Kinetics and Mechanism of Addition of Acids to Olefins. III. The Addition of Hydrogen Chloride to 2-Methyl-1-butene, 2-Methyl-2-butene, and Isoprene in Nitromethane[1]

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Abstract: The kinetics of addition of hydrogen chloride to 2-methyl-1-butene, 2-methyl-2-butene, and isoprene in nitromethane are first order in olefin but second order in acid. Added tetraethylammonium chloride suppresses the rate of addition by combining with free hydrogen chloride to produce hydrogen dichloride ions while tetraethylammonium perchlorate has no such effect. Parallel studies of conductance and of infrared and nuclear magnetic resonance spectroscopy of hydrogen and deuterium chloride solutions in nitromethane provide a control on the interpretation of kinetic results. The data enable the conclusion that the un-ionized hydrogen chloride molecule acts as the dominant proton donor in these media and that the proton transfer from acid to olefin is assisted by a second molecule of acid which hydrogen bonds to the developing chloride ion. During addition there is no detectable interconversion of 2-methyl-1-butene and 2-methyl-2-butene (kinetic control). The two isomers are, however, interconverted under conditions leading to thermodynamic control (2-methyl-2-butene:2-methyl-1-butene = 85:15). Similarly, no incorporation of deuterium into unreacted olefin could be detected during the addition of deuterium chloride to either alkene. These results are consistent with a rate-determining proton transfer from hydrogen chloride to olefin leading to the formation of a carbonium hydrogen dichloride ion pair. Under strict kinetic control, the addition of hydrogen chloride to isoprene is shown to yield predominantly (>96%) 1,2-addition product.

Special interest attaches to the study of addition of hydrogen halides to simple aliphatic alkenes and dienes in those aprotic solvents which are polar enough to sustain carbonium ions,[3,4] but which are not nucleophilic enough to react with them during the course of kinetic experiments. In addition to useful kinetic data, mechanistic information concerning the reaction may be obtained by a careful scrutiny of the rate-determining step in these media. An examination of pertinent physical parameters under similar conditions allows more precise interpretation of kinetic results.

The search for a definitive aliphatic system has led workers to investigate the methylbutenes in some detail. However, most of these studies have left many questions unanswered—often due to basically technical problems. Hence Taft's careful work in water was severely handicapped by solubility problems.[5] Whitmore's pioneering work was carried out in the absence of solvent and hence concentration changes may be important.[6] The inherent simplicity of the methylbutene system lends itself well to several different mechanistic tests, and it was principally for this reason that it was selected for this study.

The isolation of the stoichiometric composition of transition states in an acid–base reaction can be a problem of enormous complexity in protic solvents. In polar, aprotic solvents, however, the stoichiometric composition of the activated complex is obtained directly from kinetic data. Coupled with information which may be obtained by examining the products of chemical reactions in detail, it should be possible to develop a fairly concise picture of the proton-transfer step (or steps).

As part of our continuing studies of these reactions, we have examined in detail the addition of both hydrogen and deuterium chloride to 2-methyl-1-butene, 2-methyl-2-butene,[5] and isoprene in nitromethane.

Experimental Section

Materials. Eastman Spectro Grade nitromethane was purified as previously described.[1b] The purity of all olefins was checked by gas chromatography and in each case only one peak was present indicating that accompanying impurities must be present below the threshold of detection, *i.e.*, below 0.3% of the major component. The olefins, 2-methyl-1-butene, 2-methyl-2-butene (Columbia Organic Chemicals), and isoprene (Eastman White Label) were used without further purification. Tetraethylammonium chloride and perchlorate and lithium perchlorate were prepared as previously described.[3] Standard sodium methoxide solutions were prepared by adding freshly cut metal to anhydrous methanol and titrating against standard hydrochloric acid in 50 ml of methanol using Lacmoid indicator. Nitromethane solutions of hydrogen chloride were prepared by dropping concentrated sulfuric acid onto a paste made of ammonium chloride and concentrated hydrochloric acid. The hydrogen chloride gas was passed first through concentrated sulfuric acid, then through a sintered-glass plug and finally into nitromethane cooled to 0°. Deuterium chloride was prepared by dropping deuterium oxide onto benzoyl chloride heated almost to the boiling point.[7] Deuterium chloride gas was passed through a tube containing anhydrous calcium chloride, then through a trap cooled to −78°, and finally into nitromethane cooled to 0°.

2-Chloro-2-methylbutane was prepared by the action of concentrated hydrochloric acid on *t*-amyl alcohol.[8] The distilled product

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[1] (a) Support of this work by the National Science Foundation is gratefully acknowledged. (b) Paper II: Y. Pocker, Y. V. S. Devi, F. Naso, and K. D. Stevens, *Proc. Intern. Symp. Solvation Phenomena*, **1**, 27 (1963). (c) This paper is based in large part on the Ph.D. Dissertation of K. D. Stevens, University of Washington, 1966.

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[3] Y. Pocker, *J. Chem. Soc.*, 1292 (1960).

[4] Y. Pocker, *Proc. Chem. Soc.*, 216 (1960).

[5] (a) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, *J. Am. Chem. Soc.*, **75**, 1253 (1953); (b) R. W. Taft, Jr., E. L. Purlee, P. Riejz, and C. A. DeFazio, *ibid.*, **77**, 1584 (1955); (c) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956); (d) R. H. Boyd, R. W. Taft, Jr., A. D. Wold, and D. R. Christman, *ibid.*, **82**, 4729 (1960).

[6] (a) F. C. Whitmore and F. Johnston, *ibid.*, **55**, 5020 (1933); (b) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950).

