

constants

$$k = \frac{f(\text{sulfide area})}{tD_0(\text{disulfide area})}$$

where k = second-order rate constant ($1 M^{-1} \text{sec}^{-1}$), t = time (sec), f = vpc calibration factor, and D_0 = initial disulfide concentration. All calculations were performed on an IBM 360/50 computer using a least-squares program. Rate constants were calculated for the initial portion (10–50%) of the reaction for which second-order kinetics were observed to be valid.

For those experiments in which nonstoichiometric amounts of reactants were employed, sulfide and/or disulfide concentrations were calculated. This equation is valid if the conversion of phosphine to phosphine sulfide by the sulfur quench is quantitative.

$$[\text{sulfide}] = \frac{f(\text{sulfide area})[\text{phosphine}]}{(\text{phosphine sulfide area})}$$

This was demonstrated in that 0.247 g (1.00 mmol) of tris(diethylamino)phosphine (3) reacted with excess sulfur to afford 0.275 g (0.99 mmol, 99%) of tris(diethylamino)phosphine sulfide (4). These concentrations of phosphine and phosphine sulfide were measured by vpc against diphenyl sulfide as a primary standard. From the disulfide concentration thus calculated, the second-order rate constant (k) was calculated by the method of least squares.

Method B. Ultraviolet Spectrophotometry. A Coleman 124 spectrophotometer equipped with a Coleman 165 recorder and a Neslab constant-temperature regulator ($\pm 0.2^\circ$) was employed at constant wavelength to monitor the disappearance of disulfide with time. The solutions of disulfide and phosphine were equilibrated for 15–30 min at a given temperature before each run.

The requisite volumes of disulfide and phosphine stock solutions were transferred to the uv cell and allowed to equilibrate further in the cell holder for 3–5 min prior to measurement of absorbance as a function of time. Pseudo-first-order conditions were employed with an excess (at least tenfold stoichiometrically) of phosphine. All runs were performed in duplicate. The value of the pseudo-first-order rate constants (k') were calculated from plots of $\ln((A_0 - A_\infty)/(A_t - A_\infty))$ vs. time by the least-squares method. All calculations were performed by an IBM 360/50 computer. The rate constants were calculated from the initial portion of the reaction for which first-order kinetics were seen to be valid; all reactions were allowed to continue for at least six half-lives before A_∞ was recorded.

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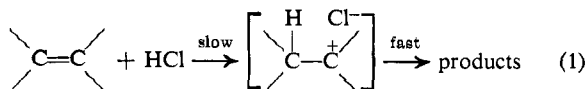
Kinetics and Stereochemistry of the Hydrochlorination of 1,2-Dimethylcyclohexene^{1a}

Robert C. Fahey*^{1b} and C. Allen McPherson^{1c}

Contribution from the Department of Chemistry, University of California, San Diego, La Jolla, California 92037. Received August 28, 1970

Abstract: Reaction of 1,2-dimethylcyclohexene with HCl in HOAc leads to the formation of *trans*-1-chloro- (TC), *cis*-1-chloro- (CC), *trans*-1-acetoxy- (TA), and *cis*-1-acetoxy-1,2-dimethylcyclohexane (CA), as well as 1,6-dimethylcyclohexene. While TC and CC are relatively stable to the reaction conditions, TA, CA, and 1,6-dimethylcyclohexene are not stable and react to yield mixtures of the other compounds. The kinetically controlled product distributions and the initial rate of addition were measured at less than 10% conversion. It was found that the fraction of TC formed increases markedly with HCl concentration and with the added chloride salt concentration, the dependence indicating that dissociated chloride ion intervenes in the formation of TC. The effect of chloride salt on the rate of reaction establishes that this intervention occurs in the rate-limiting step. These results are interpreted in terms of a carbonium chloride ion pair reaction (Ade2 mechanism) competing with a termolecular anti addition process (Ade3 mechanism), the latter dominating in the presence of large chloride salt concentrations. The products of addition were also studied in several other solvents. Addition of HCl in methanol gives primarily TC, the fraction of TC increasing with [HCl]. In contrast, addition in acetyl chloride gives ~73% CC and the product composition varies little with [HCl]. Addition in methylene chloride also gave ~74% CC while addition in pentane yielded 92% TC under conditions of kinetic control.

In an earlier series of papers, evidence was presented supporting the view that the hydrochlorination of *tert*-butylethylene and styrene in acetic acid occurs via a carbonium chloride ion pair mechanism (eq 1)²

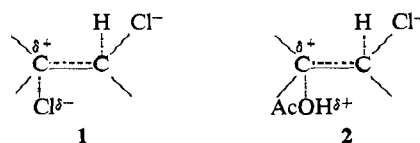


whereas the hydrochlorination of cyclohexene occurs predominantly by a termolecular (Ade3) anti addition

(1) (a) We gratefully acknowledge support of this research by the National Science Foundation and by The Research Corporation; taken in part from the Thesis of C. Allen McPherson, University of California, San Diego, Calif., 1969; (b) Alfred P. Sloan Foundation Fellow, 1966–1968; (c) National Defense Education Act Predoctoral Fellow.

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

mechanism.^{3,4} The latter process occurs via a transition state resembling 1 for formation of cyclohexyl chloride and 2 for formation of cyclohexyl acetate.



The earlier observations of anti addition of HBr to 1,2-dimethylcyclohexene by Hammond and Nevitt⁵ and of HCl to 1,2-dimethylcyclopentene by Hammond

(3) R. C. Fahey, M. W. Monahan, and C. A. McPherson, *ibid.*, **92**, 2810 (1970).

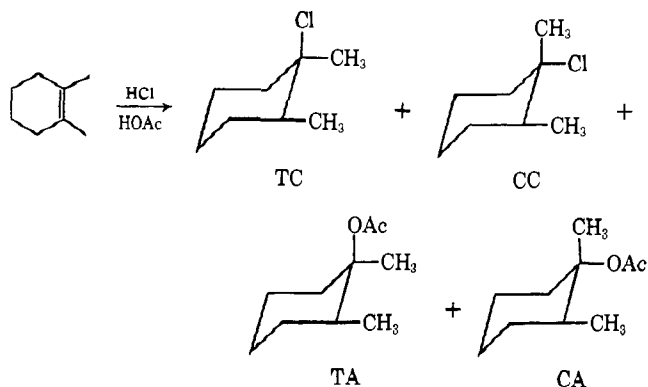
(4) R. C. Fahey and M. W. Monahan, *ibid.*, **92**, 2816 (1970).

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

and Collins⁶ also seemed consistent with a termolecular anti addition mechanism. In order to substantiate this and to obtain further information on the nature of the termolecular addition, we undertook a study of the hydrochlorination of 1,2-dimethylcyclohexene in acetic acid. This system is ideal for study in that the product stereochemistry can be determined directly and accurately by glpc analysis (a technique not available to the earlier investigators^{5,6}). We report here the results of this study.

