# Stereochemistry of the Hydrochlorination of Cyclohexene-1,3,3-$d_3$ in Acetic Acid. Evidence for Termolecular *anti* Addition of Acids to Olefins[1]

**Robert C. Fahey[2a] and Michael W. Monahan[2b]**

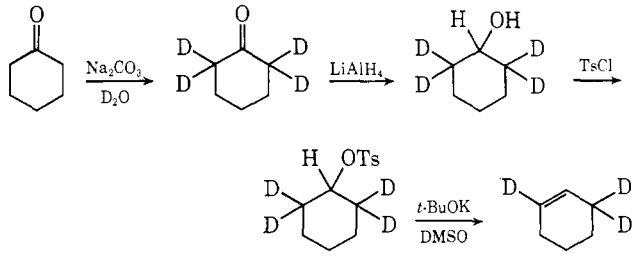
*Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92037.*
*Received September 26, 1969*

**Abstract:** The reaction of cyclohexene-1,3,3-$d_3$ with HCl in acetic acid yields a mixture of *syn*-HCl adduct SC, *anti*-HCl adduct AC, and *anti*-HOAc adduct AA under conditions of kinetic control. The ratio of AC to AA increases markedly with the HCl concentration, in the presence of tetramethylammonium chloride, or in the presence of water, while the ratio of SC to AA remains essentially unchanged. The ratio of SC to AA does, however, increase significantly with temperature. No *syn*-HOAc addition was detected. Cyclohexene-1,3,3-$d_3$ recovered after partial reaction showed no evidence of exchange or rearrangement. Analysis of these results, together with those of the preceding paper, shows that three competing reactions are involved. One involves a termolecular reaction of olefin, HCl, and dissociated chloride ion leading to AC while termolecular reaction of olefin, HCl, and acetic acid forms AA. A bimolecular reaction of HCl and olefin leads to formation of a carbonium chloride ion pair which collapses primarily to a mixture of SC and AA.

A number of years ago we reported results of a study of the stereochemistry of polar HBr addition to cyclohexene-1,3,3-$d_3$ in acetic acid.[3] Only *anti* addition of HBr was observed at temperatures between 15 and 60° as contrasted with an earlier report[4] that DBr addition to cyclohexene in acetic acid resulted in *syn* addition in amounts varying from 26 to 74% with increasing temperature between 10 and 60°. An attempt was made to study the kinetics of HBr addition to cyclohexene under the conditions employed for the stereochemical studies in order to elucidate the mechanism involved in *anti*-HBr addition, but the kinetics proved to be more complex than expected. We turned then to a study of HCl addition to cyclohexene in acetic acid which seemed a more suitable system for study. In the preceding paper[5] we reported the results of the latter study and contrasted them with results obtained from a similar study of *t*-butylethylene and styrene.[6] It was shown that the addition of HCl to cyclohexene, but not that to *t*-butylethylene or styrene, is subject to catalysis by chloride ion. In this paper we report studies of the stereochemistry of addition to cyclohexene-1,3,3-$d_3$, conducted under conditions identical with those employed in the kinetic and product studies of the preceding paper, and show that the chloride-ion catalysis is associated with stereospecific *anti* addition to cyclohexene.

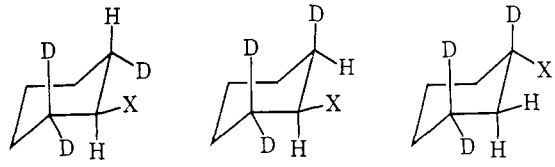
## Results

Cyclohexene-1,3,3-$d_3$ was prepared from cyclohexanone according to the following reaction sequence.[3]




The final product was purified by preparative glpc.

Reaction of cyclohexene-1,3,3-$d_3$ with HCl in acetic acid can, in principle, yield six possible addition products. Proton attack at the olefinic carbon bound to deuterium leads to the HCl adducts SC (*syn* addition) and AC (*anti* addition), and to the HOAc adducts SA (*syn* addition) and AA (*anti* addition). Proton attack at the olefinic carbon bound to hydrogen gives




rise to NC and NA. Proton attack at the two olefinic carbons is equally probable if small secondary isotope effects are neglected so that by determining the ratio of SC to AC and the ratio of SA to AA the stereochemistry of addition can be established.