[7] H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, 64, 2223 (1942).

was examined by gas chromatography on three 10 ft × 0.25 in. columns (Dow Silicone 710, Carbowax 20M, Apiezon J) at an He flow of 50 cc/min, temperature 50°, and found to give only one peak in each case. The nmr spectrum showed resonances at τ 8.92 (T with fine structure), 8.47 (S), and 8.29 (M) with areas 3, 6, and 2, respectively. 3-Chloro-3-methyl-1-butene was prepared by passing 0.66 equiv of gaseous hydrogen chloride into a solution of isoprene containing 10% by weight dry ether at −78°. The solution was allowed to stand at −35° for 36 hr and distilled rapidly under reduced pressure. Redistillation at normal pressure yielded the desired allylic chloride, bp 79.0–79.5° (lit.[9] 79.5–80.0°).

1-Chloro-3-methyl-2-butene was prepared by dissolving small amounts of hydrogen chloride into 3-chloro-3-methyl-1-butene and allowing the solution to stand for 1 hr at room temperature. Distillation yielded a product, bp 111–113° (lit.[9] bp 111–113°). The nmr spectra of both 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-1-butene unambiguously establish the identity of these compounds.[1c]

Instruments. Nmr spectra were obtained on a Varian Associates A-60 instrument. Conductance measurements were performed using an Industrial Instruments, Inc., conductivity bridge, Model RC-18. The accuracy of this instrument was 0.1% between 5×10^2 and 5×10^4 ohms. The reproducibility proved to be 0.1% in the same region.

Analytical gas chromatography was carried out using a Wilkins Aerograph Hy-Fi 600 equipped with a flame ionization detector. Preparative-scale work was performed on an Aerograph A-90P.

Mass spectra were obtained on a Consolidated Engineering Corp. Model 21-103 spectrometer.

Thermostat temperature control was maintained with a Sargent Thermonitor Model S-PN-2770. The variation in temperature was ±0.02°.

Methods. Kinetic runs for all olefins were carried out using three procedures. **Method 1.** Fresh solutions of hydrogen chloride and 2-methyl-2-butene in nitromethane were prepared having twice the desired strength and cooled to 0°. Equal amounts of these two solutions were mixed and introduced into an ice-jacketed automatic pipet equipped with a narrow delivery tip. Samples were then introduced as rapidly as possible into test tubes which had been constricted to hold a volume of 7 ml and maintained at 0°. When all of the tubes had been filled, they were frozen simultaneously in Dry Ice–ethanol and sealed. These reaction bulbs were then warmed to about 25° by vigorous shaking for two minutes in a turbulent stream of water. All of the bulbs were then placed in a thermostat kept at 25.00 ± 0.02°. To obtain the kinetic zero three bulbs were removed after 4 min and frozen to stop the reaction. Other bulbs were removed at subsequent intervals and frozen. While most runs were carried out by measuring the disappearance of acid, in some both acid and olefin were determined simultaneously. Acid was determined by first freezing the bulb, drying it thoroughly, and then breaking it in 30 ml of dry acetone at −78°. The amount of acid present was determined by titration against standard sodium methoxide using Lacmoid indicator. Alkene was determined by breaking a similarly prepared bulb in an excess of bromine–acetic acid. After reaction for 3 min, which was shown to be sufficient for complete reaction, the remaining bromine was analyzed by adding 10 ml of 10% aqueous potassium iodide and diluting the solution with 125 ml of ice water and titrating the liberated iodine with standard sodium thiosulfate to a starch end point. Except where noted samples were 5.69 ml at 25°. The analytical methods used were reproducible to better than 1%. **Method 2.** A specially constructed reaction vessel equipped with two aliquoting devices was immersed in a water bath thermostat and used for rapid reactions. Acid and olefin solutions in nitromethane were independently brought to thermostat temperature and then introduced simultaneously into the reaction vessel which was then sealed. The aliquoting devices were filled and two samples removed at the same instant. One was run into 30 ml of acetone at −78° and the other was run into excess bromine–acetic acid and the acid and olefin concentrations determined as previously described. The first acid and olefin points could be obtained roughly 15 sec after mixing was completed. Titrations were carried out in the manner described in method 1. Acid samples were 2.52 ml and olefin samples were 2.66 ml. **Method 3.** When slower runs were made using dilute acid and alkene it was possible to carry out the reaction conveniently in well-stoppered volumetric flasks. The desired solutions were prepared and mixed in the reaction flask as in method 2. Points were taken by removing an aliquot with a pipet and proceeding with the determination of acid or olefin as described above.

When kinetic runs were made with added salts, the latter were dissolved in the nitromethane solutions containing alkene prior to mixing with the corresponding acid solutions.

Using calibrated control solutions, it was shown that there was no measurable reaction of HCl with nitromethane over a period *ca.* ten times as long as the slowest kinetic experiment. There was no detectable reaction of nitromethane with Br_2 in the analysis for olefins.

Product Analysis. The product of a run with 2-methyl-1-butene = 0.25 *M* and hydrogen chloride = 0.17 *M* was isolated by gas chromatography (A90P, 50 cc/min of He, 10 ft × 0.25 in. Ucon Nonpolar, 50°). The retention time of this material was 3.6 min and identical with that of authentic 2-chloro-2-methylbutane; a mixed sample resulted in no new peaks. The retention time of 2-chloro-3-methylbutane under the same conditions was 4.6 min. The nmr spectrum of the isolated product was recorded and found to be identical with that of an authentic sample (doublets at τ 8.96 (6) and 8.58 (3), multiplets at 8.42 (1) and 6.19 (1)). The product from the addition of hydrogen chloride to 2-methyl-2-butene was found to have the same retention time on the same column and under the same conditions as used for the analysis of product with 2-methyl-1-butene (analysis performed consecutively). Nmr spectrum again was that of 2-chloro-2-methyl-butane as given above.