Results

The reaction of 1,2-dimethylcyclohexene with HCl in acetic acid proceeds rapidly at 25° to yield a mixture of addition products—*trans*-1-chloro-1,2-dimethylcyclohexane (TC), *cis*-1-chloro-1,2-dimethylcyclohexane (CC), *trans*-1-acetoxy-1,2-dimethylcyclohexane (TA), and *cis*-1-acetoxy-1,2-dimethylcyclohexane (CA). Analysis



by glpc of the reaction products showed four components to be present. The two components of longer retention time were found to be identical in retention time with authentically prepared *cis*- and *trans*-1-acetoxy-1,2-dimethylcyclohexane. Analysis at a high percentage reaction showed only the two components of shorter retention time to be present. These two products, which gave a precipitate with alcoholic silver nitrate, were also obtained by passing hydrogen chloride through a solution of 1,2-dimethylcyclohexene in dichloromethane and thus must be the isomers TC and CC.

The structures of the isomeric chlorides were assigned on the basis of ir and equilibration studies. Since the *A* value for chlorine is less than that for methyl,⁷ the most stable conformation of TC is expected to be the one with chlorine in an axial position and that of CC, the one with chlorine in an equatorial position as shown above. The same consideration predicts that TC should be the more stable isomer. Reaction of a sample of the isomeric chlorides in 1.3 *M* HCl in HOAc led to an equilibrium mixture containing 75% of the chloride with shorter retention time, indicating that this isomer is TC. A mixture rich in the isomer of longer retention time has a predominant C–Cl absorption at 752 cm^{-1} , while a mixture rich in the chloride of shorter retention time exhibits a predominant absorption at 741 cm^{-1} . Since axial C–Cl bonds are found to absorb at lower frequency

(6) G. S. Hammond and C. H. Collins, *J. Amer. Chem. Soc.*, **82**, 4323 (1960).

(7) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 44.

than equatorial C–Cl bonds,⁸ this observation confirms the assignment based on the equilibration results.

Quantitative studies of the reaction were conducted using an internal standard. Aliquots of the reaction mixture were removed at intervals, quenched in pentane-water, and then extracted with pentane. The organic fraction was concentrated and the product concentration determined by glpc. Authentic mixtures of known composition were used to correct peak area ratios to mole ratios and to show that no fractionation occurs in the work-up procedure. However, studies of the product composition as a function of reaction time showed that the product composition varies markedly with the degree of conversion indicating that secondary reactions are important. Studies of the stability of the various products under the reaction conditions were undertaken to evaluate the importance of such secondary reactions.

Control experiments with authentic samples of CC and TC showed that isomerization is the only reaction occurring under the reaction conditions and that the total rate of isomerization is only 1/100th the rate of addition to 1,2-dimethylcyclohexene under identical conditions. Thus, secondary reactions of CC and TC are unimportant in the first stages of the addition reaction.

The isomeric acetates, on the other hand, react more rapidly than 1,2-dimethylcyclohexene. The initial rates for reaction of CA and TA were found to be larger than the initial rate of addition to the olefin under the same conditions by factors of 12 and 18, respectively. The products of reaction are predominately olefins but the product composition varies with the extent of reaction. The product compositions, extrapolated to zero reaction time, are given in Table I.

Table I. The Reaction of CA and TA with 0.029 *M* Hydrogen Chloride in Acetic Acid at 25°

Products	Product composition, % ^a	
	<i>cis</i> -1-Acetoxy-1,2-dimethylcyclohexane ^b	<i>trans</i> -1-Acetoxy-1,2-dimethylcyclohexane ^c
2-Methylmethylene-cyclohexane	2	
1,6-Dimethylcyclohexene	17	8
1,2-Dimethylcyclohexene	56	76
TC	11	2
CC	7.5	4
TA	6.5	
CA		10

^a Extrapolated to zero time. ^b 0.0166 *M*, 96% CA, and 4% TA. ^c 0.0176 *M*, 99% TA, and 1% CA.

The preceding results suggested that isomerization of 1,2-dimethylcyclohexene might be important under the reaction conditions. Under the normal work-up conditions substantial loss of olefin occurs, precluding accurate measurement of olefin isomerization. In two runs, careful work-up procedures were used to minimize olefin loss and allow the determination of olefin composition. For reaction in 0.0456 *M* HCl containing 0.653 *M* tetramethylammonium chloride (TMAC) it was found that 0.5% of the 1,2-dimethyl-

(8) Reference 7, p 144.

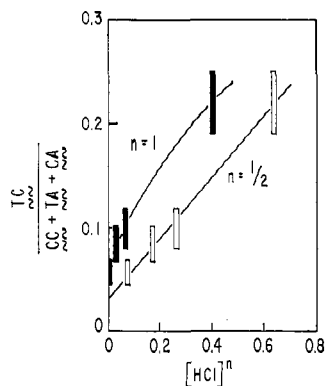


Figure 1. Variation of product distribution with HCl concentration in the absence of TMAC.

cyclohexene has been converted to 1,6-dimethylcyclohexene after 20% reaction. In another run with 0.029 M HCl and 0.0572 M TMAC, analysis showed 3% conversion to 1,6-dimethylcyclohexene after 11% reaction. No 2-methylmethylenecyclohexane was detected in either run. Clearly isomerization does occur but in order to assess its importance with regard to formation of addition products it is necessary to evaluate the relative reactivity of the two isomeric olefins. A competition experiment involving reaction of an olefin mixture containing 25% 1,6-dimethylcyclohexene and 75% 1,2-dimethylcyclohexene with 0.012 M HCl showed that 1,6-dimethylcyclohexene reacts 11 ± 2 times faster than 1,2-dimethylcyclohexene. Extrapolation of the product distribution during the early stages of the reaction to zero time led to an initial product composition of 25% TC, 38% CC, 30% TA, and 7% CA.

The foregoing results show that the isomerization of 1,2-dimethylcyclohexene to 1,6-dimethylcyclohexene followed by addition to the latter olefin and the secondary reactions of the isomeric acetates are responsible for the observed variation in product composition with per cent conversion in the addition to 1,2-dimethylcyclohexene. However, these secondary reactions become important only at higher conversions and extrapolation of the observed product composition at $\leq 10\%$ reaction to zero conversion gives the product composition derived from direct addition to 1,2-dimethylcyclohexene.

Studies of addition to 1,2-dimethylcyclohexene were carried out at less than 10% conversion and initial rates, $R = \Delta[\text{TC} + \text{CC} + \text{TA} + \text{CA}]/\Delta t$, were determined; the results are summarized in Table II. It was established that 1,2-dimethylcyclohexene undergoes no significant reaction with HOAc in the absence of HCl. In runs allowed to proceed to completion, product analysis by glpc accounted for $\geq 95\%$ of the starting olefin.

