Rates were measured by observing the rotations of materials condensed from the exit stream and purified by gas chromatography. It was shown that the gas chromatographic procedure did not cause any change in rotation. Rotations were all measured in chloroform solution in a 1-cm cell using a Bendix polarimeter.[21]

1,2-Dimethyl-2-propenyl Acetate (VII). A solution of 44.0 g (0.512 mol) of 3-methyl-3-buten-2-ol (Columbia Organic Chemicals, bp 115–117°) in 147 g (1.86 mol) of pyridine was mixed with 162.5 g (1.59 mol) of acetic anhydride and heated on a steam bath for 90 min. The reaction mixture was worked up in the usual way to yield 53.3 g (81.3%) of α,β-dimethylallyl acetate, bp 130–131°. This product appeared pure on the analytical column used for the kinetic vpc analysis and was used for some of the kinetic measurements. By use of a different analytical column, this product was shown to contain a 10.8% inert impurity.

An 8.00-g (0.0931 mol) sample of 3-methyl-3-buten-2-ol which had been purified by preparative vpc was acetylated with 32.4 g (0.318 mol) of acetic anhydride and 29.4 g (0.372 mol) of pyridine as above. The yield was 9.51 g (79.8%) of 1,2-dimethylallyl acetate which was free of the impurity mentioned above, but the rates were insensitive to this impurity.

2-Methyl-*trans*-2-butenyl Acetate (VIII) and 2-Methyl-*cis*-2-butenyl Acetate (IX). These were from a sample trapped from the passage of VII through the reactor and fractionally distilled once to give a fraction, bp 135–150°, which was separated by preparative gas chromatography into the three pure isomers VII, VIII, and IX. Compounds VIII and IX had somewhat different nmr spectra, but no firm assignment could be made, and the assignment of the *trans* structure to VIII as the predominant rearrangement product of VII is based only on analogy with the other systems.

Acknowledgment. We acknowledge support of this work by a grant from the Petroleum Research Fund of the American Chemical Society.

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[21] We acknowledge a research equipment grant to the Rice Chemistry Department from the National Science Foundation, which allowed the purchase of this instrument.

Reactions of Chloride Ion with 5-Methyl-2-cyclohexenyl Chloride. A Detailed Mechanism for Anion-Promoted Allylic Rearrangement

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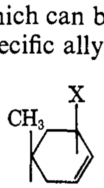
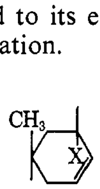
Abstract: 5-Methyl-2-cyclohexenyl chloride in the presence of a chloride salt can undergo simultaneous *cis–trans* isomerization, isotopic exchange of chloride ion, and racemization. All of these reactions are first order in tetraethylammonium chloride in acetonitrile at 65° and constant ionic strength. The most important reaction in the system is SN2 substitution on the same carbon initially containing chlorine. The rate of *cis-trans* isomerization is equal to that of isotopic exchange but less than that of mutarotation plus racemization; these observations rule out major contributions from SN2′ mechanisms. The best explanation of the racemization reaction apparently involves a "sandwich" transition state in which a chloride ion on the opposite side of the ring promotes racemization of a *cis* allylic chloride molecule. The results do not contribute to the original objective of estimating lifetimes of intimate and solvent-separated ion pairs, and studies by other investigators suggest that such lifetimes may be very short in aprotic solvents.

It has been shown that 5-methyl-2-cyclohexenyl chloride consists of *cis* and *trans* isomers (I and II) each of which can be converted to its enantiomorph by a stereospecific allylic isomerization.



I



II

Goering, Nevitt, and Silversmith[3] showed that both isomers racemized more rapidly than they were solvolyzed in either ethanol or acetic acid, but the isomers were not detectably interconverted prior to solvolysis. These observations were interpreted to involve the unimolecular formation of a racemic intimate ion pair that either collapsed or continued on a path to solvolysis products.

We selected the same compounds for an attempt to determine the lifetimes of ion pairs in a nonsolvolyzing solvent. The racemization and *cis–trans* isomerization reactions indicate differences in the extent to which the components of an ion-pair intermediate became separated before they recombined. If the reaction mixture also contained isotopically labeled chloride ion, it was reasoned that it should exchange with these ion pairs by a diffusion-controlled process whose rate constant could be estimated with moderate reliability. Comparative rates of the various processes should then permit estimates of the lifetimes of ion pairs before the components recombined to isomeric products.

Such a kinetic analysis requires that unimolecular processes make major contributions to the racemization and *cis–trans* isomerization reactions in nonsolvolyzing solvents suitable for exchange studies. Although such an expectation is encouraged by the observations of Goering and Josephson[4] about the

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[1] Based on the Ph.D. Dissertation of D. G. L. at Columbia University, May 1964.

[2] Based on the Ph.D. Dissertation of P. D. B. at the University of Oregon, Aug 1966.