A combination of nmr and glpc procedures was used to analyze the reaction products. Cyclohexene-1,3,3-$d_3$ was allowed to react with solutions of HCl in acetic acid and the solutions worked up as described previously.[5] The resulting HCl and HOAc adducts were separated by preparative glpc and their nmr spectra measured under conditions of deuterium decoupling. Neither the nmr spectrum of NC nor that of NA exhibit a low-field resonance while SC, SA, AC, and AA should exhibit low-field doublets associated

(1) (a) Reported in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) Taken in part from the Ph.D. Thesis of Michael W. Monahan, University of California, San Diego, Calif., 1968. (c) Reported in part in a preliminary communication, R. C. Fahey and M. W. Monahan, *Chem. Commun.*, 936 (1967).

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

(3) R. C. Fahey and R. A. Smith, *J. Amer. Chem. Soc.*, **86**, 5035 (1964).

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

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

(6) R. C. Fahey and C. A. McPherson, *ibid.*, **91**, 3865 (1969).

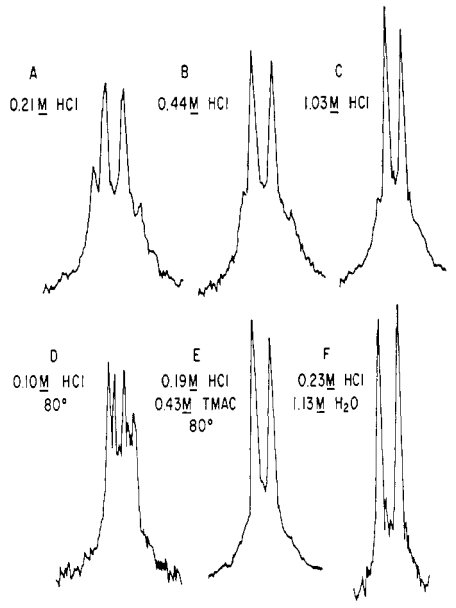



Figure 1. Resonance at $\delta$ 3.94 for HCl adduct of cyclohexene-1,3,3-$d_3$ recorded with deuterium decoupling. Sweep rates vary somewhat between samples.

with the CX–H proton. The magnitude of the splitting of these doublets can be employed to distinguish SC from AC and SA from AA.

Both cyclohexyl chloride and cyclohexyl acetate are known to exist preferentially in the *equatorial* conformation[7] and, since the *axial–axial* vicinal proton–proton coupling is rather large (~12 Hz) while the *axial–equatorial* coupling is small (~3 Hz),[8] the coupling in SC and SA, as measured in the CX–H doublet, should be larger than that in AC and AA. Representative spectra of the CX–H resonances observed for the HCl adducts obtained under various conditions are reproduced in Figure 1. In all cases, a distinct 3.5 Hz doublet is observed. At low HCl concentration and at higher temperature (Figures 1A and 1D) another doublet, symmetrically disposed about the first and having a spacing of 8.9 Hz, is observed. The former is assigned to AC and the latter to SC. The magnitudes of these couplings accord well with those found for the *anti* adduct (3.5 Hz) and the *syn* adduct (8.7 Hz) of HBr with cyclohexene-1,3,3-$d_3$.[3] As is evident in Figure 1, the resolution of the peaks is poor. This is due in part to the fact that the spectra were recorded using microtubes which do not provide optimum resolution, but the peaks may also be broadened somewhat by deviations from purely first-order spectral patterns.

The CX–H resonance of the HOAc adducts was examined in an analogous fashion and sample spectra are reproduced in Figure 2. Under all conditions the resonance appeared as a doublet of 3.2 Hz spacing. This accords well with the 3.3-Hz doublet observed for the HOAc adduct obtained from treatment of cyclohexene-1,3,3-$d_3$ with HBr in acetic acid. By analogy with the HCl and HBr adducts, this doublet can be attributed to the *anti*-HOAc adduct AA. If

(7) J. A. Hirsch in "Topics in Stereochemistry," Vol. 1, N. A. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967, p 199.

(8) A. A. Bothner-By, *Advan. Magn. Resonance*, **1**, 195 (1965).

