the rate of reaction of styrene under the same conditions. Since, as shown in Table III, the product composition is invariant to hydrogen chloride concentration the product ratios obtained must be kinetically controlled. Although the products **C** and **A** do interconvert at a significant rate at 50° the invariance in initial product composition over a tenfold change in acid concentration shows the product composition to be kinetically controlled. At 50° and high acid concentration the initial product composition undergoes a slow change to the equilibrium composition (K = [A][HCl]/[C] = ~6 × 10^{-3}).

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