[3] H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *J. Am. Chem. Soc.*, 77, 5026 (1955).

extreme facility of ionization in the 5-methyl-2-cyclohexenyl system, we have found that in acetonitrile all of the reactions of interest are cleanly first order in added chloride ion. Although this fact precluded the intended study of unimolecular ionization processes, the relative rates have provided mechanistic information concerning the bimolecular processes observed.

Preparation of Materials

Acetonitrile. The solvent was selected because of its high dielectric constant, chemical stability, and infrared properties satisfactory for analysis of the reactants. Practical grade material was shaken with saturated potassium hydroxide solution, dried, and distilled three times from phosphorus pentoxide. During storage, it was protected from moisture by a phosphorus pentoxide trap.

Tetraethylammonium Salts. Tetraethylammonium iodide (TEAI) was prepared from triethylamine and ethyl iodide by a modified procedure of Smith and Frank.[5] An aqueous solution of the salt was then converted to tetraethylammonium hydroxide with a Dowex 21K anion-exchange resin, and this solution was neutralized to pH 6 with hydrochloric or perchloric acid. In some preparations, the hydrochloric acid had been labeled with chlorine-36 from the Oak Ridge National Laboratory.

The appropriate tetraethylammonium salts were obtained by evaporation of the aqueous solution. The perchlorate (TEAClO$_4$) was recrystallized from 95% ethanol and stored under vacuum over calcium chloride. The more hygroscopic unlabeled chloride (TEACl) was recrystallized from 1,2-dichloroethane, dried at 60° by phosphorus pentoxide in an Abderhaldung pistol, and stored as acetonitrile solution. The labeled chloride was recrystallized from 1:2 acetonitrile–2-butanone to prevent loss of radioactivity by exchange with a chlorinated solvent.

5-Methyl-2-cyclohexyl Chlorides. The synthetic procedures for the desired allylic chlorides had already been developed by Goering and co-workers.[6–8] Ethyl crotonate and ethyl acetoacetate were condensed to form 5-methyl-1,3-cyclohexadione, and the dione was converted to the enol ethyl ether and reduced with lithium aluminum hydride to the allylic ketone 5-methyl-2-cyclohexenone.

This ketone was reduced to a mixture of *cis*- and *trans*-5-methyl-2-cyclohexenols. Reduction with lithium aluminum hydride gave 93% *cis* alcohol[7] and was the method of choice for this isomer. Reduction with aluminum isopropoxide gave a mixture containing 55% *cis* alcohol[7] that could be separated to prepare both isomers. The isomeric alcohols were separated both by vacuum distillation with a spinning-band column and by preparative gas chromatography, and isomeric purity was analyzed by gas chromatography. Pure *cis* isomer could be obtained satisfactorily by distillation alone; *trans* isomer was prepared by chromatography of a sample that had been enriched by distillation. All samples converted to chloride consisted of alcohol that was at least 98% a specific isomer.

The racemic isomeric alcohols were converted to their acid phthalates for resolution. The *cis* alcohol was resolved by crystallization of the cinchonidine salt from dry acetone. The brucine salt was used for resolution of the *trans* alcohol.

Samples of alcohol were converted to 5-methyl-2-cyclohexenyl chloride with thionyl chloride in anhydrous ether. The ether was then removed, and the allylic chloride was distilled as rapidly as possible.

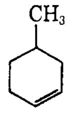
As Goering, *et al.*,[8] have noted, optically active material racemized fairly rapidly under the reaction conditions. Material with a sufficient rotation was obtained if the whole operation was conducted in 25 min or less, and optically pure samples were unnecessary for the studies of racemization kinetics.

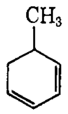
In contrast to the sensitivity to optical isomerization, Goering, *et al.*,[8] claim that the preparation is stereospecific with regard to *cis–trans* isomerism. Our own spectrophotometric observations of consecutive fractions during distillation of either isomer confirmed that the composition did not change during this operation but provided no information concerning the preparation step. Two preparations (one for each isomer) gave clear evidence of extensive isomerization that was ascribed to residual effects of acid cleaning of glassware. It was kept acid free for all subsequent preparations. Refractive index measurements on several samples gave $n^{25}\text{D}$ ranges of 1.4731–1.4734 and 1.4765–1.4770 for *cis* and *trans* chlorides, respectively. Since values quoted by Goering, *et al.*,[8] are 1.4730 and 1.4778, respectively, some isomerization may have occurred. The question of isomeric purity is discussed further below.

Chemical (as opposed to isomeric) purity was checked by commercial chloride analyses. These indicated almost 98% purity for *trans* preparations and over 99% purity for *cis*. An unknown impurity consisted of a small suspension of immiscible liquid that separated during storage at −10° and could be removed by centrifugation. Absorption at 258 mμ indicated 5-methyl-1,3-cyclohexadiene formed by elimination of HCl, and the purity of the allylic chloride could also be computed by assuming that the intensity of this band measured the only impurity. Indicated concentrations of diene were usually less than 2%.

