in Table I). A solution of the ketone **3** (2.56 g or 12.8 mmol) in 10 ml of HMP was added, dropwise and with stirring over 1.5 hr, to a cold (0°) mixture containing 2.0 g (87 mg-atom) of Na (partially dissolved), 30 ml of HMP, and 3.7 ml (2.9 g or 39 mmol) of *t*-BuOH. The resulting blue mixture containing some undissolved Na was stirred for 10 min and then methanol was added to destroy the excess Na and the resulting mixture was partitioned between pentane and H_2O. After an acetone solution of the crude neutral product had been oxidized with aqueous H_2CrO_4, distillation in a short-path still (1 mm and 140–150°) separated 2.32 g (91%) of a mixture of ketones containing (glpc) 62% of the *trans*-isomer **26** and 38% of the *cis*-isomer **25**.

Reduction of the Octalone 7 with Li and NH_3. After a solution of 1.063 g (5.16 mmol) of the ketone **7**, 1.35 ml (15 mmol) of *t*-BuOH, and 111 mg (16 mg-atom) of Li in 100 ml of liquid NH_3 and 20 ml of THF had been stirred under reflux for 1 hr, the excess Li was consumed by addition of 1.5 ml of H_2O and the NH_3 was allowed to evaporate. After the residue had been partitioned between aqueous NaCl and Et_2O, the organic layer was dried and concentrated to leave 1.031 g of yellow crystals (mp 54–65°). After the usual oxidation (H_2CrO_4 in acetone), the crude neutral product (969 mg, mp 57–68°) was distilled in a short-path still (90–100° and 0.05 mm) to separate 832 mg (77.5%) of pale yellow solid, mp 56–69°, which exhibited (glpc, silicone XE-60) one major peak (>96%) corresponding to the ketone **14**. The crude ketonic product (1.500 g or 7.19 mmol) from a comparable $Li-NH_3-THF$ reduction was treated with 2.02 g (34.3 mmol) of 85% H_2NNH_2 and 1.10 g (27.5 mmol) of NaOH in 20 ml of diethylene glycol as previously described. The crude product was collected from short-path distillation (90–100° and 0.05 mm) as 1.120 g (80%) of colorless liquid, $n^{27}D$ 1.4730, which contained (glpc, silicone XE-60) one major component (*ca.* 95%). A collected (glpc) sample of this major component was identified with the *trans*-decalin **46** by comparison of glpc retention times and ir and mass spectra.

Hydrochlorination of Cyclohexene in Acetic Acid. Kinetic and Product Studies[1]

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

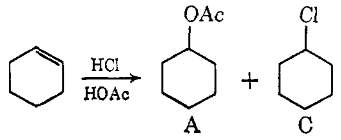
Abstract: The reaction of cyclohexene with HCl in acetic acid yields cyclohexyl chloride (C) and cyclohexyl acetate (A) under conditions of kinetic control. The reaction rate and product composition have been studied as a function of the concentration of cyclohexene, HCl, water, and tetramethylammonium chloride (TMAC). The effect of temperature as well as the deuterium isotope effect ($k_H/k_D = 1.3$) in DCl–DOAc have been determined. The ratio of C to A was found (1) to be low (∼3.0) at low [HCl] and in the absence of water or TMAC, (2) to increase significantly with the HCl concentration, with the water concentration, and with the TMAC concentration, and (3) to vary significantly with the temperature. These observations differentiate the reaction of cyclohexene from the reactions of styrene and *t*-butylethylene studied previously under similar conditions and indicate that the reaction of cyclohexene, unlike styrene and *t*-butylethylene, does not occur exclusively *via* a carbonium ion mechanism. Analysis of the rate and product data shows that there are two terms in the rate law, one involving acid and olefin and another involving acid, olefin, and dissociated chloride ion. The latter term corresponds to a termolecular mechanism leading to the formation of cyclohexyl chloride. The effect of water on the rate and product distribution is associated with its effect upon the ionization and dissociation of HCl.

This is the second in a series of studies undertaken to determine the mechanism involved in the *anti* addition of acids to olefins. In the first paper,[3] it was shown that styrene and *t*-butylethylene react with HCl in acetic acid *via* a mechanism involving rate-limiting formation of a carbonium chloride ion pair intermediate. Rapid collapse with the counterion, rapid collapse with solvent, or rapid rearrangement and collapse of this intermediate lead to the observed products. Recent studies by Pocker and coworkers[4] on HCl addition to olefins in nitromethane as solvent are in general accord with a carbonium ion mechanism. This type of mechanism is consistent with the nonstereospecific or preferential *syn* addition of acids to olefins but provides no rationalization for stereospecific *anti* addition.