Isomerization of 2-Methyl-1-butene and 2-Methyl-2-butene. 1. Absence of Isomerization during Addition (Kinetic Control). Samples of kinetic runs were injected directly into the gas chromatograph and analyzed for alkene composition during the entire course of a run. The concentrations were 2-methyl-1-butene = 0.088 *M* and HCl = 0.0153 *M* and 2-methyl-2-butene = 0.080 *M* and HCl = 0.0112 *M*. The presence of more than 1% of either alkene could be detected in a mixture of the two as was shown by preparing a synthetic mixture of the two olefins in nitromethane in the ratio 100:1 = 2-Me-1-butene:2-Me-2-butene and analyzing it under the same conditions. Vpc conditions were: Hy-Fi, Carbowax 20M, 6 ft × 1/8 in., 30°, 20 cc/min of N_2 flow; retention times: 2-Me-1-butene, 31 sec; 2-Me-2-butene, 39 sec. These peaks are so sharply defined that there is no ambiguity involved in the identification so long as control samples are injected frequently; the separation of peaks is essentially complete.

2. Isomerization under Forcing Conditions (Thermodynamic Control). Samples were prepared 1.0 *M* in 2-methyl-1-butene and 0.20 *M* in hydrogen chloride and sealed in bulbs in the usual manner. The bulbs were placed in baths at 56, 80, and 100°. Bulbs were removed periodically and analyzed for olefin composition by gas chromatography (Ucon Nonpolar, 25°). The isomerization was also shown to be catalyzed by pyridine hydrochloride with similar results.

Reaction of 2-Methyl-1-butene and 2-Methyl-2-butene with Deuterium Chloride in Nitromethane. A solution of each olefin was prepared and mixed with a solution of deuterium chloride in nitromethane such that the final olefin concentrations were 0.15 *M* and the acid was *ca.* 0.10 *M*. Small aliquots were removed periodically and the acid determined. When approximately 50% of the acid had been consumed, the unreacted olefin was removed with a nitrogen stream and trapped. A mass spectrum of the olefin collected from each reaction was obtained and compared to the mass spectrum of an authentic sample of the same olefin. The mass spectra for each pair were indistinguishable, *i.e.*, there was no detectable deuterium incorporation.

Reaction of Isoprene with HCl in Nitromethane. The product of the reaction of isoprene with HCl in nitromethane was determined by comparing the gas chromatograms of reaction solutions with those of authentic materials. It was found that the 1,2 adduct partially rearranged on the column, and after determining that there was indeed product present, the reaction solution was washed with ice water, dried, and reanalyzed. By this procedure *all* of the 1,2 adduct was removed, and the chromatogram showed *no* product peak. Control solutions of the 1,4 adduct were prepared such that the concentration of 1,4 adduct was equivalent to 2, 3, 4, and 5% of the total product observed in the reaction mixture. When the control solutions were washed, dried, and analyzed, it was possible to detect 1,4 adduct easily in the 4 and 5% solutions, barely in the 3% solution, and not at all in the 2% solution. Hence the maximum amount of 1,4 adduct that could be present in the original reaction mixture was <4% of the total product. Analyses were performed on the Hy-Fi at 25° with a 6 ft × 1/8 in. Carbowax M column, N_2

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[8] A. I. Vogel, "Textbook of Practical Organic Chemistry," Longmans, Green and Co., Ltd., London, 1948, p 275.

[9] A. J. Ultee, *J. Chem. Soc.*, 530 (1948).

Table I. Rates of Addition of HCl to 2-Methyl-1-butene and 2-Methyl-2-butene in Nitromethane at 25.0°

[Olefin], M[c]	[HCl], M	Method	10^3k_2,[a] M^{-1} sec^{-1}	k_3,[b] M^{-2} sec^{-1}
		2-Methyl-1-butene		
0.0837	0.00273	$-d[H^+]/dt$	5.19	1.90
0.0811	0.00293	$-d[H^+]/dt$	5.35	1.82
0.0544	0.00322	$-d[H^+]/dt$	6.07	1.88
0.0918	0.00352	$-d[\text{olefin}]/dt$	6.40	1.82
0.0556	0.00452	$-d[H^+]/dt$	8.55	1.89
0.108	0.00805	$-d[H^+]/dt$	15.0	1.86
0.0877	0.0153	$-d[\text{olefin}]/dt$	29.2	1.91
0.0284	0.0168	$-d[H^+]/dt$	32.3	1.92
0.0919	0.0177	$-d[H^+]/dt$	33.5	1.89
0.0872	0.0271	$-d[\text{olefin}]/dt$	51.3	1.90
0.0653	0.0283	$-d[H^+]/dt$	51.5	1.82
0.142	0.0284	$-d[H^+]/dt$	54.0	1.91
0.00920	0.0322	$-d[H^+]/dt$	59.7	1.85
0.0203	0.0329	$-d[H^+]/dt$	59.3	1.80
0.0618	0.0329	$-d[H^+]/dt$	59.0	1.79
0.0791	0.0332	Both	61.5	1.85
		2-Methyl-2-butene		
0.0734	0.00361	$d[H^+]/dt$	1.99	0.550
0.0835	0.00432	$d[\text{olefin}]/dt$	2.40	0.555
0.118	0.00574	$d[H^+]/dt$	3.13	0.545
0.0797	0.00590	$d[H^+]/dt$	3.32	0.562
0.0479	0.00641	$d[H^+]/dt$	3.44	0.538
0.0791	0.0112	Both	5.98	0.534
0.119	0.0134	$d[H^+]/dt$	7.22	0.540
0.0952	0.0144	$d[H^+]/dt$	7.95	0.551

[a] The second-order coefficients are obtained from the initial slope of a plot of log $[(a - x)/(b - x)]$ *vs.* time where $a - x$ and $b - x$ represent the concentrations of reactants at time t; possible error in measurement of initial slopes ±3%. [b] Values obtained from the equation, $k_3 = k_2^i/[\text{HCl}]$. [c] The addition of HCl to these alkenes at 25° proceeds to more than 99% completion as indicated by the following experiments. After ten half-lives a run initially 0.066 M in 2-Me-1-Bu and 0.034 M in HCl showed no detectable acid. Since the indicator method is sensitive to HCl concentrations around 6×10^{-5} M (*i.e.*, *ca.* 0.2% of the initial HCl in the above experiment) we conclude that the addition of HCl is essentially complete. Similarly, when HCl was in excess ([2-Me-1-Bu] = 0.0092 M; [HCl] = 0.032 M) no olefin could be detected after ten half-lives at 25°.

flow 20 cc/min; retention times observed: isoprene, 42 sec; 3-chloro-3-methyl-1-butene, 96 sec (1,2 adduct); 1-chloro-3-methyl-2-butene, 264 sec (1,4 adduct).