Solutions of allylic chloride in acetonitrile were prepared by weight, and concentrations were corrected for the results of chloride or diene analyses. When both values were available for the same sample, the lower indicated purity was used in the calculations.

5-Methyl-1,3-cyclohexadiene. The possible HCl-elimination product was synthesized by the method of Mousseron and Winternitz.[9] 4-Methylcyclohexene (III) was brominated; the bromines were substituted with sodium ethoxide, and the product was dethoxylated by add-


III


IV

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(4) H. L. Goering and R. R. Josephson, *J. Amer. Chem. Soc.*, **84**, 2779 (1962).

(5) P. A. S. Smith and S. Frank, *ibid.*, **74**, 509 (1952).

(6) J. P. Blanchard and H. L. Goering, *ibid.*, **73**, 5863 (1951).

(7) H. L. Goering and J. P. Blanchard, *ibid.*, **76**, 5405 (1954).

(8) H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *ibid.*, **77**, 4042 (1955).

(9) M. Mousseron and F. Winternitz, *Bull. Soc. Chim. France*, 232 (1946).

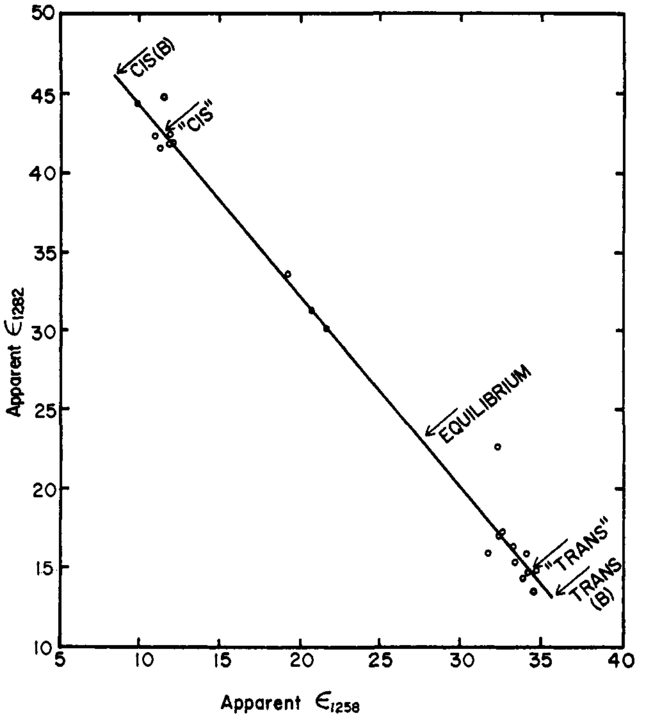

Figure 1. Apparent extinction coefficients (in l. mole^{-1} cm^{-1}) for different preparations of 5-methyl-2-cyclohexenyl chlorides. Points designated "*cis*" and "*trans*" are assignments for pure isomers according to assumption A and are used to calculate all quantities enclosed in quotation marks. Points designated *cis*(B) and *trans*(B) are assignments for pure isomers required by assumption B that rates of isomerization and exchange are equal in all solutions.

ing it dropwise to sodium bisulfate at 190°. The resulting 5-methyl-1,3-cyclohexadiene (IV) formed a maleic anhydride adduct apparently identical with that from the diene prepared by Goering, *et al.*[10] It also formed a tetracyanoethylene adduct of proper chemical analysis that melted at 217.5-218.5°. The nmr spectrum indicated that four of the hydrogens were vinylic and confirmed which of the possible conjugated methylcyclohexadienes had been prepared.

The diene could be analyzed by absorbance at 258 mμ in ethanol. The extinction coefficient of 4470 ± 80 l./mole cm in ethanol is in rather poor agreement with the value of 4910 reported previously.[10]

Experimental Section

Kinetic Conditions. Most solutions were 0.16–0.18 *M* in allylic chloride, but a few isomerization and exchange runs at other concentrations established that the reactions were indeed first order in this species. Concentrations of tetraethylammonium chloride varied from 0 to 0.06 *M* for isomerization and exchange runs and to 0.10 *M* for polarimetric runs. When necessary, tetraethylammonium perchlorate was added so that the total salt concentration was always 0.10 *M*.

All runs were at 65.0 ± 0.1°. *cis-trans* isomerization and exchange runs were in sealed glass ampoules that were quenched in ice as soon as they were removed from the thermostat and were analyzed within 3 hr. Polarimetric runs were thermostated by water pumped through a jacket surrounding the cells.