The results of Table II show that the rate of reaction of 1,2-dimethylcyclohexene increases somewhat faster than the HCl concentration. At HCl concentrations greater than 0.2 M the acidity of the medium increases faster than the HCl concentration and it is useful to measure the dependence of rate upon the acidity function, A ,⁹ determined¹⁰ for HCl-HOAc solutions. A plot of $\log(R/[\text{C}_8\text{H}_{14}])$ vs. $\log A$ has a

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

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

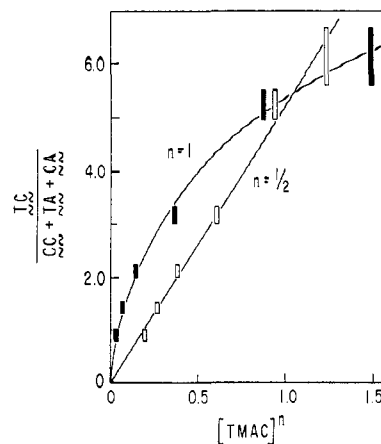


Figure 2. Variation of product distribution with TMAC concentration at $[\text{HCl}] = 0.0685 \text{ M}$.

slope of 1.2, the same as found earlier for the hydrochlorination of cyclohexene.³

The product composition also varies with the HCl concentration, the most striking feature being a marked increase in the amount of TC formed as the HCl concentration is increased. This effect is best seen in the plot of the ratio $\text{TC}/(\text{CC} + \text{TA} + \text{CA})$ vs. $[\text{HCl}]^n$ shown in Figure 1. The plot vs. $[\text{HCl}]^{1/2}$ is more linear than that vs. $[\text{HCl}]$. Because HCl is little dissociated in acetic acid the concentration of dissociated chloride ion increases with the square root of the stoichiometric HCl concentration. Thus, the foregoing result suggests that dissociated chloride ion can intervene in the formation of TC. However, the fact that the intercept in Figure 1 is nonzero shows that some TC is formed by a process that does not involve dissociated chloride ion.

Table II. The Hydrochlorination of 1,2-Dimethylcyclohexene in Acetic Acid at 25°

[C ₈ H ₁₄], M	[HCl], M	[TMAC], M	10 ³ R, ^a M sec ⁻¹	Product composition, % ^b			
				TC	CC	TA	CA
0.0477	0.0057		0.60	5.5	37	49	8.5
0.0507	0.029		3.17	8	37	44	11
0.0457	0.0685		8.8	9	39	42	10
0.0405	0.40		77	18	40	36	6
0.0472	0.0685	0.036	21	48	18	28	5.5
0.049	0.0685	0.072	37	59	16	21	4
0.049	0.0685	0.144	58	68	10	19	2.5
0.0466	0.0685	0.36	136	76	7	15	2
0.0354	0.0685	0.866	140	83	4	11	1.5
0.0382	0.0685	1.48	171	86	3	10	1
0.0438	0.0456	0.653	70	80	5	13	1.5
0.0401	0.0456	0.857	82	83	4	11	1.5
0.0498	0.029	0.0572	10.3	58	16	22	4
0.0451	0.029	0.572	52	80	3	16	1
0.0621	0.0685	0.0425 ^c	25	56	18	22	4
0.0412	0.0685	0.170 ^c	46	76	8	14	2
0.0474	0.0685	0.425 ^c	74	80	4	13	1
0.0427	0.0685	0.722 ^c	61	84	4	12	0.5

^a Maximum error $\pm 10\%$. ^b Extrapolated to zero time. ^c Tetra-*n*-butylphosphonium chloride.

Addition of TMAC to the reaction solution has a marked effect upon both the product composition and upon the reaction rate. A plot of $\text{TC}/(\text{CC} + \text{TA} + \text{CA})$ vs. $[\text{TMAC}]^{1/2}$ (Figure 2) is linear with an intercept near zero, whereas the same function plotted vs.

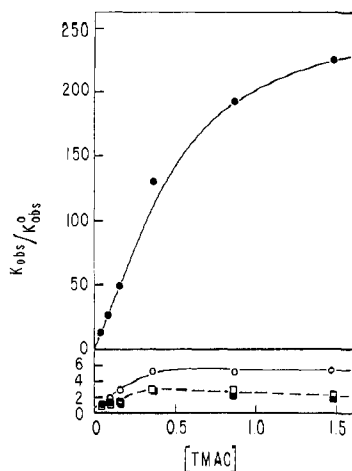


Figure 3. Dependence of $k_{\text{obsd}}/k_{\text{obsd}}^0$ upon TMAC concentration for individual addition products: ●, TC; ○, TA; □, CC; ■, CA; $[\text{HCl}] = 0.0685 M$.

$[\text{TMAC}]$ exhibits distinct curvature. In the presence of both HCl and TMAC, the dissociated chloride ion concentration is given by

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

where K_{HCl} and K_{TMAC} are the dissociation constants of HCl and TMAC, respectively. A value of $2.8 \times 10^{-9} M$ has been determined¹¹ for K_{HCl} but K_{TMAC} has not been directly measured. However, K_{TMAC} should be significantly larger than K_{HCl} and most of the points in Figure 2 are for $[\text{TMAC}] > [\text{HCl}]$. Under these conditions the dissociated chloride ion concentration increases with $[\text{TMAC}]^{1/2}$ and the straight line plot *vs.* $[\text{TMAC}]^{1/2}$ in Figure 2 therefore further confirms the view that dissociated chloride ion intervenes in the formation of TC.

It is possible to empirically estimate a value of K_{TMAC} from the results obtained here and the measured value of K_{HCl} . The foregoing observations imply that eq 3 should be followed with *C* and *D* being con-

$$\text{TC}/(\text{CC} + \text{TA} + \text{CA}) = C/[\text{Cl}^-] + D \quad (3)$$

stants. Equations 2 and 3 can be combined leading to an expression which can be solved using the data of Table II for the value of $K_{\text{TMAC}}/K_{\text{HCl}}$. Least-squares analysis gave a value of 260 ± 130 for this ratio from which we calculate $K_{\text{TMAC}} = 7 \times 10^{-7} M$. Within the error, this agrees with the value of $5 \times 10^{-7} M$ determined in a similar fashion in our study of the hydrochlorination of cyclohexene.³

That the intervention by chloride ion occurs in the rate-limiting step for the formation of TC is evident from the effect of TMAC upon the reaction rate. The reaction rate increases by a factor of more than 20 in the presence of 1.48 *M* TMAC. This is much too large an effect to be ascribed to a salt effect upon the reaction rate² and it must, therefore, derive from chloride ion catalysis of the reaction. It is instructive to examine the effect of TMAC on the rate of formation of each product independently. For this purpose we define an observed first-order rate constant, $k_{\text{obsd}} = R/[\text{C}_8\text{H}_{14}]$, and calculate the ratio of k_{obsd} in the presence

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

of TMAC to k_{obsd}^0 in the absence of TMAC. Figure 3 shows a plot of this ratio *vs.* $[\text{TMAC}]$ at constant $[\text{HCl}]$ for each of the four products. While this ratio increases by a factor of over 200 for the formation TC, it increases only by a factor of between 2 and 5 for the formation CC, CA, and TA. Thus, the effect of TMAC on the rate of formation of CC, CA, and TA is that expected for a salt effect² while the much larger effect upon the rate of formation of TC implies catalysis by chloride ion. Further analysis of the rate and product studies is deferred to the Discussion.