Conductance Measurements in Nitromethane. Duplicate samples were prepared for all measurements. The conductance of salts was measured by successively diluting stock solutions. Conductance of HCl and DCl was carried out using solutions taken directly from the acid generators.

Results

Addition of Acids to Olefins. The kinetics of addition of hydrogen chloride to olefins in nitromethane were studied using titrimetric methods in which the rate of both acid and olefin disappearance were identical within experimental error (Table I). The stoichiometry of addition is such that each molecule of olefin reacts with one molecule of acid. However, the kinetics reveal that the initial second-order rate coefficients, first order in olefin and first order in hydrogen chloride, are not constant, but rise linearly as the initial concentration of acid rises. The reaction follows accurate third-order kinetics of the form $v_{\text{addition}} = k_3[\text{olefin}][\text{HCl}]^2$, as can be seen from the constancy in third-order rate coefficients, k_3, obtained by dividing the initial second-order coefficient by the initial acid concentration or directly from the integrated rate expression given by eq 1 (see Table I).

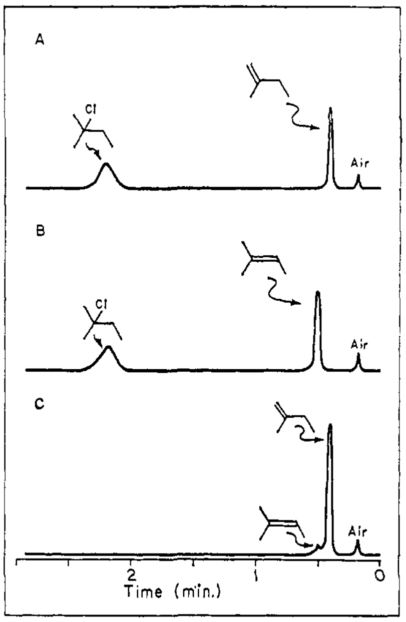

Figure 1. Vapor phase chromatograms of reactions carried out in nitromethane: (A) 2-methyl-1-butene (initially 0.08 M), HCl (initially 0.10 M), after *ca.* 30% reaction; (B) 2-methyl-2-butene (initially 0.08 M), HCl (initially 0.10 M), after *ca.* 30% reaction; (C) control, 2-methyl-1-butene (0.08 M), 2-methyl-2-butene (0.0008 M), *i.e.*, olefin ratio 100:1.

$$k_3 = \frac{1}{t(b - a)}\left[\frac{x}{a(a - x)} + \frac{1}{b - a}\ln\frac{b(a - x)}{a(b - x)}\right] \quad (1)$$

In those runs to which tetramethylammonium chloride had been added, the apparent value of k_2 for any run was found to be lower than in the corresponding case with no added salt. In the concentration range [HCl] > [Et$_4$NCl] this decrease could be satisfactorily treated by assuming that the added chloride ions combine with free hydrogen chloride to produce hydrogen dichloride ions. Thus the value of the second-order rate coefficient is restored if a is taken to mean the concentration of free hydrogen chloride given by ($[\text{HCl}]_{\text{stoich}} - [\text{HCl}_2^-]$). Similarly, the value of k_3 (apparent) is changed to its usual value if k_{2f} is divided by ($[\text{HCl}]_{\text{stoich}} - [\text{HCl}_2^-]$). The addition of tetraethylammonium perchlorate did not have any measurable effect on the rate of reaction (Table II).

The product of addition of HCl to both 2-methyl-1-butene and 2-methyl-2-butene was found to be 2-chloro-2-methylbutane. At the same time, there was no interconversion of these isomeric olefins during the course of addition. The gas chromatograms of reaction solutions after *ca.* 30% reaction are shown in Figure 1. Under conditions leading to thermodynamic control, the ratio of 2-methyl-2-butene to 2-methyl-1-butene is 85:15. The gas chromatograms of a nitromethane solution, initially 1.0 M in 2-methyl-1-butene and 0.2 M in HCl that was heated at 80° for 2 days are shown in Figure 2. There was essentially no change in olefin composition after 24 hr. When DCl was added to 2-methyl-1-butene or 2-methyl-2-butene, there was no detectable incorporation of deuterium into unreacted olefin at *ca.* 50% reaction. Thus the addition of a proton (or deuteron) leads essentially completely to product formation.

Table II. Rate of Addition of HCl to 2-Methyl-1-butene in the Presence of Tetramethylammonium Salts in Nitromethane

a. Et_4NCl

[Olefin], M	[HCl], M	[Et_4NCl], M	10^3k_2[a,b]	k_3[c]	10^3k_{2f}[a,b,d]	k_{3f}[c,d]
0.0164	0.00932	0.00234	9.49	1.02	12.7	1.82
0.00962	0.0192	0.00682	14.7	0.768	22.8	1.84
0.0283	0.0154	0.00730	7.94	0.515	15.1	1.86
0.0356	0.0216	0.0103	11.2	0.520	21.4	1.90
0.0344	0.0223	0.0194	0.655	0.0294	5.05	1.74
0.0570	0.0367	0.0143	26.6	0.727	43.2	1.93
0.0376	0.0531	0.0343	12.0	0.226	33.8	1.90

b. Et_4NClO_4

[Olefin], M	[HCl], M	[Et_4NClO_4], M	10^3k_2[a,b]	k_3[c]
0.0134	0.00767	0.00629	14.3	1.86
0.119	0.0150	0.00642	27.8	1.85
0.00863	0.0165	0.00783	31.2	1.89
0.0545	0.0179	0.00926	32.6	1.82
0.0683	0.0263	0.01191	50.0	1.90
0.0427	0.0303	0.0176	54.1	1.80

[a] Possible error in measurement of initial slopes ±3%. [b] M^{-1} sec^{-1}. [c] M^{-2} sec^{-1}. [d] Calculated on the basis of free HCl, using the equation $[HCl]_f = [HCl]_{titrable} - [Et_4NCl]_0$.