***cis-trans* Composition.** Extent of isomerization was measured by infrared spectrophotometry at 1258.0 and 1282.5 cm^{-1}. A double-beam Beckman IR-7 instrument was used, and the 0.935-mm cells had barium fluoride windows. The reference cell contained a solution of tetraethylammonium salts at the same concentration as the sample.

Quantitative interpretation suffered from lack of any objective criterion for identifying pure *cis* and *trans* isomers. All preparations absorbed somewhat at both analytical frequencies but obeyed Beer's law well. Apparent extinction coefficients at these frequencies are plotted in Figure 1 for several preparations including those that gave evidence of acid-catalyzed isomerization. The data fall reasonably on the straight line anticipated if isomeric composition is the only variable among preparations. Extinction coefficients for the individual isomers were then identified as the extreme positions on this line validated by duplicate preparations. The values, in l./mole cm, are "$\epsilon_{1282}{}^{cis}$" = 42.57, "$\epsilon_{1282}{}^{trans}$" = 14.87, "$\epsilon_{1258}{}^{cis}$" = 11.23, and "$\epsilon_{1258}{}^{trans}$" = 34.22.

All quantities calculated for the isomers assigned by Figure 1 are enclosed in quotation marks. Theoretical quantities derived for the pure isomers are undesignated. Let γ be the mole fraction of *trans* in the "*cis*" material, and let τ be the mole fraction of *cis* in the "*trans*." Then the true composition of any analyzed mixture is given by

$$[cis] = (1 - \gamma)[\text{“}cis\text{”}] + \tau[\text{“}trans\text{”}] \qquad (1)$$

$$[trans] = (1 - \tau)[\text{“}trans\text{”}] + \gamma[\text{“}cis\text{”}] \qquad (2)$$

Absorbance measurements at the two analytical frequencies permit concentrations of both "isomers" to be calculated. Such uncritical calculations suggested increases of up to 7% in total allylic chloride concentration during a run, while titrations of free chloride ion indicated slight decomposition of allylic chloride. When a mixture corresponding to the equilibrium isomeric composition was heated as in a run, the absorbances at both frequencies increased at equal rates and changed a total of 9% while the concentration of free chloride ion changed an amount corresponding to 4% decomposition of the allylic chloride. The absorbance increase was attributed to the formation of decomposition products (although the diene IV is almost transparent at the analytical wavelengths).

This effect of decomposition was corrected for in the following way. At the end of each isomerization kinetic run the total concentration of allylic chloride was calculated as the difference between the initial concentration and the increase in titratable chloride ion. The measured absorbances were then decreased by a correction (the same for each analytical wavelength) such that the total allylic chloride concentration calculated from the corrected absorbances equaled that calculated from the chloride ion titration. The absorbance correction was assumed to vary linearly with time, and concentrations of "isomers" at other points of the run were computed from measured absorbances on this assumption. Total allylic chloride concentrations obtained in this way for the intermediate points never differed by more than 1.5% from the values indicated by titration of chloride ion.

Isotopic Exchange. Radioactive chlorine was initially present only as the tetraethylammonium salt. The solution from a kinetic run was diluted tenfold with ethyl ether and extracted with distilled water. Tests indicated that this procedure removed more than 99% of the salt present without significantly hydrolyzing the allylic chloride.

The aqueous extract was made slightly basic, evaporated almost to dryness, and diluted to exactly 25 ml with water. The radioactivity of this solution was measured with a thin-walled Geiger-Mueller counter. Counting efficiency was only about 1.5%, but at least 10,000 counts were accumulated for each solution.

Polarimetric Measurements. Optical rotation was followed with a Perkin-Elmer Model 141 polarimeter. Most measurements were made with the 365-mμ mercury line, which gave the largest angle for any wavelength intense enough to use, but some runs at other wavelengths exhibited quantitatively identical kinetic behavior. Initial angles ranged from 0.1 to 2°, and rotations could be measured to 0.002° under the best conditions.

At the end of a run, the concentration of free chloride ion was determined by titration of an aqueous extract, and the concentration of cyclohexadiene IV was estimated by absorbance at 258 mμ. The concentration of free acid was also sometimes measured by titration with standard sodium hydroxide, but this titration always agreed with the increase in chloride concentration and added no new information.

Chloride Titration. Decomposition of allylic chloride was estimated by measuring free chloride ion in an aqueous extract obtained as for an exchange measurement. The potentiometric procedure was based on that of Shiner and Smith.[11] Changes in

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[10] H. L. Goering, J. P. Blanchard, and E. F. Silversmith, *J. Am. Chem. Soc.*, **76**, 5409 (1954).

[11] V. J. Shiner, Jr., and M. L. Smith, *Anal. Chem.*, **28**, 1043 (1956).

chloride concentration of the original acetonitrile solution could apparently be measured with an accuracy of 2×10^{-4} *M*.