In order to prepare samples of TC and CC, a variety of conditions was examined for addition of HCl to 1,2-dimethylcyclohexene. The product distributions were determined by glpc and are summarized in Table III. It is of interest to note that in methanol

Table III. The Hydrochlorination of 1,2-Dimethylcyclohexene in Various Solvents

Temp, °C	[HCl], <i>M</i>	Solvent	% TC ^a
25	0.45	MeOH	70 ^b
25	4.5	MeOH	90 ^b
25	9.0	MeOH	91 ^b
25	4.5	MeOH ^c	95 ^b
25	Saturated	AcCl	26
25	$\frac{1}{8}$ saturated	AcCl	26
25	$\frac{1}{2}$ saturated	AcCl	27
25	$\frac{1}{8}$ saturated	AcCl	29
0	Saturated at 25°	AcCl	24
-78	Saturated at 25°	AcCl	27
25	Saturated	(CH ₂ Cl ₂ , 2 hr)	26
25	Saturated	(CH ₂ Cl ₂ , 12 hr)	36
25	Saturated	Sulfolane	47
25	Saturated	Sulfolane ^c	61
0	Saturated	Pentane	92
25	Saturated	Pentane	86

^a Other product CC except as noted. ^b Other products CC plus unidentified compounds. ^c Saturated solution of calcium chloride.

anti-HCl addition predominates and increases with the HCl concentration in much the same fashion as found for addition in acetic acid. In contrast to this, *syn* addition predominates in acetyl chloride as solvent and the fraction of TC formed varies little with the concentration of HCl or with temperature. In methylene chloride, *syn* addition also predominates while in sulfolane *syn* and *anti* addition occur to a roughly equal extent. In view of the above results, we were somewhat surprised to find that *anti* addition predominates in pentane as solvent; that this is the result of kinetic control was demonstrated by showing that a mixture rich in CC is stable to the reaction conditions.

Discussion

The hydrochlorination of 1,2-dimethylcyclohexene differs from that of *tert*-butylethylene² and of styrene² in two ways. First, the product composition varies markedly with the concentration of HCl and of TMAC in the reaction of 1,2-dimethylcyclohexene but not in that of *tert*-butylethylene or styrene. Secondly, TMAC has a substantially larger effect on the rate of reaction of 1,2-dimethylcyclohexene than on that of *tert*-butylethylene or styrene. In these respects, addition to 1,2-dimethylcyclohexene more closely resembles the hydrochlorination of cyclohexene.^{3,4} However, even

in the absence of TMAC, anti addition to cyclohexene predominates whereas substantial syn addition occurs with 1,2-dimethylcyclohexene under these conditions. The general mechanism for addition to 1,2-dimethylcyclohexene implied by the present results is essentially the same as that derived earlier for the hydrochlorination of cyclohexene but the relative importance of the several competing processes is different.

The Rate Law. There are good reasons to believe that the rate law for addition to 1,2-dimethylcyclohexene is the same as for addition to cyclohexene and contains three terms¹² as shown in eq 4;^{3,4} here A is an

$$R = k_{2c}[\text{olefin}]A^k + k_3^{\text{HOAc}}[\text{olefin}]A^l[\text{HOAc}] + k_3^{\text{HCl}}[\text{olefin}]A^m[\text{Cl}^-] \quad (4)$$

acidity function for HCl-HOAc solutions.^{9,10} The effect of chloride ion on the reaction rate and product distribution requires the presence of the last term which is associated solely with formation of TC. The first two terms are kinetically indistinguishable in acetic acid as solvent if $k \approx l$, but the presence of these two terms can be indirectly inferred. Thus, if the apparent second-order term is associated entirely with a carbonium chloride ion pair mechanism (see below), then we must conclude that the major addition product of this reaction is TA and that more acetate (TA + CA) than chloride (TC + CC) is formed. This is in contradiction to the results found under similar conditions for *tert*-butylethylene and styrene (which have been shown to react *via* a carbonium chloride ion pair mechanism) where the chloride to acetate ratios were observed to be ~ 2 and ~ 13 , respectively. Since 1,2-dimethylcyclohexene is more reactive than styrene and forms a carbonium ion of comparable stability, a high ratio of chloride to acetate should have been observed. This inconsistency suggests that the major fraction of TA is formed *via* a mechanism analogous to the chloride ion catalyzed process leading to TC but with acetic acid serving as nucleophile, and this in turn implies the presence of the second term in eq 4. The first term is associated with the carbonium chloride ion pair mechanism.

A quantitative test of eq 4 is complicated by the possibility that the three terms may involve different acidity dependence ($k \neq l \neq m$) and different salt effects, as well as by the uncertainty in the value of K_{TMAC} . The larger apparent effect of TMAC upon the formation of TA than upon CC or CA (Figure 3) does indicate that different salt effects are involved. Also, the rate of formation of CC varies with $A^{1.15}$ while that of TA varies with $A^{1.05}$. These observations provide further support for the view that CC and TA are formed by different mechanisms.

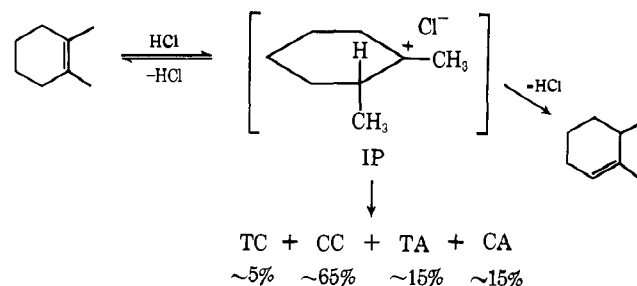
Allowing for slightly different values for k , l , and m , and different salt effects on the three terms, the data of Table II can obviously be fit to eq 4. This would, however, simply be an exercise in data fitting and for our purpose it is satisfactory to estimate the rate constants from the results without added salt assuming that $k = l = m = 1.1$.

The Carbonium Chloride Ion Pair Mechanism. There are several reasons for believing that the first term in eq 4 is associated with this type of mechanism. First, the kinetics at low HCl concentrations are consistent

(12) The dependence upon olefin was not experimentally tested in these studies and was assumed to be first order.

with such a mechanism. Secondly, since *tert*-butylethylene and styrene react *via* this type of mechanism,² such a mechanism should be available for addition to 1,2-dimethylcyclohexene. Finally, at low HCl concentrations substantially more CC than TC is formed, which is consistent with reaction *via* a carbonium chloride ion pair. Scheme I outlines such a mechanism as it applies to 1,2-dimethylcyclohexene.