The product of the reaction of HCl with isoprene in nitromethane was found to be 96 ± 4% 3-chloro-3-methyl-1-butene, the 1,2 adduct. The 1,2-addition product was found to rearrange partially during analysis and a technique was developed which removed this compound prior to analysis. Authentic samples of 3-chloro-3-methyl-1-butene and 1-chloro-3-methyl-2-butene were compared with samples obtained from the reaction mixture.

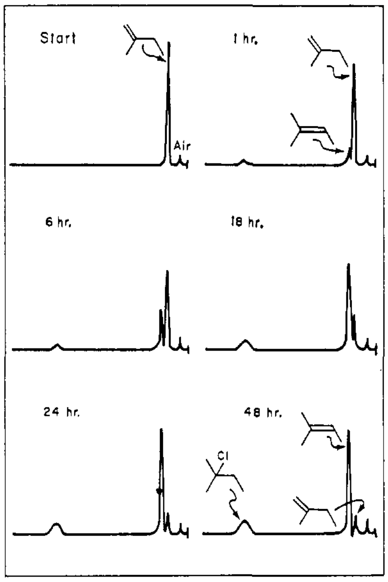

Figure 2. The change in olefin composition in a solution heated in a sealed bulb at 80°. Initially, 2-methyl-1-butene, 1.0 M, and HCl, 0.2 M. The composition at equilibrium is 85% 2-methyl-2-butene and 15% 2-methyl-1-butene.

It is concluded that to the limit of the measurements made kinetic control leads to the production of 1,2 adduct. Treatment of a nitromethane solution containing 3-chloro-3-methyl-1-butene with hydrogen chloride, or allowing such a solution to stand for extended periods at room temperature with no added acid leads to the formation of the more stable 1-chloro-3-methyl-2-butene quantitatively.

The reaction was shown to result in the addition of only 1 × equiv of acid and to follow the expression $V = k_3[\text{isoprene}][HCl]^2$ (see Table III).

Table III. Rate of Addition of HCl to Isoprene in Nitromethane at 25°

a. No Salt Added

[Olefin], M	[HCl], M	10^3k_2,[a] M^{-1} sec^{-1}	k_3, M^{-2} sec^{-1}
0.0119	0.0303	4.73	0.164
0.0205	0.0344	6.19	0.180
0.0193	0.0352	5.49	0.156
0.0326	0.0447	7.61	0.170
0.0294	0.0533	8.67	0.163
0.0297	0.0545	8.41	0.155
0.130	0.0683	10.52	0.154
0.0731	0.0854	16.87	0.173
0.0803	0.0956	16.0	0.167
0.0736	0.0993	15.1	0.157
0.0704	0.101	16.6	0.164
0.0900	0.103	16.6	0.161

b. Added Et_4NCl

[Olefin], M	[HCl], M	[Et_4-NCl], M	10^3k_2,[a] M^{-1} sec^{-1}	k_3, M^{-2} sec^{-1}	k_{2f},[a] M^{-1} sec^{-1}	k_{3f}, M^{-2} sec^{-1}
0.0647	0.0953	0.0105	9.62	0.0101	13.7	0.162
0.0797	0.123	0.0141	16.7	0.136	18.7	0.172
0.0321	0.0585	0.0150	5.49	0.0938	7.70	0.177
0.0327	0.0611	0.0150	6.23	0.102	8.10	0.176
0.0315	0.0628	0.0150	6.15	0.0980	8.17	0.171
0.0300	0.0790	0.0150	7.98	0.101	10.1	0.158
0.0789	0.110	0.0282	8.40	0.0764	12.7	0.155
0.0357	0.0932	0.0304	6.38	0.0684	9.76	0.155
0.0585	0.108	0.0314	8.06	0.0749	12.0	0.156
0.0629	0.102	0.0314	6.95	0.0683	11.1	0.157

c. Added Et_4NClO_4

[Olefin], M	[HCl], M	[Et_4NClO_4], M	10^3k_2,[a] M^{-1} sec^{-1}	k_3, M^{-1} sec^{-1}
0.0720	0.0993	0.0101	15.3	0.154
0.0736	0.0993	0.0201	15.1	0.152
0.0704	0.101	0.0301	16.2	0.160
0.0728	0.101	0.0502	15.7	0.156

[a] Possible variation in k_2 due to error in measurement of initial slopes is ±4%.

The conductances of several electrolytes in nitromethane were measured at 25°. For hydrogen and deuterium chloride, the equivalent conductances were abnormal in that above 0.01 *M* they became essentially independent of concentration. The data were analyzed in terms of the equilibrium $CH_3NO_2 + 2HCl \rightleftharpoons CH_3NO_2H^+ + HCl_2^-$ and an approximate value for K_{diss} was calculated. The data for hydrogen chloride are shown graphically in Figure 3.

For several salts it was found that the conductances measured were normal. The data are given in Table IV for Et_4NCl, Et_4NClO_4, and $LiClO_4$. Table V is included for comparison of the relative amounts of dissociation at several concentrations for the species examined.