In this paper we report rate and product studies for the hydrochlorination of cyclohexene in acetic acid and show that the reaction of cyclohexene differs from that of *t*-butylethylene and of styrene in several important respects. In the following paper we examine the stereochemistry of addition to cyclohexene-1,3,3-d_3 and show that cyclohexene reacts almost entirely by a different mechanism from that involved for *t*-butylethylene and styrene.

Results

General Procedure. The reaction of cyclohexene with HCl in acetic acid occurs slowly at 25° to yield cyclohexyl acetate (A) and cyclohexyl chloride (C). The reaction kinetics were studied by the method of initial rates. After 1–5% reaction, portions of the reaction were quenched and worked up, and the composition was analyzed by glpc. The concentrations of A



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[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.

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

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

[4] Y. Pocker, K. D. Stevens, and J. J. Champoux, *ibid.*, **91**, 4199 (1969); Y. Pocker and K. D. Stevens, *ibid.*, **91**, 4205 (1969).

and C were determined by comparison of the peak area of each product with that of an internal standard. The glpc procedure was standardized with samples of known composition and peak area ratios correlated to known mole fractions; control experiments demonstrated that the method yields correct values for product concentrations. The initial rate, R, determined at time t, was calculated according to the expression

$$R = \mathrm{d[product]}/\mathrm{d}t \cong ([\mathrm{A}] + [\mathrm{C}])/t$$

It was shown that cyclohexyl chloride and cyclohexyl acetate are not interconverted under the reaction conditions, and that no significant reaction of cyclohexene with acetic acid occurs in the absence of HCl. In runs allowed to proceed to more than 60% completion, over 90% of the starting material was accounted for as products or unreacted cyclohexene.

Dependence upon Cyclohexene. The olefin concentration was varied between 0.196 and 0.587 M and the rates and product compositions determined (Table I).

Table I. Dependence of Rate and Product Composition upon Cyclohexene Concentration[a]

[Cyclohexane], M	10^8R^b/[cyclohexene], sec^{-1}	%C:%A
0.196	18	0.31 ± 0.02
0.391	19	0.32 ± 0.02
0.587	20	0.34 ± 0.02

[a] At 25° with 0.56 M HCl. [b] Average deviation ±5% based on at least three analyses.

In order to offset dielectric effects due to changing the hydrocarbon content of the medium, pentane was added to solutions containing less than 0.587 M olefin; in all cases, the hydrocarbon content was maintained at 6% by volume. Nevertheless, it is evident from Table I that R increases slightly faster than the cyclohexene concentration. This is reasonably explained by assuming that pentane and cyclohexene have slightly different effects on the reaction medium, pentane being less polar than cyclohexene. We conclude from these results that the reaction is first order in cyclohexene. It is evident that the ratio of C to A is little affected by the cyclohexene concentration.

Dependence upon Hydrogen Chloride and upon Temperature. The reaction was studied as a function of hydrogen chloride concentration and temperature. That R increases faster than the HCl concentration is evident from the results in Table II. In the concentration region in which the rate was studied (0.06–1.0 M HCl), nonlinearity in such a plot might be expected since the concentration and the activity of HCl are unlikely to be equivalent over this range. It is preferable to compare the rate with some function of the activity of HCl rather than with the stoichiometric concentration of HCl. Satchell has measured the extent of protonation of aniline bases in solutions of HCl in acetic acid at 18°.[5] From his results an "effective acidity function," log A, similar to Hammett's $-H_0$ function, can be defined as described previously.[6]

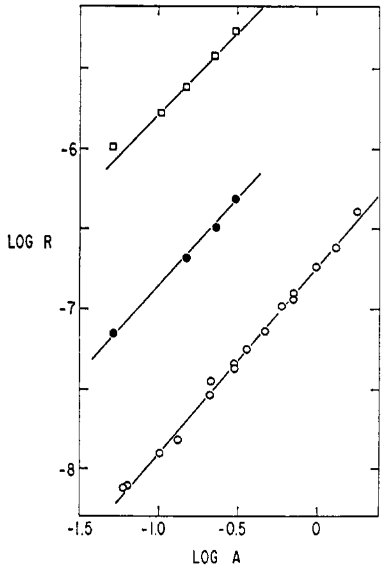

Figure 1. Plot of log R vs. log A for the hydrochlorination of cyclohexene (0.587 M) in acetic acid at 25.0° (○), 50.0° (●), and 80.0° (□).

Plots of log R vs. log A (Figure 1) are reasonably linear with slopes of 1.2, 1.1, and 1.0 at 25, 50, and 80°, respectively.