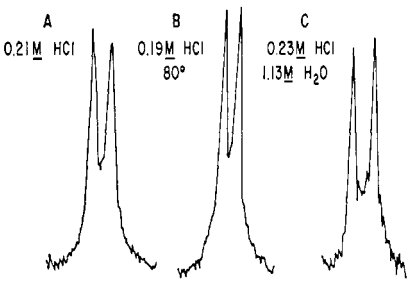
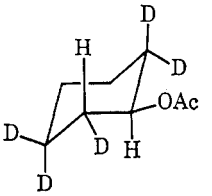



Figure 2. Resonance of $\delta$ 4.67 for HOAc adduct of cyclohexene-1,3,3-$d_3$ recorded with deuterium decoupling. Sweep rates vary somewhat between samples.

the *syn*-adduct SA had been formed in significant amounts it would certainly have been detected since it would have a CX–H doublet with a splitting of 8.7 Hz, the value obtained by Wolfe and Campbell[9] for the *anti*-HOAc adduct (A) isolated from reaction of cyclohexene-3,3,6,6-$d_4$ with DBr in DOAc.




A

The stereochemical results may be put on a semiquantitative basis by integrating the doublet peak areas. This was accomplished by decomposing the superimposed peaks into separate doublets which, when added, would reproduce the observed spectrum. The line shapes were assumed to conform to those observed when only the smaller doublet was found to be present. The relative areas were measured by cutting out and weighing the separately reconstructed doublets. The stereochemical results were combined with the observed ratios of HCl to HOAc addition[5] to give the product compositions listed in Table I.

**Table I.** Variation of the Stereochemistry of Addition with Reaction Conditions

| $T$, °C | [HCl], $M$ | % SC | % AC | % AA[a] |
|---|---|---|---|---|
| 25.0 | 0.21 | 4 | 14 | 82 |
| 25.0 | 0.44 | 4 | 19 | 77 |
| 25.0 | 1.03 | 3 | 28 | 69 |
| 25.0 | 0.15[b] | ≤4 | ≥67 | 30 |
| 80.0 | 0.19[b] | ≤4 | ≥65 | 31 |
| 80.0 | 0.10 | ~18 | ~18 | 65 |
| 80.0 | 0.19 | 15 | 18 | 68 |
| 25.0 | 0.23 | ≤3 | ≥54 | 43 |
| 25.0 | 0.13[c] | *d* | *d* | 96 |

[a] Nmr analysis of the deuterated cyclohexyl acetate revealed no *syn*-HOAc adduct within the limits of detection (*ca.* 5% of the total acetate). [b] With 0.43 $M$ TMAC. [c] With 0.193 $M$ $LiClO_4$. [d] Not determined.

The results of Table I show that, while HOAc addition occurs predominantly *anti* under all conditions, the stereochemistry of HCl addition is a marked function

(9) Private communication from Professor Saule Wolfe, Queens University, Kingston, Ontario.

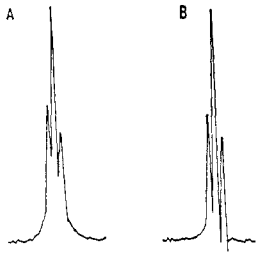



Figure 3. Resonance at $\delta$ 5.57 for cyclohexene-1,3,3-$d_3$ recorded with deuterium decoupling: (A) recovered after 60% reaction in 0.1 *M* HCl at 80°; (B) starting material.

of the reaction conditions. The increase in cyclohexyl chloride formation associated with an increase in the HCl concentration, with the presence of tetramethylammonium chloride (TMAC) in the reaction mixture, or with a high water content, is seen to involve an increase in the amount of *anti*-adduct AC which is formed. An increase in the reaction temperature, on the other hand, results in an increase in the fraction of cyclohexyl chloride formed primarily as a result of an increase in the fraction of *syn*-adduct SC which is formed. In the presence of lithium perchlorate, the fraction of chloride formed is markedly reduced.[10]

It is important to know whether the formation of *syn*-HCl adduct results from kinetically controlled *syn* addition or from secondary isomerization of the *anti*-addition product. The fact that addition in 0.1 *M* HCl at 80° yields nearly equal amounts of SC and AC while addition in 0.19 *M* HCl and 0.43 *M* TMAC at 80° (during a comparable reaction interval) gives only AC indicates that the products are stable to the reaction conditions since the presence of TMAC could only accelerate product isomerization. The fact that cyclohexyl chloride and cyclohexyl acetate are not interconverted under the reaction conditions[5] accords with this conclusion.