Scheme I



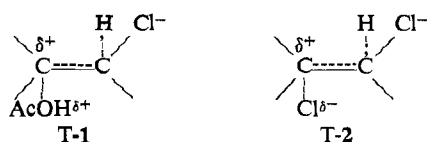
Attack on the olefin by hydrogen chloride (molecular or ionized) leads to the carbonium chloride ion pair IP. Direct collapse of IP to adduct is expected to yield primarily CC and possibly TA, but isomerization or dissociation of IP can also result in the formation of TC and CA. There is also the possibility that attack by molecular HCl and ionized HCl lead to discretely different ion pair intermediates. The limited studies of olefin isomerization show that 2,3-dimethylcyclohexene is also formed in the reaction of 1,2-dimethylcyclohexene and that this process is not chloride ion catalyzed. It seems reasonable to assume that this olefin derives from loss of HCl from IP and the results indicate that this process occurs to roughly the same extent as collapse of IP to addition products. Finally, if IP loses HCl to form isomerized olefin, then it should logically also lose HCl to regenerate starting material, a process which is not detected. Since, 1,2-dimethylcyclohexene is more stable than 2,3-dimethylcyclohexene, regeneration of the starting material from IP may occur many times for each time IP forms isomerized olefin or collapses to addition product. This corresponds simply to IP being a reversibly formed intermediate. In this regard, the reaction of 1,2-dimethylcyclohexene apparently differs from that of cyclohexene-1,3,3-*d*₃ since in the latter case olefin isomerization was not observed to compete with addition.

The observed results allow us to make an estimate of the addition product composition derived from collapse of IP. The fraction of TC formed can be determined from the intercept in Figure 2. All of the CC and CA formed are presumed to derive from this intermediate. It is more difficult to evaluate how much TA is formed *via* Scheme I and we arbitrarily assume this to be an amount equal to the amount of CA formed.¹³ On this basis the percentage figures given in Scheme I were calculated. These values, along with the data of Table II obtained in the absence of added salt, allow us to estimate a value for k_{2c} of $2.2 \times 10^{-4} M^{-1} \text{sec}^{-1}$. It should be emphasized that this is the value

(13) Actually this should be a lower limit for the amount of TA formed in the carbonium chloride ion pair process. A reasonable upper limit might be obtained by assuming that the amount of TA formed is equal to the amount of CC formed by this mechanism. The uncertainty in this assignment introduces some error into the value estimated for k_{2c} and leads to an even greater uncertainty in the estimate of k_3^{HOAc} .

for the rate of formation of addition products *via* IP. The total rate of formation of IP cannot be accurately determined from the present results but is clearly substantially greater than k_{2c} . If one assumes that the overall salt effect¹⁴ on this term is the same as found for the reaction of *tert*-butylethylene ($R/R_0 \approx 2.5$ at 1.0 *M* TMAC), then this value of k_{2c} also accommodates the results obtained in the presence of TMAC.

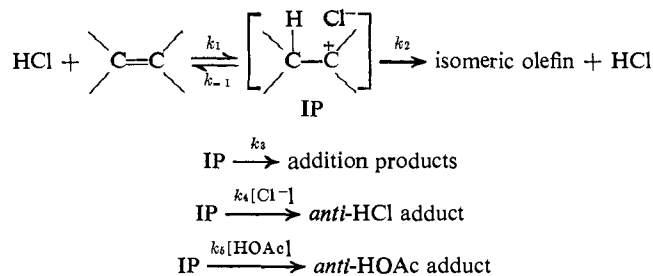
The Third-Order Anti Addition Mechanism. Having estimated a value for k_{2c} and assigned the product distribution associated with this term in the rate law, it is now possible to estimate values for the third-order rate constants of eq 4. Thus, from the excess rate of formation of TA and TC over that assigned to the second-order term, we calculate the values of $k_3^{\text{HOAc}} = 7 \times 10^{-6} M^{-2} \text{ sec}^{-1}$ and $k_3^{\text{HCl}} = 1.8 M^{-2} \text{ sec}^{-1}$ from the data obtained in the absence of TMAC and the determined value of K_{HCl} . These rate constants will also adequately accommodate the results in the presence of TMAC if it is assumed that the overall salt effects¹⁴ on the third-order terms in eq 4 are larger ($R/R_0 \approx 5-6$ at 1.0 *M* TMAC) than for the second-order term and with K_{TMAC} taken as $6 \times 10^{-7} M$, the average of the value estimated in this and in an earlier study.³ The third-order terms of eq 4 are associated with transition states resembling T-1 and T-2 which lead to formation of TA and TC, respec-



tively. Evidence analogous to that reported here has been presented^{3,4} for reaction *via* this type of transition state in the anti addition of HCl and of HOAc to cyclohexene-1,3,3-*d*₃.

Is There a Common Intermediate? The view that there are three competing reactions in the hydrochlorination of both cyclohexene and 1,2-dimethylcyclohexene in acetic acid poses problems for the development of a simple overall understanding of acid additions and one would like to be able to link these reactions in some coherent fashion. One possibility is that IP is a reversibly formed precursor to transition states resembling T-1 and T-2; the mechanism could then be formulated as outlined in Scheme II. Since no olefin isomerization

Scheme II



was detected in the hydrochlorination of cyclohexene-1,3,3-*d*₃, IP cannot be a mandatory intermediate in the anti addition to cyclohexene. Olefin isomerization does occur, however, in the reaction of 1,2-dimethyl-

(14) The effect upon the rate constant together with the effect upon the acidity of the medium.

cyclohexene which makes the mechanism of Scheme II more plausible in this case.

A definitive way to demonstrate that IP is a mandatory intermediate in the formation of TC and TA would be to show that k_1 of Scheme II becomes rate limiting at high chloride ion concentration. The results provide no indication that this occurs but admittedly the test is not very sensitive.¹⁵

However, an indirect argument can be given that IP is not a precursor of transition states such as T-1 and T-2. A bimolecular reaction of IP with nucleophile would normally involve an entropy change of about -15 eu contributing about 4.5 kcal to the free energy for this reaction.¹⁶ The free energy contribution associated with formation of the C-Cl bond may be favorable but it is difficult to see why this would be appreciably more favorable in reaction 4 of Scheme II than in reaction 3 involving collapse to the *syn*-HCl adduct (CC). It follows that k_4 would be expected to be very much smaller than k_3 , if Scheme II is correct, and third-order terms should never be observed. If, on the other hand, IP is not a precursor of transition state T-2 leading to TC, then the carbonium ion is circumvented and the energy gain in C-Cl bond formation can offset the unfavorable entropy effect of the higher order reaction.

Until such time as definitive evidence is presented that IP or some other cationic intermediate is a required common species in these reactions we feel that it is best to consider them as discrete reactions: an ADE2 carbonium chloride ion pair mechanism (Scheme I) and the ADE3 termolecular anti addition mechanisms represented by transition states T-1 and T-2.