Table II. Dependence of Rate and Product Composition upon Acidity[a]

[HCl], M	10^9R,[b] M sec^{-1}	%C:%A	Log A[c]
		25.0°	
0.062	7.8	0.28 ± 0.03	−1.21
0.064	8.0	0.28 ± 0.03	−1.19
0.104	12.7	0.29 ± 0.03	−0.99
0.134	15.5	0.20 ± 0.02	−0.88
0.208	28.7 ± 1.7	0.32 ± 0.04	−0.68
0.213	35	0.22 ± 0.02	−0.67
0.294	44	0.29 ± 0.03	−0.50
0.295	43	0.23 ± 0.02	−0.50
0.336	56	0.30 ± 0.03	−0.43
0.410	73	0.30 ± 0.03	−0.32
0.51	104	0.32 ± 0.04	−0.20
0.56	117	0.34 ± 0.03	−0.14
0.57	126	0.34 ± 0.03	−0.14
0.59	137	0.36 ± 0.04	−0.11
0.70	184	0.37 ± 0.03	0.00
0.83	248	0.34 ± 0.04	0.12
1.03	405	0.44 ± 0.04	0.27
		50.0°	
0.053	70	0.32 ± 0.05	−1.28
0.147	210	0.36 ± 0.03	−0.83
0.218	325	0.38 ± 0.04	−0.64
0.294	490 ± 37	0.43 ± 0.10	−0.50
		80.0°	
0.053	1020 ± 130	0.43 ± 0.04	−1.28
0.104	1650[d]	0.42[d]	−0.99
0.147	2430	0.48 ± 0.07	−0.83
0.218	3880	0.45 ± 0.03	−0.64
0.294	5429	0.47 ± 0.05	−0.50

[a] [Cyclohexane] = 0.587 M. [b] Average deviation ±5% based on at least three analyses except as noted. [c] Values calculated from the data at 18° in D. P. N. Satchell, *J. Chem. Soc.*, 1916 (1958). [d] Single analysis.

The partitioning between products depends upon the HCl concentration and the temperature. At 25°, the ratio of cyclohexyl chloride to cyclohexyl acetate is

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(5) See Table II, footnote c.

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

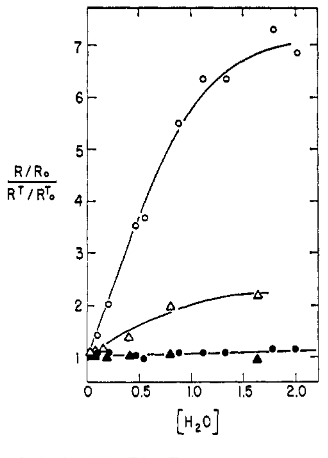


Figure 2. Plot of $(R/R_0)/(R^T/R_0^T)$ *vs.* $[H_2O]$ at 25.0° for the formation of C (△, 0.064 *M* HCl; ○, 0.22 *M* HCl) and A (▲, 0.064 *M* HCl; ●, 0.22 *M* HCl).

found to slightly but significantly increase with the acid concentration (Table II). At a given acid concentration this ratio clearly increases with temperature, roughly doubling between 25 and 80°.

The Effect of Water. Water has a marked effect upon the reaction rate as well as upon the product distribution and the magnitude of these effects varies with the hydrogen chloride concentration (Table III).

Table III. Dependence of Rate and Product Composition upon Water Concentration[a]

$[H_2O]$, *M*	10^9R,[b] *M* sec^{-1}	%C:%A
	0.22 *M* HCl	
<0.01	35	0.22 ± 0.02
0.110	44	0.30 ± 0.03
0.225	52	0.42 ± 0.04
0.463	68	0.76 ± 0.06
0.56	68	0.86 ± 0.10
0.89	88	1.13 ± 0.09
1.12	85	1.33 ± 0.12
1.34	77	1.30 ± 0.13
1.79	62	1.33 ± 0.11
2.02	50	1.32 ± 0.12
	0.064 *M* HCl	
<0.01	8.0	0.28 ± 0.03
0.052	8.3	0.29 ± 0.04
0.104	8.5	0.30 ± 0.03
0.207	9.8	0.31 ± 0.05
0.415	11.7	0.38 ± 0.03
0.83	13.2	0.58 ± 0.04
1.66	8.5	0.70 ± 0.05

[a] At 25° with 0.587 *M* cyclohexene. [b] Average deviation ±5% based on at least three analyses.

This behavior is in contrast to that found[3] for *t*-butylethylene where water was observed to have a significant effect upon the reaction rate but little effect upon the product distribution. The significance of the results obtained with cyclohexene becomes clear when they are compared directly with those previously reported for *t*-butylethylene. To do this we define R^C = d[C]/d*t* and R^A = d[A]/d*t* for addition to cyclohexene and R^T = −d[*t*-butylethylene]/d*t* for addition to *t*-butylethylene; a naught subscript is used to refer to the rate without added water. Figure 2 shows plots of $(R/R_0)/(R^T/R_0^T)$ for cyclohexyl chloride and cyclohexyl acetate formation as a function of the water concentration. The effect of water upon the rate of cyclohexyl acetate formation is essentially identical with the effect upon the reaction of *t*-butylethylene and is not dependent upon the HCl concentration. The effect of water on the rate of formation of cyclohexyl chloride, however, is more pronounced and is strongly dependent upon the acid concentration.