It was also of interest to ascertain whether exchange in or rearrangement of the starting olefin accompanies addition. In the reaction of cyclohexene-1,3,3-$d_3$ with 0.1 *M* HCl at 80°, the unreacted olefin was recovered after 60% reaction and its nmr spectrum recorded under conditions of deuterium decoupling. The observed olefinic resonance is compared in Figure 3 with that of the starting material. The spectrum of the recovered olefin, measured in a microtube, exhibits somewhat broader lines than that of the starting material, measured in a precision 5-mm sample tube. It is evident, however, that there is no other significant difference in the patterns, both being triplets as the result of a 2.0-Hz coupling to the C-6 methylene group. If appreciable (~10%) exchange or rearrangement had occurred, new signals or significant perturbations in the triplet structure would have been observed.

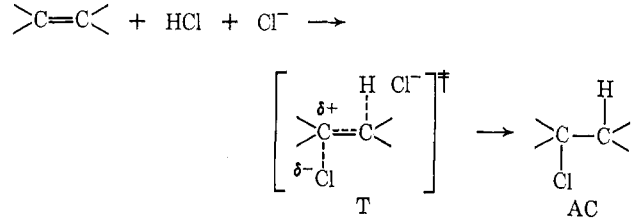
## Discussion

The results presented in this paper, when coupled with those of the preceding paper, greatly clarify the mechanism involved in the *anti* addition of acids to olefins. Thus, it was shown[5] that the rate law for the hydrochlorination of cyclohexene is given by eq 1[11]

$$-d[C_6H_{10}]/dt = k_2A^{1.1}[C_6H_{10}] + k_3A^{1.1}[C_6H_{10}][Cl^-] \quad (1)$$

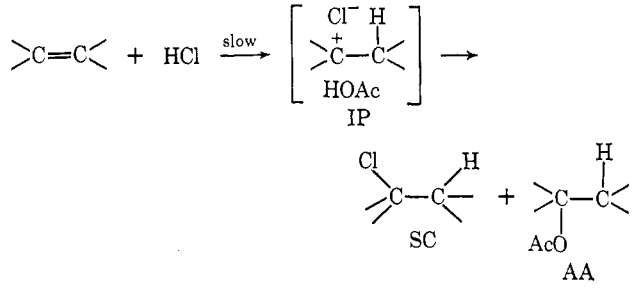
where the third-order term is associated exclusively with formation of cyclohexyl chloride. The results of Table I involving the effect of HCl concentration, TMAC, and water upon the stereochemistry of addition show further that this term is associated with stereospecific *anti*-HCl addition. It is clear then that this component of the reaction is best described as involving a termolecular mechanism ($Ad_E3$) proceeding *via* a transition state resembling T (Scheme I).

**Scheme I**




The second-order kinetic term, which is associated with the formation of ~5% *syn*-HCl adduct SC, 0–5% *anti*-HCl adduct AC, and 90–95% *anti*-HOAc adduct AA, involves at least two different mechanisms. The *syn* addition of HCl might, in principle, arise by a direct molecular addition of HCl to cyclohexene, but such a mechanism is unprecedented for reactions of acids with unstrained olefins in solution.[12] Alternatively, and more reasonably, the *syn*-HCl adduct may arise *via* a carbonium ion mechanism ($Ad_E2$) of the type previously demonstrated for addition to styrene and *t*-butylethylene under comparable conditions (Scheme II). The ion pair intermediate IP would be expected to collapse to a mixture of SC and AA. Both cyclohexene and *t*-butylethylene form secondary cations in such a mechanism and their rates should, therefore, be similar under comparable conditions. The results show that *t*-butylethylene reacts at about 12 times the rate at which cyclohexene forms SC and this observation supports the view that Scheme II is the mechanism

**Scheme II**




leading to SC. Some AC may also be formed in this mechanism *via* isomerization of the ion pair prior to collapse but the stereochemical results show only that the amount of AC formed by such a process must be less than or equal to the amount of SC formed.

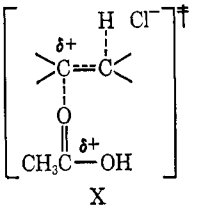
It is clear, however, that AA cannot be formed exclusively by the $Ad_E2$ mechanism of Scheme I. Col-

(10) Lithium perchlorate has been found to have a marked effect upon the rate and products formed in the addition of HCl to a variety of olefins in acetic acid. The nature of these effects will be the subject of a future paper.