The nmr data obtained with HCl solutions in nitromethane are summarized in Table VI. The data for HCl with added Et_4NCl are presented. It was determined that the absorption due to hydrogen chloride alone or with added Et_4NClO_4 was not sensitive to concentration changes of acid.

Table IV. Conductance of Several Salts in Nitromethane at 25°

[MX], *M*	Λ^a	[MX], *M*	Λ^a
	a. Et_4NCl		
0.0000250	102.6	0.0100	86.2
0.000100	101.7	0.0196	79.3
0.000400	99.9	0.0357	73.9
0.00160	96.5	0.0596	68.2
0.00640	89.6	0.0993	62.1
	$\Lambda_0{}^b$ = 103.4 ohm^{-1} cm^{-1}		
	b. Et_4NClO_4		
0.0000250	112.0	0.0101	92.5
0.000100	110.8	0.0202	86.6
0.000400	108.4	0.0404	82.0
0.00160	103.7	0.0808	72.1
0.00640	94.3		
	$\Lambda_0{}^b$ = 113.2 ohm^{-1} cm^{-1}		
	c. $LiClO_4$		
0.0000250	108.8	0.00617	55.0
0.000100	104.9	0.0123	42.1
0.000400	97.1	0.0247	31.3
0.00160	81.6	0.0493	23.0
0.00360	66.3	0.0986	17.0
	$\Lambda_0{}^b$ = 112.7 ohm^{-1} cm^{-1}		

[a] ohm^{-1} cm^2 mol^{-1}. [b] By extrapolation to infinite dilution.

Table V. Per Cent Dissociation of Several Electrolytes in Nitromethane[a] at 25°

	% dissociation at *M*			
MX	0.1	0.01	0.001	0.0001
HCl	0.076	0.083	0.48	1.13
DCl	0.046	0.071	...	...
Et_4NCl	59.6	83.4	94.5	98.4
Et_4NClO_4	61.3	81.7	93.3	97.9
$LiClO_4$	14.8	46.1	77.9	93.1

[a] Values obtained from conductivity data.

Discussion

The addition of hydrogen chloride to simple olefins in the gas phase has a high energy of activation, and at the temperature at which it can be conveniently studied, the equilibrium lies largely toward elimination rather than addition.[10] On the other hand, addition proceeds smoothly and in good yield at temperatures between −80 and 80° in aprotic solvents. The orientation of addition follows Markovnikov's rule, but factors which affect other details of the mechanism are not completely understood.

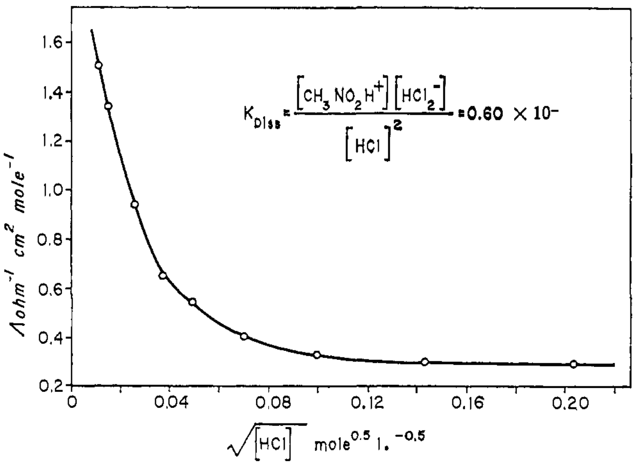

Figure 3. A plot of equivalent conductance *vs.* the square root of the concentration for HCl in CH_3NO_2 $K_{diss} = \alpha^2/(1 - 2\alpha)^2$ where $\alpha = \Lambda/\Lambda_0$.

Table VI. Effect of Added Chloride on the Hydrogen Chloride Nmr Absorption[a,b]

[HCl] = 0.13 ± 0.01 *M*		[Et_4NCl] = 0.0914 *M*	
[Et_4NCl], *M*	Shift,[c] cps	[HCl], *M*	Shift,[c] cps
0.00	0	0.015	−47.0
0.00683	−12.5	0.028	−81.5
0.0137	−31.5	0.042	[−110 − (−101)][d]
0.0139	−35.5	0.063	−146
0.0205	−41.5	0.092	−159
0.0278	−71.0	0.13	−148
0.0417	−96.0		
0.110	−291		
0.221	−413		
0.331	−429		

[a] The hydrogen chloride absorption was found to be concentration independent over the range 0.1–0.9 *M*. [b] Added Et_4NClO_4 was found to cause no shift in the HCl absorption over the range [Et_4NClO_4] = 0.005–0.1 *M*. [c] From HCl with no salt present. [d] In solvent peak.

One important consideration in any mechanistic study is the understanding of the catalytic species present. In the present case it has been shown that hydrogen chloride exists largely as undissociated molecules in nitromethane, in agreement with earlier work.[8,11] The conductance data for hydrogen chloride in nitromethane provide a means of calculating an approximate K_{diss}. The equilibrium $2HCl \rightleftharpoons H^+_{solv} + HCl_2^-$ best describes the situation in nitromethane. Using standard formulations, the approximate value of K_{diss} is found to be $K_{diss} = 6.0 \times 10^{-7}$ in the region [HCl] $\geqslant$ 0.015 *M*.[12] At lower concentrations, *i.e.*, [HCl] < 0.005*M*, there is a concentration dependence, indicating that the dissociation $HCl \rightleftharpoons H^+_{solv} + Cl^-$ may be taking place. The fact that conductance measurements show that the amount of dissociation reaches a constant value is supported by the complete

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(10) E. J. Stamburger, *Rec. Trav. Chim.*, **85**, 167 (1904).

(11) C. P. Wright, O. N. Murray-Rust, and H. Hartley, *J. Chem. Soc.*, 199 (1931).