The Effect of Solvent. The observed effect of solvent upon the product distribution (Table III) can, for the most part, be understood in terms of the foregoing mechanistic considerations. Addition in methanol gives primarily TC with more TC being formed at higher HCl concentrations. Since methanol is more ionizing and more dissociating than acetic acid, the dissociated chloride ion concentration is higher in methanol than acetic acid at a given HCl concentration and ADE3 addition of HCl logically competes more effectively with the other processes. Acetyl chloride, on the other hand, is expected to be less ionizing than acetic acid and little dissociated chloride ion should be present in this solvent. Under these circumstances it is reasonable that predominant, but not exclusive, *syn* addition occurs *via* a carbonium chloride ion pair mechanism with the HCl concentration having little effect upon the product distribution. We note also that the product distribution is, in this case, invariant with reaction temperature, a phenomenon that we observed previously for carbonium chloride ion pair addition to *tert*-butylethylene and to styrene.² The limited results for addition in methylene chloride suggest that the carbonium chloride ion pair mechanism dominates in this solvent also.

An observation which is not so easily understood is the $\sim 90\%$ anti addition observed in pentane. This is virtually the same result as found by Hammond and

(15) If $k_{-1} \geq 10 \times k_2$, which is a reasonable possibility, a steady-state analysis shows that the apparent total rate neglecting salt effects would increase by a factor of ≥ 3.5 in the range of chloride ion concentration studied. A salt effect of a factor of six would then account for the observed rate increase.

(16) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966, p 124.

Collins⁶ for HCl addition to 1,2-dimethylcyclopentene in pentane solvent. There is certainly little dissociation of HCl in pentane so that catalysis by dissociated chloride ion seems highly improbable. In this case, an ADE3 mechanism involving two molecules of HCl may be involved as suggested by Hammond and Collins.⁶

The Effect of Structure upon Reactivity. A summary of the rate data determined in this and previous studies is given in Table IV and these values allow us to draw

Table IV. Estimated Rate Constants for Addition to Olefins in HCl-HOAc Solutions at 25°

Olefin	$10^8 k_{2c}$, $M^{-1} \text{ sec}^{-1}$	k_3^{HCl} , $M^{-2} \text{ sec}^{-1}$	$10^8 k_3^{\text{HOAc}}$, $M^{-2} \text{ sec}^{-1}$
1,2-Dimethylcyclohexene ^a	22,000	1.8	700
Styrene	2,300 ^b	<0.1	
<i>tert</i> -Butylethylene	8 ^b	<10 ⁻⁵	
Cyclohexene ^c	2.4	1.0×10^{-3}	1.3

^a This work. ^b From $R = k_{2c}[\text{olefin}][\text{HCl}]$ at $[\text{HCl}] < 0.15 M$; ref 2. ^c From ref 4.

some useful conclusions concerning the effect of structure upon the several processes involved. It must be emphasized that many of these numbers are estimates and are based on a series of assumptions, not all of which are likely to be strictly valid. However, the conclusions to be drawn from Table IV are qualitatively evident in the observed results themselves; the use of these estimated rate constants merely serves to simplify the discussion.

The most important features derive from a comparison of the variations in k_{2c} with those in k_3^{HCl} . Thus, 1,2-dimethylcyclohexene is 10^4 and styrene 10^3 more reactive than cyclohexene *via* the carbonium ion mechanism (k_{2c}), this being consistent with the relative stabilities of the carbonium ions formed.¹⁷ The variation in k_3^{HCl} is smaller, with 1,2-dimethylcyclohexene being 1800 times more reactive than cyclohexene, but the rather large rate increase does show that transition state T-2 has substantial carbonium ion character. Although k_{2c} for *tert*-butylethylene is about three times that for cyclohexene, the corresponding value of k_3^{HCl} is less than 1/100th that of cyclohexene, a change which presumably reflects the unfavorable steric effect of the *tert*-butyl group on the ADE3 reaction. It is also clear that the resonance effect of the phenyl group has less influence upon k_3^{HCl} than upon k_{2c} . From these comparisons it is clear that while the ADE3 addition does have carbonium ion character the effect of substituents upon the ADE3 rate can be quite different than upon the ADE2 rate.

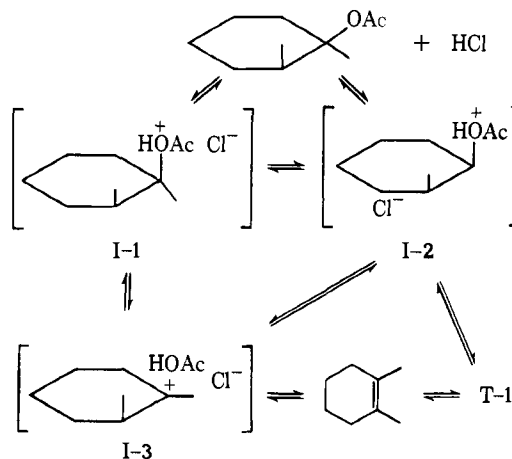
There also appears to be a difference in the termolecular HOAc and HCl additions. Note that $k_3^{\text{HCl}}/k_3^{\text{HOAc}} = 7.7 \times 10^4$ for cyclohexene but 26×10^4 for 1,2-dimethylcyclohexene. Put another way k_3^{HCl} increases by a factor of 1800 in going from cyclohexene to 1,2-dimethylcyclohexene but k_3^{HOAc} increases by a factor of only ~ 500 . Since our estimate of k_3^{HOAc} for 1,2-dimethylcyclohexene must be close to an upper limit, this difference is real. This observation suggests that transition state T-1 for HOAc addition

(17) Actually the relative rate value of 10^4 for 1,2-dimethylcyclohexene is only a lower limit for carbonium ion formation since it does not reflect olefin isomerization *via* this mechanism.

has less carbonium ion character than transition state T-2 for HCl addition.

The Reverse Reaction. It is instructive to call attention to a few aspects of the reverse reaction, specifically to the reaction of TA with HCl to form 1,2-dimethylcyclohexene (Table I). Since the reaction conditions employed are almost identical with those for addition, the principle of microscopic reversibility should apply and, if our analysis for the addition reaction is correct, there must be two mechanisms involved in the elimination. One involves the transition state T-1 and the other a carbonium ion intermediate. Scheme III outlines the essentials of this process.

Scheme III



In Scheme III, protonation by HCl leads to I-1 but the immediate precursor of T-1 must be I-2 in which chloride ion is near the proton to be removed. I-2 differs from I-1 in that charge separation is much greater and this presumably means I-1 is the more stable of the two. Ionization of either I-1 or I-2 leads to a carbonium chloride ion pair I-3,¹⁸ where the chloride ion in this species is difficult to say but acetic acid must occupy the position defined by C-O bond cleavage. If chloride ion is at the other face of the carbonium ion then I-3 and IP (Scheme I) are essentially identical. But IP cannot be the sole intermediate in both the reaction of TA with HCl and the carbonium chloride ion pair addition to 1,2-dimethylcyclohexene since, if it were, the ratio of CA to CC would be the same in both reactions and this is not found. Thus, there must be more than one ion pair involved in both reactions. Actually, there are probably several discretely different carbonium chloride ion pairs involved but the present results do not justify further speculation as to their nature. Cristol, Morrill, and Sanchez¹⁹ have previously called attention to the potential importance of multiple ion pair intermediates in connection with a study of the addition of acetic acid to norbornadiene.