Diene Analysis. Elimination of HCl from the allylic chloride presumably forms 5-methyl-1,3-cyclohexadiene (IV) which absorbs strongly at 258 mμ. This absorption was considered for monitoring extent of decomposition.

In solutions of freshly prepared samples of allylic chloride, absorption attributable to diene correlated well with deviations of chlorine analyses from predictions for pure material. When kinetic runs were examined at 258 mμ, the absorption increased to a maximum and then decreased while chloride ion production continued to increase. The diene apparently underwent further reaction such as polymerization, and its concentration could not be used to measure extent of allylic chloride decomposition.

Computational Procedures and Results

Conventions for Kinetic Quantities. The kinetic measurements can be used to derive or infer many different rate constants of potential interest. In order to reduce confusion, the following conventions have been adopted.

Quotation marks are used to set off quantities derived on the assumption that the arrows so labeled in Figure 1 do indeed designate the extinction coefficients of the pure isomers. No quotation marks are used for hypothetical rate constants involving pure isomers or for quantities whose values are unaffected by the incorrect identification of those isomers.

Both expectation and experiment concur that all of the processes are first order in allylic chloride. A *preceding superscript asterisk* designates a first-order rate constant computed on this assumption. The results indicate that most of these processes are also first order in added tetraethylammonium chloride, TEACl. *Absence of an asterisk* designates a second-order rate constant defined by

$$k_i = {}^*k_i/[\mathrm{TEACl}] \qquad (3)$$

The various processes to which the rate constants refer are designated by *following subscripts*. A *three-letter* subscript designates a quantity derived from measurements of a single type such as exchange or polarimetry. An *Arabic numeral* subscript designates a stereospecific process whose measurement requires combination of isomerization and polarimetry measurements.

Isomerization Kinetics. *cis–trans* isomerization is a typical relaxation process.[12] If Y is any property linearly related to the mole fraction of one isomer, and if Y_{eq} is the value at equilibrium

$$^*k_{\mathrm{iso}} = -\frac{\mathrm{d} \ln (Y - Y_{\mathrm{eq}})}{\mathrm{d}t} \qquad (4)$$

Let K be the equilibrium constant for the conversion of *cis* isomer to *trans*, and let k_{cis} and k_{tis} be the rate constants for the forward and reverse reactions. Then

$$k_{\mathrm{iso}} = k_{\mathrm{cis}} + k_{\mathrm{tis}} = k_{\mathrm{tis}}(1 + K) \qquad (5)$$

If the approach to equilibrium can be identified, the value of k_{iso} calculated from any data will be independent of whether or not the pure isomers have been correctly identified. If "K" is the ratio of "isomers" at equilibrium, we can define "k_{tis}" by

$$\text{“}k_{\mathrm{tis}}\text{”} = k_{\mathrm{iso}}/(1 + \text{“}K\text{”}) \qquad (6)$$

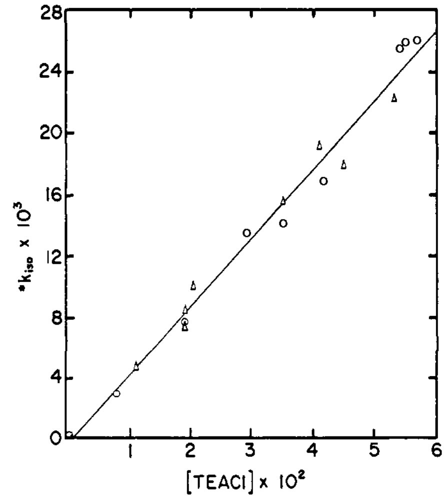

Figure 2. Variation of $^*k_{\mathrm{iso}}$ with [TEACl]: ○, runs initially rich in *cis* material; △, initially rich in *trans*.

Because decomposition products contributed to the absorption spectrum as described above, determination of the equilibrium composition was complicated. For any single run, good linear plots corresponding to different values of $^*k_{\mathrm{iso}}$ could be obtained for a moderate range of assumed equilibrium constants. However, for two runs with the same TEACl concentration but starting from different isomers, only one value of "K" leads to identical values of $^*k_{\mathrm{iso}}$ for both runs. A total of nine runs at four different TEACl concentrations were paired in this way to calculate the equilibrium mole fraction of "*cis*." Results ranged from 0.271 to 0.314 with an average of 0.296.

Another run with initial mole fraction 0.307 "*cis*" gave almost linear absorbance changes at the two analytical frequencies. The deviations from linearity were ascribed to a small shift in isomeric composition, and extrapolation back to zero time indicated an equilibrium value of 0.293 "*cis*."

From these data, the equilibrium mole fraction of "*cis*" was taken to be 0.295; then

$$\text{“}K\text{”} = \text{“}k_{\mathrm{cis}}\text{”}/\text{“}k_{\mathrm{tis}}\text{”} = 2.39 \qquad (7)$$

The scatter of individual measurements of equilibrium composition indicates a standard deviation of 0.09 in the averaged "K."