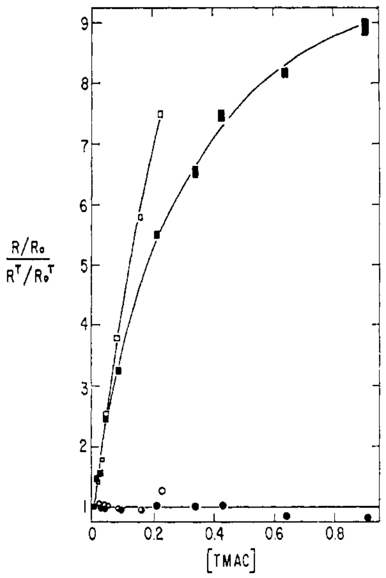


Figure 3. Plot of $(R/R_0)/(R^T/R_0^T)$ *vs.* [TMAC] at 25.0° for the formation of C (□, 0.062 *M* HCl; ■, 0.57 *M* HCl) and of A (○, 0.062 *M* HCl; ●, 0.57 *M* HCl).

The Effect of Tetramethylammonium Chloride (TMAC). TMAC has a marked effect upon both the reaction rate and the product ratio (Table IV). This effect of chloride salt, like that of water, contrasts with the behavior found[3] with *t*-butylethylene and styrene where TMAC accelerates the rates of reaction but does not appreciably change the product ratios. The effects upon the cyclohexene and *t*-butylethylene reactions can be compared, as above, in terms of the ratios $R:R_0$ where the naught in this case refers to the rate in the absence of TMAC. Figure 3 shows that the rate of cyclohexyl acetate formation is affected by TMAC in the same fashion as is the reaction of *t*-butylethylene, while the rate of cyclohexyl chloride formation is markedly accelerated. Note, however, that the accelerating effect upon cyclohexyl chloride formation is definitely not linear in the TMAC concentration.

Table IV also includes results obtained as a function of HCl concentration at a constant and fairly high (0.43 *M*) TMAC concentration. It is seen that the rate increases with HCl concentration in a fashion similar to that found without added TMAC. A plot (not shown) *vs.* the values of log *A* for solutions not containing TMAC has a slope of 1.1 as compared with the value 1.2 found without added TMAC. No detectable reaction occurs in the presence of TMAC without added HCl.

The Deuterium Isotope Effect. The deuterium isotope effect on the reaction was studied using DCl–DOAc solutions. Deuterated acetic acid containing 0.5 *M* DCl was prepared by allowing D_2O to react with the appropriate amount of acetyl chloride and acetic anhydride. Control experiments demonstrated that exchange of acetic acid methyl protons with hydroxylic

Table IV. Dependence of Rate and Product Distribution upon Tetramethylammonium Chloride (TMAC) Concentration[a]

[HCl], M	[TMAC], M	10^9R,[b,c] M sec^{-1}	% C:% A[b,d]
0.57	0	126	0.34
	0.0086	151	0.47
	0.0172	162	0.59
	0.043	219	0.87
0.56	0.086	305	1.15
0.58	0.212	520[c]	1.86
0.56	0.344	640	2.26
0.58	0.424	730	2.48
0.57	0.645	780[e]	3.33[e]
	0.902	780[e]	3.50[e]
0.062	0	7.8	0.28
	0.0101	9.1	0.37
	0.0202	10.6	0.51
	0.0404	13.4	0.74
	0.081	18.4	1.07[c]
	0.162	29.0	1.57[c]
	0.226	37.9	1.96[c]
0	0.43	<0.1[e]	
0.156	0.43	128	2.4
0.290	0.424	290	2.8
0.405	0.43	420	2.4

[a] At 25° with 0.587 M cyclohexene. [b] Based upon three analyses except as noted. [c] Average deviation ±5%. [d] Average deviation ±10%. [e] Based upon two analyses.

protons does not occur at a significant rate. A solution of 0.5 M HCl in acetic acid was prepared in a similar fashion from acetyl chloride, acetic anhydride, and water. Table V gives the results of rate and product studies obtained with these solutions. From these data a kinetic isotope effect, k_H/k_D, of 1.3 ± 0.1 is obtained for reaction without added TMAC as well as for reaction in the presence of 0.43 M TMAC. The solutions used contain significant amounts of water and, since water affects the reaction rate, the observed rates should be corrected for the effect of water. However, the water content of the DCl and HCl solutions is relatively low and very nearly the same so that this correction does not lead to a significant change in the calculated isotope effect.