(11) In the presence of TMAC, a correction for salt effects must be included. See ref 5.

(12) There is evidence, however, for concerted *syn* addition of electrophilic reagents to strained bicyclic olefins. For references see: T. G. Traylor, *Accounts Chem. Res.*, 2, 152 (1969).

lapse of IP would give at most equal amounts of acetate and chloride while much more acetate than chloride is actually formed. Moreover, the ratio of SC to AA increases markedly with temperature (Table I) corresponding to a large apparent difference in activation enthalpy for formation of these two products ($\Delta H_{SC}^{\ddagger} - \Delta H_{AA}^{\ddagger} \approx 5$ kcal/mol). Collapse of a reactive intermediate such as IP should occur at nearly diffusion-controlled rates and two competing reactions of this type could not reasonably differ in activation enthalpy by as much as 5 kcal.[6] Thus, it is necessary to postulate that most of the *anti*-HOAc adduct AA is formed by a termolecular addition of acetic acid analogous to that of Scheme I for HCl addition. For this process the transition state is presumed to resemble **X**.



X

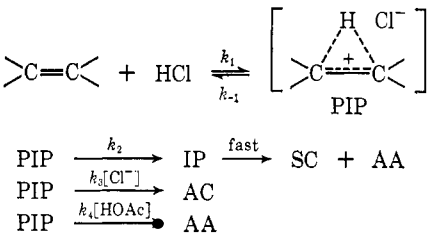
Explicit evaluation of the rate constants associated with each of these reactions is complicated by the lack of a precise value for the dissociation constant of TMAC ($K_{TMAC}$), by the deviation of effective acidity from stoichiometric acid concentration, and by the complex salt effects which operate in the concentration range studied. It might seem that these difficulties could be overcome by studying the reaction at much lower reactant concentrations but the rather slow reaction rate and the necessity to isolate significant amounts of product for stereochemical analysis make this totally impractical. Although precise evaluation of the rate constants is not possible, it is possible, with some assumptions, to estimate their values.

In the preceding paper, values of $k_2$ and $k_3$, applicable in eq 1 at 0.06–1.0 *M* HCl, were obtained based upon an estimate of $K_{TMAC}$ and the assumption that the salt effects upon the various reactions are identical. The value of $k_3 = 1.0 \times 10^{-3}\ M^{-2}\ \text{sec}^{-1}$ is the rate constant for the termolecular *anti*-HCl addition in Scheme I; we will henceforth designate this rate constant $k_3^{HCl}$. The rate constant for the carbonium ion process of Scheme II, $k_{2c}$, can be estimated if we assume that equal amounts of SC and AA are formed in this reaction; thus, $k_{2c} \cong 0.1\ k_2 \cong 2.4 \times 10^{-8}\ M^{-1}\ \text{sec}^{-1}$. The remainder of $k_2$ is assigned to termolecular *anti*-HOAc addition with rate constant $k_3^{HOAc} \cong 0.9\ k_2/[\text{HOAc}] \cong 1.3 \times 10^{-8} M^{-2}\ \text{sec}^{-1}$.

These estimates of the rate constants may be used to make some useful comparisons. The value of $k_{2c}$ for cyclohexene can be compared with the corresponding values calculated from the data obtained with *t*-butylethylene and styrene[6] leading to relative rates of 1, 4, and ~1900 for cyclohexene, *t*-butylethylene, and styrene, respectively. No termolecular addition of HCl to *t*-butylethylene or styrene was detected but upper limits for the values of $k_3^{HCl}$ can be calculated from the results reported; we obtain $k_3^{HCl} \leqslant 9 \times 10^{-6}\ M^{-2}\ \text{sec}^{-1}$ for *t*-butylethylene and $10^{-1}\ M^{-2}\ \text{sec}^{-1}$ for styrene. We see, then, that termolecular HCl addition to *t*-butylethylene occurs at a rate at least 80-fold less than that to cyclohexene, a fact which can be attributed to an unfavorable steric interaction of the *t*-butyl group with chloride ion in the transition state for addition (Scheme I). Termolecular addition to styrene occurs at most about 150-fold faster than that to cyclohexene compared with a factor of ~1900 for reaction *via* Scheme II. This indicates that the phenyl group has a smaller rate-enhancing effect upon the termolecular addition, as expected if the bonding of chloride ion to carbon is significantly developed in the transition state (Scheme I).