Values of $^*k_{\mathrm{iso}}$ in min^{-1} are plotted against [TEACl] in Figure 2. The first-order dependence on added chloride is readily apparent. A two-parameter least-squares fit to Figure 2 gives

$$k_{\mathrm{iso}} = 0.449 \text{ l./mole min} \qquad (8)$$

$$\text{“}k_{\mathrm{cis}}\text{”} = 0.317 \text{ l./mole min} \qquad (9)$$

$$\text{“}k_{\mathrm{tis}}\text{”} = 0.132 \text{ l./mole min} \qquad (10)$$

The standard deviation of k_{iso} is 0.016 l./mole min. A one-parameter fit constrained to pass through the origin gives $k_{\mathrm{iso}} = 0.441$ l./mole min.

For reasons that will become apparent in comparison with exchange, it is also convenient to compute "k_{eqi}," the apparent rate constant for the total change in

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(12) M. Eigen and L. de Maeyer, "Technique of Organic Chemistry. Volume VIII. Investigation of Rates and Mechanisms of Reactions," 2nd ed, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 895–966.

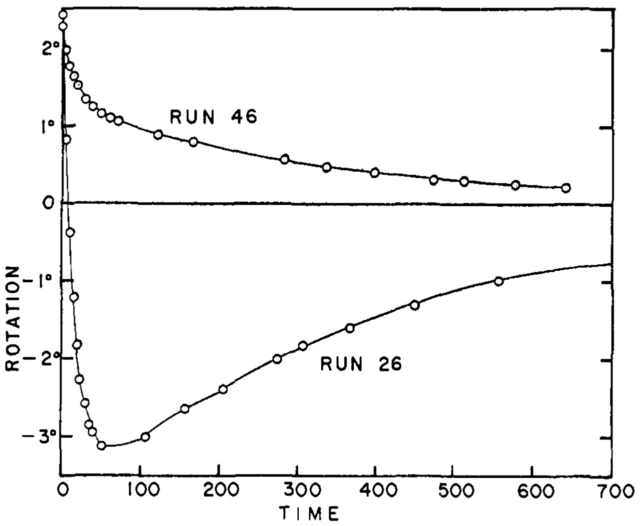


Figure 3. Behavior of two typical polarimetric runs. Run 26 (true rotations one-tenth of those indicated) was 0.132 M in *cis* allylic chloride and 0.099 M in TEACl. Run 46 was 0.153 M in *trans* allylic chloride and 0.0995 M in TEACl.

isomeric composition of individual molecules in a system at isomeric equilibrium. The equation is

$$\text{“}k_{\text{eqi}}\text{”} = \frac{\text{“}k_{\text{cis}}\text{”} + \text{“}K\text{”“}k_{\text{tis}}\text{”}}{1 + \text{“}K\text{”}} = \frac{2\text{“}k_{\text{cis}}\text{”}}{1 + \text{“}K\text{”}} = 0.187 \text{ l./mole min} \quad (11)$$

Exchange Kinetics. The exchange experiments measured the rate at which chloride initially present in the salt became incorporated in allylic chloride. Since the isomers exchange with different rate constants, and since there is no *a priori* evidence of the extent to which exchange and isomerization are simultaneous processes, no rigorous mathematical treatment is possible. Even if an assumption about the extent of simultaneity is made, the resulting differential equations are nonlinear and insoluble in closed form.

Assumptions about the extent of simultaneity were avoided by designing exchange experiments so that rates could be measured while the systems were as far from isomeric equilibrium as possible. The concentration of allylic chloride was usually at least three times that of TEACl. Hence a considerable change in the distribution of radioactivity must have occurred before a significant fraction of previously exchanged allylic chloride molecules exchanged again with inactive TEACl. The large difference in concentrations also permitted a large fraction of the radioactive salt to exchange during a time in which the isomeric composition of the allylic chloride was little altered. The effect of changing isomeric composition could therefore be handled fairly well by assuming that composition to be constant at the average value existing during the run.

The validity of these approximations was supported by the fact that excellent linear plots were obtained when data for individual runs were treated by standard equations appropriate to exchange of a single pure compound. These plots were used to calculate k_{uex}, the second-order rate constant for exchange of allylic chloride of an undifferentiated composition.

Table I contains values of k_{uex} for several runs initially enriched in each isomer. The average mole fractions of "*cis*" were computed from the starting composition and the value of $^{*}k_{\text{iso}}$.