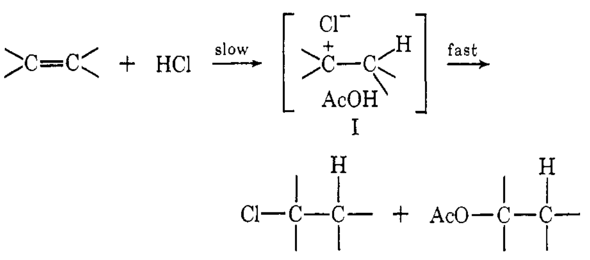
Table V. Solvent Kinetic Isotope Effect[a]

Acid	Water,[b] M	[TMAC], M	10^9R,[c] M sec^{-1}	% C:% A[d]
HCl	0.031	0	126 ± 9	0.34
HCl	0.031	0.43	596 ± 37	2.1
DCl[e]	0.042	0	98 ± 2	0.30
DCl[e]	0.042	0.43	464 ± 13	2.0

[a] At 25°, 0.5 M HCl, and 0.587 M cyclohexene. [b] Determined by Karl Fisher method. [c] Average deviations of three analyses are listed. [d] Average deviation ±5% in three analyses. [e] In acetic acid-O-*d* of 98.8% isotopic purity.

Discussion

Some of the results reported here for the hydrochlorination of cyclohexene are similar to those reported earlier for the hydrochlorination of *t*-butylethylene and styrene.[3] The reaction is first order in olefin and the reaction rate exhibits an acidity dependence similar to that found for styrene. The isotope effect upon the reaction rate (k_H/k_D) is found to be 1.3 for cyclohexene compared with 1.2 for *t*-butylethylene and 1.4 for styrene. From these observations alone we might assume that the addition to cyclohexene occurs *via* the same type of carbonium ion mechanism demonstrated earlier for addition to *t*-butylethylene and styrene (eq 1). The fact that, under comparable conditions, cyclohexene reacts at five times the rate of *t*-butylethylene but at only $^1/_{60}$ the rate of styrene would seem in accord with this assumption.



(1)

There are, however, a number of features of the present results which are not entirely consistent with this mechanism. First, the observed ratio of hydrogen chloride addition to acetic acid addition is substantially less for cyclohexene (~0.3) than for *t*-butylethylene (~2) or styrene (~13). We would expect the ion pair I to collapse preferentially to form chloride or, if the cation is especially reactive, to form roughly equal amounts of acetate and chloride. The preferential formation of acetate in the addition to cyclohexene is difficult to reconcile in terms of an intermediate ion pair resembling I.

Secondly, the ratio of chloride to acetate formed in the reaction of cyclohexene exhibits a small but definite dependence upon the HCl concentration and a marked dependence upon the TMAC concentration. This might be attributed to capture of the intermediate ion pair by external chloride ion. However, no such effect was observed in the hydrochlorination of styrene and, if external chloride ion is unable to capture a resonance-stabilized benzylic cation of the type formed from styrene, it seems unreasonable to suppose that under identical conditions it could capture the less stable secondary cation formed from cyclohexene.

Thirdly, and finally, the observed ratio of cyclohexyl chloride to cyclohexyl acetate exhibits a significant temperature dependence which is larger than that of the corresponding ratios observed with *t*-butylethylene or styrene. It is difficult to see why partitioning of the ion pair formed from cyclohexene should involve substantially different enthalpy effects from the comparable processes involving styrene or *t*-butylethylene.

We conclude that the mechanism of eq 1 cannot accommodate the results obtained with cyclohexene and that some other mechanism must be involved. The most significant difference between the present results and those obtained with *t*-butylethylene and styrene is the marked effect of TMAC upon the reaction rate and the product ratio. The specific acceleration of the formation of cyclohexyl chloride by TMAC (Figure 3) indicates that this process involves catalysis by chloride ion. Such catalysis might involve either undissociated HCl and TMAC, or dissociated chloride ion. In the first case, the ratio of cyclohexyl chloride to cyclohexyl acetate (C/A) should

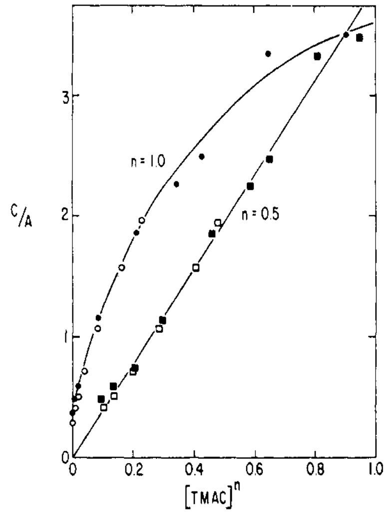


Figure 4. Plot of C/A *vs.* [TMAC]^n for the hydrochlorination of cyclohexene (0.587 *M*) at 25.0° (○□, 0.062 *M* HCl; ●, ■, 0.57 *M* HCl).