It is often tempting to assume that the important reacting species in a reaction are those which are most abundant. This is, of course, exceedingly hazardous and the conclusion that I-2, though not the most stable

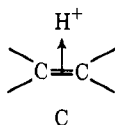
(18) In this discussion we have intentionally omitted conformational considerations. If I-1 and I-2 have different conformations then they will not necessarily ionize to the same intermediate I-3. While specific consideration of conformational problems does complicate the argument, it does not change the conclusions.

(19) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Org. Chem.*, 31, 2719 (1966).

form of the protonated acetate, is nevertheless an important reactant species illustrates this point. The fact that dissociated chloride ion, though not the dominant form of chloride in solution, catalyzes the addition to form TC is another case in point.

Conclusions. The present study provides further evidence for the involvement of both AdE2 and AdE3 mechanisms in the addition of hydrogen chloride to olefins and in the acid-catalyzed addition of acetic acid to olefins. It seems to us that the AdE3 mechanism should also be important in the acid-catalyzed addition of alcohols and water to olefins. Unhappily, this mechanism cannot be detected kinetically when the reagent that adds is itself the solvent and other tests must be devised to distinguish it from the AdE2 mechanism.

It now seems virtually certain that the anti addition of HBr to 1,2-dimethylcyclohexene observed by Hammond and Nevitt⁵ involves an AdE3 mechanism. The involvement of a reversibly formed proton-olefin complex C as postulated by these authors is not re-



quired by our results or theirs, nor is it ruled out providing that it is formed as an ion pair. A future paper in this series will describe our own studies of HBr addition to mono- and dialkylethylenes in acetic acid.

Experimental Section

An Aerograph Hy-FI III Model 1200 chromatograph equipped with a flame ionization detector, linear temperature programmer, and capillary-splitter injector was employed with two 150 ft \times 0.01 in. stainless steel columns, one coated with XF-1150 and the other with Carbowax 400. For analytical measurements either the Carbowax 400 column (column A) or the two columns in series (column B) were used. Preparative separations were accomplished on a 20 ft \times 1/4 in. column packed with XF-1150 on HMDS treated Chromosorb P (column C) using an Aerograph Model 202 chromatograph with thermal conductivity detectors. Nmr spectra were measured on approximately 10% w/v solutions in carbon tetrachloride using a Varian T-60 spectrometer. Chemical shifts are reported in parts per million downfield from TMS as internal standard.

Materials. 2-Methylcyclohexanone was purchased from Columbia Organic Chemicals, iodomethane from Matheson Coleman and Bell, and magnesium from Mallinckrodt Products. Glacial acetic acid (Allied Chemical) was titrated for water by the Karl-Fisher method; slightly more than 1 equiv of acetic anhydride was added and the mixture allowed to stand until reaction with the water was complete. Tetramethylammonium chloride (Matheson Coleman and Bell) was recrystallized from water and dried at 150° in a vacuum oven prior to its use.

1,2-Dimethylcyclohexene. A mixture of *cis*- and *trans*-1,2-dimethylcyclohexanol was prepared by reaction of methylmagnesium iodide with 2-methylcyclohexanone according to the procedure of Hammond and Nevitt.⁵ A portion of this product was fractionally distilled to give *cis*- (bp 90° (60 mm)) and *trans*-1,2-dimethylcyclohexanol (bp 91° (62 mm)). Dehydration of the mixture of *cis* and *trans* alcohols was accomplished by heating the mixture with a few crystals of iodine and distilling. Collection of the fraction boiling from 135.5 to 137° followed by preparative glpc purification (column C) gave 1,2-dimethylcyclohexene in $\geq 99.8\%$ purity.

***cis*- and *trans*-1-Acetoxy-1,2-dimethylcyclohexane (CA and TA).** In accordance with the procedure of Nevitt and Hammond,²⁰ addition of acetyl chloride to a solution of *cis*-1,2-dimethylcyclo-

hexanol in dimethylaniline yielded CA, bp 72° (5 mm). Analogous treatment of the *trans* alcohol yielded TA, bp 81° (25 mm).

***cis*- and *trans*-1-Chloro-1,2-dimethylcyclohexane (CC and TC).** 1,2-Dimethylcyclohexene (0.6 g) was dissolved in 50 ml of a solution of 0.14 M HCl and 1.8 M TMAC in HOAc and allowed to react for 2 days. Extraction with pentane-water followed by evaporation of the pentane gave a mixture (0.7 g) of TC (93%) and CC (7%). Hydrogen chloride was bubbled through a solution of 1,2-dimethylcyclohexene (0.5 g) in acetyl chloride (20 ml) at 0° for 4 hr. Careful addition to a cold water-pentane mixture followed by extraction and evaporation of the pentane gave a mixture (0.6 g) of CC (73%) and TC (27%). The mixture containing 93% TC exhibited a predominant ir absorption at 741 cm^{-1} (axial C-Cl) while the mixture containing 73% CC exhibited a predominant ir absorption at 752 cm^{-1} (equatorial C-Cl). Equilibration of the mixture containing 73% CC in 1.3 M HCl-HOAc leads to an equilibrium mixture of 75% TC and 25% CC. The nmr spectra of CC, CA, and *cis*-1,2-dimethylcyclohexanol all exhibit a sharp upfield doublet corresponding to the resonance of the C-2 methyl group. By contrast the nmr spectra of TC, TA, and *trans*-1,2-dimethylcyclohexanol all exhibit a broad multiplet for the C-2 methyl group. The glpc retention times on column A of the three *trans* compounds are in all cases shorter than the corresponding *cis* compounds. The assignment of stereochemistry is entirely consistent with the almost exclusive formation of *trans*-1-chloro-1,2-dimethylcyclohexane from 1,2-dimethylcyclohexene and hydrogen chloride at high TMAC concentrations.

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

The reaction solutions were prepared by mixing a stock solution of the acid with the glpc purified olefin, internal standard, and salt solution in a 25-ml volumetric flask; the flask was transferred to a constant temperature bath (25.0 \pm 0.01°) after rapid mixing of the solutions. Aliquots (5 ml) were withdrawn at intervals and mixed with pentane (10 ml) and 10% aqueous sodium chloride solution (20 ml). The organic layer was separated and the water layer washed with two 5-ml portions of pentane. The combined organic layers were washed with a dilute solution of sodium bicarbonate, dried over anhydrous sodium carbonate, and concentrated on a rotary evaporator.

The concentrated samples were analyzed by glpc on column A at 60° with a nitrogen flow rate of 3 ml/min. Retention times (minutes) as measured from the injection point were: 1,2-dimethylcyclohexene, 4.5; TC, 8.7; CC, 10.2; TA, 20.0; CA, 26.5; tetralin (internal standard), 40.3. Reaction mixture compositions were calculated from the peak area ratios using correction factors determined with mixtures of known composition. Analysis of synthetic mixtures showed that CC, TC, CA, TA, and *cis*- and *trans*-1,2-dimethylcyclohexanol are all stable to the work-up procedure.