Table I. Rates of Exchange

[TEACl], mole/l.	[Allylic chloride], mole/l.	Mole fraction "*cis*"	k_{uex}, l./mole min
0.0151	0.100	0.931	0.254
0.0151	0.171	0.880	0.276
0.0202	0.174	0.835	0.267
0.0350	0.041	0.700	0.252
0.0348	0.174	0.836	0.276
0.0548	0.180	0.748	0.265
0.0625	0.170	0.731	0.285
0.0108	0.172	0.123	0.141
0.0202	0.169	0.140	0.138
0.0330	0.171	0.101	0.184
0.0409	0.166	0.179	0.156
0.0525	0.171	0.122	0.167
0.0516	0.170	0.122	0.181

Values of k_{uex} from Table I were plotted against mole fraction "*cis*," and the intercepts of the least-squares line were identified as "k_{cex}" and "k_{tex}," the rate constants for exchange of "*cis*" and "*trans*" allylic chlorides, respectively. The values obtained are

$$\text{“}k_{\text{cex}}\text{”} = (1 - \gamma)k_{\text{cex}} + \gamma k_{\text{tex}} = 0.295 \text{ l./mole min} \quad (12)$$

$$\text{“}k_{\text{tex}}\text{”} = (1 - \tau)k_{\text{tex}} + \tau k_{\text{cex}} = 0.143 \text{ l./mole min} \quad (13)$$

The standard deviation of each intercept is 0.010 l./mole min, but these deviations are not independent. A positive error in one rate constant will almost certainly be accompanied by a negative error in the other. If mole fractions and rate constants were averaged for the runs rich in each isomer, the resulting simultaneous equations gave 0.298 and 0.140 for "k_{cex}" and "k_{tex}," respectively. The correction to obtain k_{cex} and k_{tex}, the rate constants for the pure isomers, is discussed below.

Let k_{eqe} be the rate constant for exchange in a system at isomeric equilibrium. Then

$$k_{\text{eqe}} = \frac{k_{\text{cex}} + Kk_{\text{tex}}}{1 + K} \quad (14)$$

The numerical value computed will be the same independent of the correctness with which the pure isomers have been identified and whether or not all quantities on the right side are enclosed in quotation marks. Then the exchange data indicate

$$k_{\text{eqe}} = 0.188 \text{ l./mole min} \quad (15)$$

Polarimetry Kinetics. Figure 3 illustrates typical behavior for the angle of rotation during runs initially rich in each isomer. Each curve involves a fast initial mutarotation and a slow subsequent racemization. Readings at long times could be fitted to the equation

$$^{*}k_{\text{rac}} = -\frac{\mathrm{d}\ln|\alpha_{\text{E}}|}{\mathrm{d}t} \quad (16)$$

where α_{E} is the angle of rotation in this region. Values

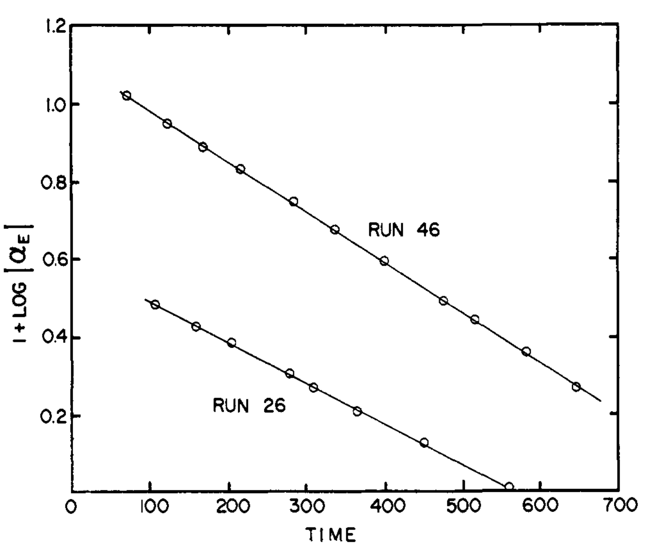


Figure 4. Fit of typical polarimetric data at long times to eq 16.

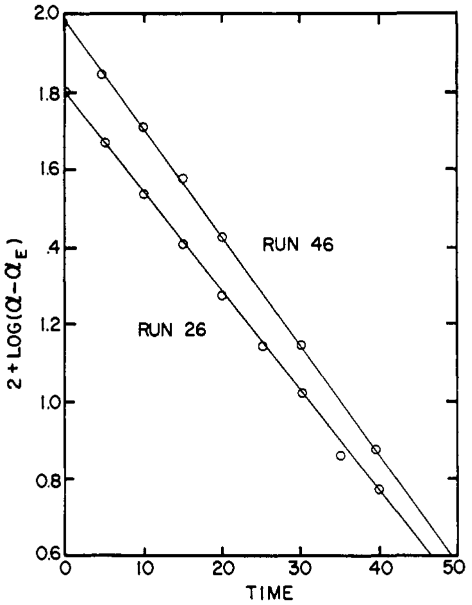


Figure 5. Fit of typical polarimetric data at short times to eq 17.

of α_E could be extrapolated back to short times and the data fitted by

$$^*k_{\text{mut}} = -\frac{d \ln (\alpha - \alpha_E)}{dt} \tag{17}$$

Figures 4 and 5 illustrate the accuracy with which the runs in Figure 3 could be fitted in this way.