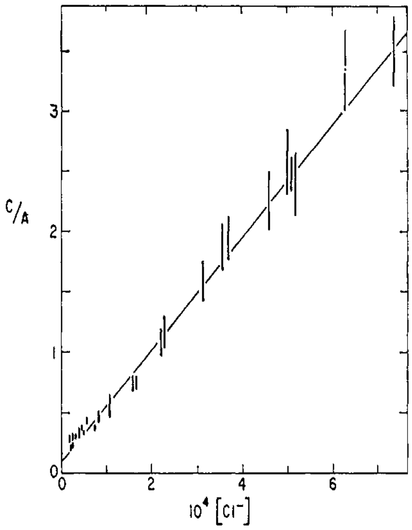


Figure 5. Plot of C/A *vs.* calculated [Cl⁻] for the hydrochlorination of cyclohexene at 25.0°.

increase linearly with the HCl concentration in the absence of TMAC and linearly with the TMAC concentration at constant acid concentration. Unfortunately, the precision of the data is inadequate to definitively test the dependence of the small variation of C/A with [HCl]. The dependence of C:A upon [TMAC] is clearly not linear, as is evident in Figure 4. A good linear dependence is observed, however, in the plot of C/A *vs.* [TMAC]$^{1/2}$. This is expected at high [TMAC] if dissociated chloride ion is the effective nucleophile since the concentration of dissociated chloride ion is given by

$$[\mathrm{Cl}^-] = (K_{\mathrm{HCl}}[\mathrm{HCl}] + K_{\mathrm{TMAC}}[\mathrm{TMAC}])^{1/2} \qquad (2)$$

where K_{HCl} and K_{TMAC} are the dissociation constants of HCl and TMAC, respectively.

The involvement of dissociated chloride ion in the reaction suggests that a rate law of the form

$$R = K_2A^m[\mathrm{C_6H_{10}}] + K_3A^n[\mathrm{C_6H_{12}}][\mathrm{Cl}^-] \qquad (3)$$

should be followed with the third-order term associated exclusively with cyclohexyl chloride formation. Combining eq 2 and 3, we obtain

$$R = k_2A^m[\mathrm{C_6H_{10}}] + k_3A^n[\mathrm{C_6H_{10}}](K_{\mathrm{HCl}}[\mathrm{HCl}] + K_{\mathrm{TMAC}}[\mathrm{TMAC}])^{1/2} \qquad (4)$$

To test eq 4 it is necessary to know both K_{HCl} and K_{TMAC}. A value of 2.8 × 10^{-9} *M* has been determined[7] for K_{HCl} but K_{TMAC} has not been measured.

A value for K_{TMAC} can be indirectly estimated from the present results. If we assume that $m = n$ in eq 4 and that salt effects upon k_2 and k_3 are the same, then the ratio C/A is given by

$$\mathrm{C{:}A} = \frac{f}{1-f} + \frac{k_3(K_{\mathrm{HCl}}[\mathrm{HCl}] + K_{\mathrm{TMAC}}[\mathrm{TMAC}])^{1/2}}{k_2(1-f)} \qquad (5)$$

where f is the fraction of C formed in the second-order process. A plot of C:A *vs.* [HCl]$^{1/2}$ in the absence of TMAC should have slope $k_3(K_{\mathrm{HCl}})^{1/2}/k_2(1-f)$ while the slope in Figure 4 gives $k_3(K_{\mathrm{TMAC}})^{1/2}/k_2(1-f)$ The square of the ratio of the latter slope to the former thus gives $K_{\mathrm{TMAC}}/K_{\mathrm{HCl}}$. If a square-root dependence is assumed for the data of Table II at 25.0°, then a slope of 0.3 is estimated. The slope in Figure 4 is 3.9 so that $K_{\mathrm{TMAC}}/K_{\mathrm{HCl}} = 170$ and $K_{\mathrm{TMAC}} = 5 \times 10^{-7}$ *M*. A value of $K_{\mathrm{TMAC}} = 7 \times 10^{-7}$ *M* has been calculated from the data obtained in a study of the hydrochlorination of 1,2-dimethylcyclohexene in a fashion analogous to that given above.[8] Using an average value of 6 × 10^{-7} for K_{TMAC} and the known value of K_{HCl}, the concentration of dissociated chloride ion can be calculated for all of the points of Tables II and IV. A plot of C/A *vs.* [Cl⁻] is shown in Figure 5. The plot is linear within experimental error indicating that eq 3 satisfactorily accommodates the data. The slope of this plot gives $k_3/k_2(1-f) = 4.6 \times 10^3\ M^{-1}$ while the intercept gives $f/(1-f) = 0.1$; thus, $f = 0.09$ and $k_3/k_2 = 4.2 \times 10^3\ M^{-1}$.