Several experiments were conducted to test the stoichiometry of addition to 1,2-dimethylcyclohexene and the stability of CC and TC. A solution of 0.044 g of 1,2-dimethylcyclohexene and 10 ml of 1.3 M hydrogen chloride in acetic acid was reacted for 5 hr at 25°. Analysis by glpc on column A showed that 1,2-dimethylcyclohexene had been converted $\geq 95\%$ to a mixture of 55% TC and 45% CC. Analysis after 35 days reaction showed that the product composition was 75% TC and 25% CC. Reaction of a solution of 0.1 g of 73% CC and 27% TC in 10 ml of 1.3 M hydrogen chloride in acetic acid leads to a mixture of 60% CC after 3 days reaction and 25% CC after 58 days reaction. Reaction of a solution of 0.0474 M 1,2-dimethylcyclohexene, 0.0685 M hydrogen chloride, and 0.425 M tetrabutylphosphonium chloride for 7 days at 25° converts the olefin (83%) to a mixture of 88% TC and 12% CC. Analysis of the same solution after 25 days reaction shows that the olefin is converted ($\geq 95\%$) to a mixture of 81% TC and 19% CC.

Similar studies were conducted with CA and TA. Aliquots of a solution of the acetate in 0.029 M HCl were taken over 5 hr, worked up, and analyzed as described above. Analysis of a mixture of 1,6-dimethylcyclohexene, 1,2-dimethylcyclohexene, and tetralin (internal standard) before and after work-up showed that from 15 to 20% of the olefin was lost during work-up but that the ratio of 1,2- to 2,3-dimethylcyclohexene before (10.1:1) was essentially the same as after work-up (10.3:1). Thus, the product compositions from the reactions of TA and CA were obtained by setting the difference between the initial reactant concentration and the sum of the concentrations of reactants and products at a later time equal

(20) T. D. Nevitt and G. S. Hammond, *J. Amer. Chem. Soc.*, **76**, 4124 (1954).

to the amount of olefin lost. The initial product distributions were obtained by extrapolating the product distribution to zero reaction time. The results of these studies are given in Table I.

Additions in methanol were conducted similarly to additions in acetic acid. The hydrogen chloride was bubbled into anhydrous methanol with cooling and the concentrations determined by titration with a standardized solution of sodium hydroxide. A few drops of 1,2-dimethylcyclohexene were added to the solutions of hydrogen chloride in methanol. Aliquots of the reaction solution were taken and added to a mixture of pentane-water. Separation and concentration of the organic layer followed by analysis on column A gave the percentages of TC and CC.

Reaction of 1,2-dimethylcyclohexene with hydrogen chloride in acetyl chloride was accomplished by saturating acetyl chloride with hydrogen chloride at room temperature. Portions of the saturated solution were removed, cooled to the indicated temperature, or diluted with additional acetyl chloride to the indicated concentration (Table III); a few drops of 1,2-dimethylcyclohexene were then added. Aliquots of the reaction solution were withdrawn and

added cautiously to a mixture of ice-cold pentane-water with shaking. Extraction and concentration of the organic layer followed by analysis of glpc of the products gave the indicated percentages of TC. Additions in sulfolane were carried out in a similar manner.

Reactions in dichloromethane and pentane were carried out by bubbling hydrogen chloride through a solution of a few drops of 1,2-dimethylcyclohexene in pentane or dichloromethane at the indicated temperature. Although no rate measurements were attempted, the rate appeared to be slower at 25° than at 0° in pentane, and an increase in percentage of TC was noted at longer reaction times in dichloromethane. A solution of 73% CC and 27% TC in pentane at 0° was saturated with hydrogen chloride and allowed to stand for 2 hr; no detectable change in the product composition was observed.

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Substituent Effects on Silver-Olefin Complexation¹

C. F. Wilcox, Jr.,* and W. Gaal

Contribution from the Department of Chemistry, Cornell University, Ithaca, New York 14850. Received June 25, 1970

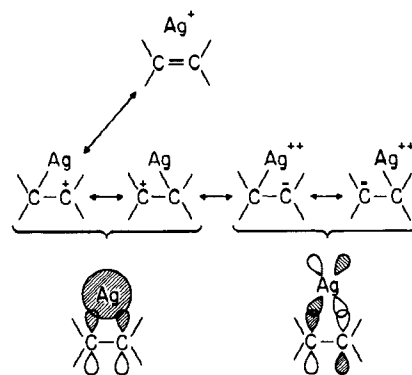
Abstract: The argentation constants in aqueous silver nitrate have been measured for several exo- and endo-substituted norbornenes as well as similarly substituted ethylenes. The constants are correlated by a modified Kirkwood-Westheimer cavity model. The validity of this model for argentation equilibria is discussed.

A classical technique for the study of reaction mechanisms is the determination of the effect of substituents. As the questions asked about transition states become finer it is essential that there be a parallel development in the precision of predictions of quantitative models of substituent effects. With this in mind, the stability of silver complexes of olefins holds promise of being a valuable addition to the physical organic chemists' arsenal of substituent-sensitive reactions because of the rapidity with which the complexes are formed and the ease of measurement.

Because of the well-known analogy of silver ion complexes to carbonium ions,² a study of substituent effects on complexation is particularly relevant to the broad area of carbonium ion chemistry. The argentation reaction, for example, might reveal (under easily controlled equilibrium conditions) the effect of structure on the solvation of charges embedded in a mixed hydrocarbon-aqueous environment analogous to that of a carbonium ion reaction.

A concern in studying substituent effects on argentation is the distribution of charge in the complex. The electronic structure of the complex has been described in terms of both resonance² and molecular orbital³ symbolisms. These descriptions are summarized below (Chart I). The usual abbreviated resonance description has been augmented by the pair of right-hand structures in order to bring out the close parallel between the two descriptions.

Chart I



It can be seen that depending on the relative importance of the $2p\pi \rightarrow 5s$ charge transfer and $4d \rightarrow 2p\pi^*$ charge transfer (or equivalently the relative importance of the left-hand pair of resonance structures *vs.* the right-hand pair of structures) the argentation equilibrium might be either enhanced or diminished by electron-withdrawing substituents. Semiquantitative molecular orbital calculations based on a configuration interaction model suggest⁴ that the charge-transfer contributions are both small and closely balanced so that the substituent effect should be largely determined by the uppermost structure (or its molecular orbital equivalent) in which the electron con-

(1) Based in part on the Ph.D. Thesis of W. Gaal, Cornell University, Ithaca, N. Y., Sept 1968.

(2) S. Winstein and H. J. Lucas, *J. Amer. Chem. Soc.*, **60**, 836 (1938).

(3) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951).

(4) H. Hosoya and S. Nagakura, *Bull. Chem. Soc. Jap.*, **37**, 249 (1964); T. Fueno, T. Okuyama, and J. Furukawa, *ibid.*, **39**, 2094 (1966). These articles describe quantitative treatments of silver complexation.