(12) The equivalent conductance for hydrogen chloride is given by the expression $\Lambda_0{}^{HCl} = \Lambda_0{}^{HClO_4} + \Lambda_0{}^{Et_4NCl} - \Lambda_0{}^{Et_4NClO_4} = 117$ ohm^{-1} cm^{-1}.

lack of sensitivity of the HCl nmr signal to concentration changes. The nmr signal is very sensitive to even small amounts of added chloride ions, moving toward regions of increased deshielding of the proton as chloride ion concentration increases. Added perchlorate ions have no effect, indicating that a general salt effect is not resoponsible for these observations.

These data are readily accommodated in terms of the following equilibria.

$$HCl \rightleftharpoons H^+ + Cl^- \text{ (far to left)}$$

$$HCl + Cl^- \rightleftharpoons HCl_2^- \text{ (far to right)}$$

$$HCl + ClO_4^- \rightleftharpoons ClHClO_4^- \text{ (no detectable reaction)}$$

Thus the dominant species capable of donating protons in nitromethane is seen to be undissociated hydrogen chloride molecules (Table V). It has previously been shown that there is very little association (dimerization) of hydrogen chloride in nitromethane.[3]

The kinetics of addition of hydrogen chloride to all of the olefins is rate $= k_3[\text{olefin}][HCl]^2$. The kinetic results do not define the form in which hydrogen chloride enters the rate expression, but they do define the stoichiometry of the activated complex as olefin, 2HCl. As has been previously described,[3] the species $CH_3NO_2H^+$ (free ion) cannot be the dominant proton-donating species, as this leads to a first-order dependence on hydrogen chloride. Additionally, a proton transfer from such a species would have to be extremely rapid to compete with the process represented by the third-order term.[13]

It thus appears that the prevalent species in solution, hydrogen chloride, is also the dominant proton donor. The kinetic results are consistent with such a scheme and contrast with the conductance data which show that at kinetically useful concentrations, the concentration of the dissociated species, $CH_3NO_2H^+$, is proportional only to the first power of hydrogen chloride concentration.

$$[CH_3NO_2H^+] = [HCl_2^-] = \sqrt{K_{\text{diss}}[HCl]^2} = \sqrt{K_{\text{diss}}}[HCl]$$

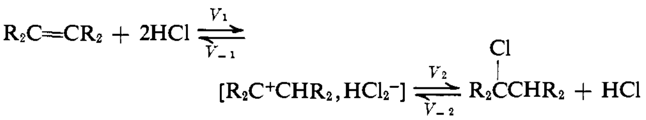
Account being taken of the low degree of dissociation of hydrogen chloride in nitromethane, the type ground state for these electrophilic addition reactions is thus more accurately represented by olefin + 2HCl rather than by olefin + $CH_3NO_2H^+$ + HCl_2^-. Additionally, since the infrared spectra of freshly prepared solutions of hydrogen chloride in nitromethane do not show any new bands which could be associated with either $CH_3NO_2H^+$ or HCl_2^-,[3] the concentration of $CH_3NO_2H^+,HCl_2^-$ ion pairs must also be very low, a conclusion which is entirely consistent with our preferred representation of the ground state as olefin + 2HCl rather than as olefin + $CH_3NO_2H^+,HCl_2^-$. Further support for molecular hydrogen chloride as the proton donor is offered by the observed effect of added salts on the rate of reaction. Recalling that the equilibrium $HCl + Cl^- \rightleftharpoons HCl_2^-$ is far to the right, it is apparent that added chloride ions will act to remove molecular hydrogen chloride from solution essentially on a one-to-one basis. Thus examination of Table II leads us to conclude that only molecular acid is acting as a proton donor.

The addition of any substantially dissociated salt should increase the ionizing capacity of the medium and enhance any process that either proceeds to form ions or depends on an ionic equilibrium in the ground state. Thus the total lack of effect of added tetraethylammonium perchlorate leads to two conclusions: (1) prior dissociation of hydrogen chloride is not an important factor *and* (2) the salt must effect the transition state and ground state in substantially the same way.

That the rate-determining step in the addition process is the initial proton transfer is supported by three observations. The first of these is that there is no interconversion of the two isomeric 2-methylbutenes during the course of reaction starting with either isomer, while under conditions leading to thermodynamic control, an equilibrium mixture of 2-methyl-2-butene: 2-methyl-1-butene of 85:15 is obtained. Thus the first step in the reaction does not appear to be a rapid and reversible protonation to form a carbonium ion; since both olefins give the same ion, equilibration should occur in that event. The second observation supports this conclusion. In the addition of deuterium chloride to either olefin there is no deuterium incorporation into unreacted olefin at partial reaction, a result only possible if there is no detectable return once protonation has been accomplished.[14]

The final observation is that the addition of hydrogen chloride results in essentially complete kinetic control since only the *less* stable 1,2-addition product is obtained. A reversible protonation would give both 1,2- and 1,4-addition products. Thus if we agree that the carbonium ions are indeed intermediates in this reaction, the possibility that the transfer of chloride to carbonium ion could be rate determining is excluded. The most attractive mechanism consistent with all of the data involves a rate-determining proton transfer from molecular hydrogen chloride to olefin with a second molecule of acid acting to assist the proton transfer by hydrogen bonding to the developing chloride ion.[15]

A path consistent with the data presented is



$$R_2C{=}CR_2 + 2HCl \underset{V_{-1}}{\overset{V_1}{\rightleftharpoons}} [R_2C^+CHR_2,HCl_2^-] \underset{V_{-2}}{\overset{V_2}{\rightleftharpoons}} R_2\overset{\displaystyle Cl}{C}CHR_2 + HCl$$

The rates of the various steps are given by

$$V_1 = k_1[R_2C{=}CR_2][HCl]^2$$

$$V_{-1} = k_{-1}[R_2C^+CHR_2,HCl_2^-]$$

$$V_2 = k_2[R_2C^+CHR_2,HCl_2^-]$$

and

$$V_{-2} = k_{-2}[R_2CClCHR_2][HCl]$$

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[13] At very low acid concentrations ([HCl] < 0.001 *M*) a very small second-order term is observed. It is too small to be accurately measured, and with [HCl] > 0.001 *M* it accounts for less than 1% of the total reaction.