One additional problem complicates the test of the rate expression (eq 3); TMAC has a salt effect upon the rate constants and may also affect the acidity function. If we assume that the effect of TMAC upon the rate of reaction of *t*-butylethylene (which is not catalyzed by chloride ion), is the same as that upon cyclohexene, then eq 3 can be corrected for the salt effect as indicated in eq 6 where $R^{\mathrm{T}}/R_0^{\mathrm{T}}$ is the ratio of the rate in

$$R = \frac{R^{\mathrm{T}}}{R_0^{\mathrm{T}}}(k_2A^m[\mathrm{C_6H_{10}}] + k_3A^n[\mathrm{C_6H_{10}}][\mathrm{Cl}^-]) \qquad (6)$$

the presence of TMAC to that in the absence of TMAC for the hydrochlorination of *t*-butylethylene. We find that eq 6 with $m = n = 1.1$, $k_2 = 2.4 \times 10^{-7}\ M^{-1}\ \mathrm{sec}^{-1}$, and $k_3 = 1.0 \times 10^{-3}\ M^{-2}\ \mathrm{sec}^{-1}$, fits the rate data at 25° of Tables I, II, and IV with an average deviation of ±7%. In view of the assumptions inherent in eq 6, the agreement appears satisfactory.

Although the salt effects upon the various reactions should be similar, it is unlikely that they are identical. Note that the ratio $(R/R_0)/(R^{\mathrm{T}}/R_0^{\mathrm{T}})$ for formation of A does drop below unity at high TMAC concentration

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

(8) R. C. Fahey and C. Allen McPherson, unpublished results.

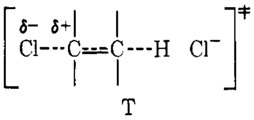
(Figure 3). The observed rates for these points at 0.645 and 0.902 M TMAC fall below those given by eq 6 by 16 and 26%, respectively. Thus, while the rate law of eq 6 does accommodate the rather complex behavior observed for the hydrochlorination of cyclohexene, k_2 and k_3 cannot be determined with high precision and the values reported above should be viewed as estimates.

The effect of water upon the rate and product composition is consistent with the foregoing analysis. Hydrogen chloride is only partially ionized in acetic acid and is very little dissociated.[7] Water is more basic than acetic acid and should, therefore, promote the ionization of HCl (eq 7) and thus increase the concentration of

$$\mathrm{HCl} + n\mathrm{H_2O} \rightleftharpoons [(\mathrm{H_2O})_n\mathrm{H^+Cl^-}] \rightleftharpoons (\mathrm{H_2O})_n\mathrm{H^+} + \mathrm{Cl^-} \quad (7)$$

dissociated chloride ion. We see in Table III that the ratio C:A observed at >1.0 M water concentration nearly doubles with an almost 4-fold increase in acid concentration, suggesting that this ratio increases with the $[\mathrm{HCl}]^{1/2}$ rather than [HCl]. This indicates that in ~1 M H_2O the hydronium chloride ion pair (eq 7) is largely undissociated. The ratio of C to A at >1 M water is significantly higher for 0.22 M HCl (Table III) than at 0.22 M TMAC (Figure 4) suggesting either that the dissociation constant of the hydronium chloride ion pair is larger than that of TMAC or, more likely, that water increases the dielectric constant of the solvent and thus the dissociation constants of all salts.

Mechanistically the third-order kinetic term in eq 3 corresponds to a termolecular addition reaction proceeding *via* a transition state resembling T and leading to cyclohexyl chloride. One might be tempted to



T

associate the second-order term in eq 3 with a mechanism of the type given in eq 1 but the results show that the ratio of C to A associated with this rate term is only 0.1 and, as explained above, this low ratio is inconsistent with such a mechanism. That the second-order kinetic term actually involves at least two different competing reactions will be shown in the following paper which is concerned with the stereochemistry of addition to cyclohexene. A more detailed discussion of the mechanism is given in that paper.

Experimental Section

An Aerograph Model 202 gas chromatograph, equipped with thermoconductivity detectors and a Sargent Model SR recorder, fitted with a Disc Integrator, was employed for glpc analysis. Analytical measurements were made on a mixed column consisting of 20 ft × 1/8 in. 30% diethyleneglycol succinate (DEGS) on Chromosorb P regular and 10 ft × 1/8 in. 20% DEGS on the same solid phase (Column I). Nmr spectra were measured on a Varian Associates HR-60 spectrometer.