The *anti* addition of acids to olefins has been frequently attributed to reaction *via* a protonium ion intermediate. In the reaction of cyclohexene, it is possible that the bimolecular and termolecular transition states are preceded by the rapid reversible formation of a protonium chloride ion pair PIP which is a common intermediate to both reactions (Scheme III);

**Scheme III**



such a scheme is similar to that discussed some years ago by Taft, *et al.*,[13] for the hydration of olefins. This more elaborate mechanism is consistent with all of the present results. Observation of a large primary isotope effect ($k_H/k_D > 2$) might have excluded such a mechanism but the observed isotope effect ($k_H/k_D = 1.3$) does not allow a definite conclusion to be drawn. In fact, it would seem that the only way to definitively prove the mechanism of Scheme III would be to demonstrate a change in the rate law with changing reaction conditions corresponding to $k_1$ becoming rate limiting. As pointed out in the preceding paper, the two runs at highest TMAC concentration did have lower rates than predicted by eq 1, but this more likely results from salt-effect phenomenon than from a change in the rate law. In the absence of definite evidence for the mechanism of Scheme III, the reaction is best described as involving the competing reactions shown in Schemes I and II. It is, of course, probable that a weak molecular complex between olefin and HCl[14] is involved in a preequilibrium step, but the intermediacy of a protonium ion remains purely speculative.[15]

A number of other preferential or stereospecific *anti* additions of acids to olefins have been reported. These include the polar additions of HBr to 1,2-dimethylcyclohexene[16] and to cyclohexene-1,3,3-$d_3$,[3] of DBr to *cis*- and *trans*-2-butene,[17] and of HCl to 1,2-dimethylcyclopentene.[18] It now seems probable that

(13) R. H. Boyd, R. W. Taft, A. P. Wolfe, and D. R. Christman, *J. Amer. Chem. Soc.*, **82**, 4729 (1960), and references therein.
(14) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).
(15) It has been shown that the acid-catalyzed hydration of the relatively reactive olefin *p*-methoxy-α-methylstyrene is subject to a general acid catalysis showing that reversible formation of a protonium ion is not involved in this reaction. See: W. M. Schubert, B. Lamm, and J. R. Keeffe, *ibid.*, **86**, 4727 (1964).
(16) G. S. Hammond and T. D. Nevitt, *ibid.*, **76**, 4121 (1954).
(17) D. J. Pasto, G. R. Meyer, and S.-Z. Kang, *ibid.*, **91**, 2163 (1969).
(18) G. S. Hammond and C. H. Collins, *ibid.*, **82**, 4323 (1960).

these reactions involve a termolecular mechanism similar to that shown in Scheme I.

A recent report[19] of *anti* addition of HCl to 1-methylcyclopentene-1,3,3-$d_3$ in nitromethane has, however, been interpreted in terms of a carbonium ion mechanism. The reaction follows a third-order rate law, first order in olefin and second order in HCl, and the mechanism was described as involving rate-limiting formation of a carbonium hydrogen dichloride ion pair; the observed *anti* addition was attributed to orientational effects upon the collapse of the ion pair to products. There are two problems associated with these results and conclusions. First, the stereochemistry was studied at high acid concentration ($\sim$0.8 *M*) while the kinetics were studied at low acid concentration (<0.1 *M*) so that it is not entirely clear that the observed stereochemistry is actually associated with the observed rate law. Second, if it is assumed that *anti* addition does occur at lower acid concentrations according to a third-order rate law, it could well be that it occurs by a termolecular mechanism involving *anti* attack by dissociated $H^+$, and dissociated $HCl_2^-$ upon the olefin. A process of this type fits the observed kinetics and seems more consistent with stereospecific *anti* addition than a mechanism involving a carbonium ion intermediate.

The results and conclusions reported in this series of papers generally parallel those reported earlier[20] for addition of HCl to acetylenes. However, for addition to 3-hexyne[20b] it was observed that the total rate increased linearly with the concentration of added TMAC at constant HCl and acetylene concentrations and this observation led to the conclusion that undissociated TMAC is the effective nucleophile. The results of the present more detailed studies suggest that this linear dependence of the rate upon TMAC may have been a fortuitous result arising from the complications associated with ion pair dissociation and with nonlinear salt effects upon the reaction rate. This problem will be considered further in a future paper reporting additional studies of acid additions to acetylenes.