[14] This is not the case with species which form more stable carbonium ions. In the case of styrene, for example, a small but detectable amount of return is observed [Y. Pocker, F. Naso, and G. Tocchi, *Proc. XIXth Intern. Congr. Pure Appl. Chem.*, A1-42, 45 (1963); Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 50-M, and unpublished observations].

[15] Actually, other species capable of hydrogen bonding may work. In the presence of phenol, the addition of hydrogen chloride to styrene in nitromethane becomes first order in hydrogen chloride and first order in phenol, *cf.* ref 1b and unpublished observations.

The reverse process has been shown to be very slow at 25°.[4,16]

In the present work V_{-1} has been shown to be appreciably smaller than V_2 and V_2 has been shown to be greater than V_1 which leads to

$$V_{\text{addition}} = V_1 = k_1[R_2C{=}CR_2][HCl]^2$$

The kinetic description of the reaction path does not describe the structure of the transition state nor the position of the hydrogen dichloride anion in it. These questions will be the subject of future studies in this area.

The possibility has recently been raised that addition of acids to olefins might involve synchronous addition of proton and anion by two different molecules of acid.[17,18] On the basis of the evidence given in this paper such a process is not required in nitromethane solvent. The stereochemistry of addition and the definitive demonstration or exclusion of a carbonium ion intermediate are required prior to reaching any conclusion on this point. At present, the formation of an ion pair intermediate seems the simplest scheme which accords with all of the data presented in this paper.

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(16) Y. Pocker, *J. Chem. Soc.*, 1972 (1960).

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

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Kinetics and Mechanism of Addition of Acids to Olefins. IV. The Addition of Hydrogen and Deuterium Chloride to 3-Methyl-1-butene, 3,3-Dimethyl-1-butene, 1-Methylcyclopentene, and 1-Methylcyclopentene-2,5,5-d_3[1]

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Abstract: The addition of hydrogen and deuterium chloride to 3-methyl-1-butene, 3,3-dimethyl-1-butene, 1-methylcyclopentene, and 1-methylcyclopentene-2,5,5-d_3 has been studied in nitromethane at 25.0°. In the initial stages of the reaction, 3-methyl-1-butene is shown to form 40% normal addition product, 2-chloro-3-methylbutane, and 60% rearranged product, 2-chloro-2-methylbutane, while 3,3-dimethyl-1-butene is shown to form only 17% normal addition product, 2-chloro-3,3-dimethylbutane, and 83% rearranged product, 2-chloro-2,3-dimethylbutane. Hydrogen chloride catalyzes the rearrangement of 2-chloro-3-methylbutane but control experiments show that the rate of this Wagner–Meerwein rearrangement is too slow to account for the observed product ratio during the initial stages of the addition reaction. Under similar conditions the rearrangement of 2-chloro-3,3-dimethylbutane is very slow and can be neglected. The addition of deuterium chloride to 1-methylcyclopentene and of hydrogen chloride to 1-methylcyclopentene-3,5,5-d_3 is shown to lead to 96 ± 4% *trans*-addition product.

For the addition of hydrogen chloride to aliphatic alkenes in nitromethane, kinetics alone do not allow a distinction to be made between a one-step and a two-step process.[1b] Thus the rate law, $V = k_3[\text{alkene}][HCl]^2$, allows us to deduce the stoichiometric composition of the activated complex but does not provide any compelling evidence as to whether the reaction takes place in two discrete steps, with transfer of Cl^- from HCl_2^- to carbonium ion following the proton transfer from acid to alkene or as a concerted one-step process. For the addition of DCl and TCl to styrene[3] the small but measurable incorporation of tracer into alkene which *accompanies* addition is best interpreted in terms of a two-step addition process. This test fails, however, in the case of simple aliphatic alkenes. Thus starting with the two isomeric olefins, 2-methyl-2-butene and 2-methyl-1-butene, in nitromethane we have shown (see preceding paper) that at 30% reaction neither olefin has been *measurably* converted to the other isomer in spite of the fact that the addition of a proton to either of these olefins leads to the same carbonium ion. This observation was also substantiated by showing that no H–D exchange occurs in either unreacted olefin during an essentially irreversible addition. These results made it necessary for us to apply more direct tests for the presence of carbonium ion intermediates. Consequently we have examined the addition of hydrogen chloride to 3-methyl-1-butene and 3,3-dimethyl-1-butene in nitromethane, since these are reactions which could provide a special piece of evidence for an ionic two-stage process, if accompanied by Wagner–Meerwein rearrangements.

Whitmore and Johnston[4] have shown that the addition of HCl to 3-methyl-1-butene (neat) and 3,3-di-

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(1) (a) This research was supported by a grant from the National Science Foundation. (b) Part III of this series: Y. Pocker, K. D. Stevens, and J. J. Champoux, *J. Am. Chem. Soc.*, **91**, 4199 (1969). (c) Taken from the Ph.D. Thesis of K. D. Stevens, University of Washington, 1966.

(2) Weyerhaeuser Research Fellow, 1963–1964; National Science Foundation Cooperative Research Fellow, 1964–1965.

(3) Y. Pocker, F. Naso, and G. Tocchi, *Proc. XIXth Intern. Congr. Pure Appl. Chem.*, **A1-42**, 45 (1963); Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p 50M.

(4) (a) F. C. Whitmore and F. Johnston, *J. Am. Chem. Soc.*, **55**, 5020 (1933); (b) G. G. Ecke, N. C. Cook, and F. C. Whitmore, *ibid.*, **72**, 1511 (1950).