Materials. Chromatoquality cyclohexene, anhydrous hydrogen chloride, cyclohexyl chloride, cyclohexanol, chromatoquality cyclohexane, chromatoquality pentane, chromatoquality dichloromethane, tetramethylammonium chloride (TMAC), acetic anhydride, *p*-cymene, and 99.7% acetic anhydride were all purchased from Matheson Coleman and Bell. Other sources were: cyclohexyl acetate (Eastman); reagent grade glacial acetic acid (B and A); zone refined durene, 99.99% (Columbia Organic Chemicals); deuterium oxide, 99.8% (Diaprep); acetyl chloride (J. T. Baker).

Kinetic and Product Studies. The water content of the stock acid solutions was determined by the Karl Fisher titration method using a Labindustries aquametry potentiometer. To obtain anhydrous acetic acid, a 0.01 M excess of acetic anhydride was added to the stock reagent, and either a trace of mineral acid was added (0.005 M hydrogen chloride), or the solution was refluxed to facilitate hydrolysis. In every case, the final stock solutions contained less than 0.01 M water. Solutions of hydrogen chloride were prepared by bubbling anhydrous hydrogen chloride into dry acetic acid. Hydrogen chloride concentrations were determined by addition of a measured aliquot of the solution to an excess of standard lithium acetate solution in acetic acid and subsequent potentiometric titration with standard *p*-toluene sulfonic acid in acetic acid.

Reaction solutions were prepared by adding known amounts of cyclohexene, internal standard, and hydrogen chloride in acetic acid to clean, dry 50-ml volumetric flasks. These were immediately diluted to the mark, mixed by shaking, and placed in a constant temperature bath maintained at 25.0 ± 0.01°. For the studies at 50 and 80°, the solutions were prepared at 25°, and aliquots sealed in clean dry ampoules. The ampoules were placed in the bath and one sample was immediately quenched by immersion of the ampoule in ice water. The latter was then worked up and analyzed for the initial concentrations of product, which proved to be negligible in all cases. The work-up consisted of quenching 5 ml of reaction solution by shaking with 50 ml of 10% sodium chloride and 10 ml of pentane or dichloromethane in a 250-ml separatory funnel. The organic layer was separated and the aqueous layer was extracted twice more with 5-ml portions of organic solvent. The combined organic layers were washed with 5 ml of saturated sodium bicarbonate and dried over anhydrous sodium carbonate. The organic solvent was then evaporated, leaving about 1 ml of solution whose composition was determined by glpc. In most cases, three aliquots of each reaction mixture were taken at intervals, worked up, and analyzed. The extracts were analyzed on column I (column temperature, 140°; He flow, 16 ml/min). Retention times, measured from the air peak, were: cyclohexyl chloride, 5 min; cyclohexyl acetate, 13 min; durene, 17 min. The glpc procedure was calibrated with known mixtures of products and internal standard.

In control experiments it was shown that no fractionation occurs during the work-up, that cyclohexyl chloride and cyclohexyl acetate are stable to the reaction conditions, and that no significant reaction between cyclohexene and acetic acid occurs in the absence of HCl. In runs allowed to proceed to high conversion >90% of the starting cyclohexene was accounted for as unreacted cyclohexene, cyclohexyl chloride, and cyclohexyl acetate. In runs containing high water concentrations, cyclohexanol might reasonably have been a side product but none was detected and it was shown that cyclohexanol is stable to the reaction conditions.

Isotope Effects. A solution of acetic acid-O-*d* was prepared by slowly adding 1.35 mol of 99.8% D_2O to a stirred solution of 1.26 mol of acetic anhydride containing 0.087 mol of acetyl chloride. The final solution was analyzed for proton content by integration of the OH nmr resonance and the methyl group resonance. Analysis by glpc demonstrated that the resulting solution contained no detectable unreacted anhydride; nmr analysis showed that the acetic acid-O-*d* prepared in this way contained 1.2% hydroxylic protons. Titration revealed that the final solution was 0.53 M in DCl. The water content of this solution was 0.042 M by Karl Fisher titration. When TMAC was added to a DCl–acetic acid-O-*d* solution, no exchange of deuterium with protons was observed after 5 days' contact time.

An identical procedure was followed in the preparation of an acetic acid–HCl solution, so as to assure identical conditions for rate comparisons. Four runs were made, all in 25-ml volumetric flasks. TMAC (1.25 g) was placed in two of the flasks. To one of these, 0.53 M DCl in DOAc was added, and to the other, 0.53 M HCl in HOAc was added. When the TMAC dissolved, all four flasks were diluted to the mark with the appropriate acid containing solvent, and 1.5 ml of solution was removed from each flask. Finally, 1.5 ml of cyclohexene was added to each to initiate the reaction; the flasks were then shaken well and placed in the 25° constant temperature bath. The work-up was the same as in all other runs, except that internal standard was added volumetrically to a separatory funnel which contained a known aliquot of the reaction mixture.

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