## Experimental Section

An Aerograph Model 202 gas chromatograph equipped with thermoconductivity detectors was used with a 10 ft × 1/4 in. column packed with Apiezon L on Chromosorb G (DMCS, acid washed) for preparative glpc separations. Nmr spectra were recorded with a Varian HR-60 spectrometer equipped with a Nuclear Magnetic Resonance Specialties, Inc., Model SD-60 heteronuclear spin decoupler.

**Materials.** Lithium aluminum hydride was obtained from Metal Hydrides, Inc., lithium perchlorate from G. Frederick Smith Chemical Co., and *p*-toluene sulfonyl chloride from Matheson Coleman and Bell. Cyclohexanone-2,2,6,6-$d_4$ was that prepared by R. A. Smith by exchange of cyclohexanone with $D_2O$.[3] All other materials were as described in the preceding paper.[5]

**Cyclohexene-1,3,3-$d_3$.** Cyclohexanone-2,2,6,6-$d_4$ (0.1515 mol) was added to a stirred mixture of 0.37 mol of lithium aluminum hydride in ether over 1 hr, after which the solution was allowed to come to room temperature. After 5 hr of stirring at room temperature, the solution was neutralized with 1 *M* $H_2SO_4$, and the organic layer extracted several times with ether. The combined ether extracts were dried over anhydrous sodium carbonate. The ether was evaporated, leaving a crude yield of 15.6 g of cyclohexanol-2,2,6,6-$d_4$. The latter was treated with a slight excess of *p*-toluene sulfonyl chloride in pyridine to yield 25.8 g of crude tosylate. The tosylate was reacted with potassium *t*-butoxide in dimethyl sulfoxide at 55–60° for 10 hr, after which the mixture was quenched in water and extracted with pentane. Most of the pentane was removed from the dried organic layer by distillation and the residue was purified by preparative glpc. The total yield of purified cyclohexene-1,3,3-$d_3$ (99.9% pure by glpc analysis) was 4.7 g (36%). Nmr analysis showed 96% isotopic purity of product assuming an aliphatic to olefinic peak area ratio of 6:1. The olefinic proton resonance at 5.57 ppm downfield from TMS was a sharp triplet (1:2:1) of 2.0-Hz spacing (Figure 3A).

**Stereochemical Studies.** A typical stereochemistry determination consisted of weighing the appropriate amount of cyclohexene-1,3,3-$d_3$ in a volumetric flask, adding the appropriate volume of hydrochloric acid of predetermined concentration, and diluting to the mark. The volumetric flasks were then stoppered and placed in a 25° constant temperature bath. Runs at 80° were made in sealed ampoules. The work-up consisted of quenching the contents of the reaction vessels in 10% sodium chloride and extracting several times with pentane or dichloromethane. The solvent was then removed by flash distillation and the residue purified by preparative glpc. Purified cyclohexyl acetate and chloride (20–100 mg) were collected in each run. Nmr spectra were measured in microtubes (purchased from NMR Specialties, Inc.), utilizing sideband calibration and deuterium double resonance. The chemical shifts (TMS internal standard) are 3.94 and 4.67 ppm for cyclohexyl chloride and acetate, respectively (both neat). The resonance at 4.67 ppm consists of a sharp doublet of 3.2-Hz spacing in all cases. The resonance at 3.94 ppm consists of two doublets with spacing of 3.5 Hz and 8.9 Hz. The relative intensity of the latter two doublets is dependent upon the reaction conditions under which the chloride product is formed. Cyclohexene-1,3,3-$d_3$ was recovered from one run at 80° in the same way as were cyclohexyl acetate and chloride; after 60% reaction the recovered cyclohexene-1,3,3-$d_3$ exhibited nmr spectral properties nearly identical with those of authentic starting material. The resonance at 5.57 ppm remained a sharp triplet (1:2:1) of 2.0-Hz spacing (Figure 3A).

**Acknowledgment.** We are grateful to the National Science Foundation for support of this research and for a grant (GP-2137) assisting the purchase of the nmr equipment used in these studies.

(19) Y. Pocker and K. D. Stevens, *J. Amer. Chem. Soc.*, **91**, 4205 (1969).

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