Apparent rate constants were constant over a fourfold range in allylic chloride concentration. Figures 6 and 7 show the dependence of $^*k_{\text{mut}}$ and $^*k_{\text{rac}}$ on [TEACl]. Two-parameter least-squares fits give

$$k_{\text{mut}} = 0.618 \text{ l./mole min} \tag{18}$$

$$k_{\text{rac}} = 0.0243 \text{ l./mole min} \tag{19}$$

The standard deviation of k_{mut} is 0.033 l./mole min, and that of k_{rac} is 0.0021. One-parameter fits passing through the origin gave 0.600 and 0.0268 l./mole min for k_{mut} and k_{rac}, respectively. Since values of $^*k_{\text{rac}}$ are based on observations at times so long that isomeric equilibrium had been attained, it is not clear why runs initially rich in *trans* material usually gave somewhat higher rates than runs initially rich in *cis*. Thus the value of k_{rac} computed for the *trans* runs differs from that for the *cis* runs by 2.7 times the standard deviation of the value in eq 19 computed for all runs.

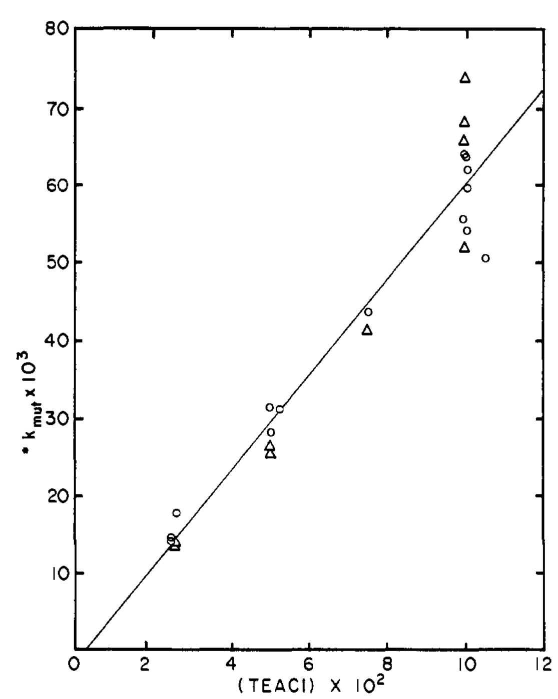


Figure 6. Variation of $^*k_{\text{mut}}$ with [TEACl]: ○, runs initially rich in *cis* material; △, initially rich in *trans*.

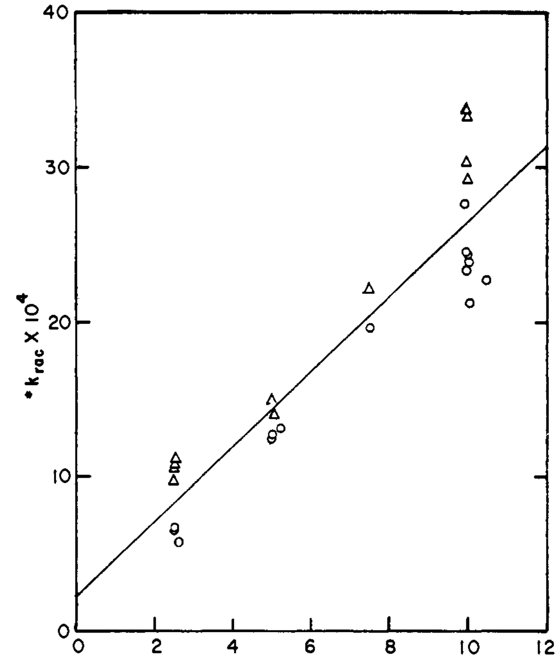


Figure 7. Variation of $^*k_{\text{rac}}$ with [TEACl]: ○, runs initially rich in *cis* material; △, those initially rich in *trans*.

As is shown in Figure 3, for typical runs starting with *cis* isomer the angle of rotation reversed its sign before the final racemization to optically inactive material. This fact demonstrates that the stereospecific mutarotation reaction forms a species with opposite sign of rotation from the initial reactant. Different behavior was observed with the first preparation of apparently *cis* allylic chloride. With this preparation, the initially positive angle of rotation *increased* to a maximum and then declined to approach a slightly negative value at long times. This behavior was observed in several runs made with this first preparation, and the rates of mutarotation and pseudo-racemization were roughly proportional to the concentrations of added chloride. As is indicated by the subsequent discussion, increase in angle of rotation due to allylic chloride could only occur if *trans*-SN2′ substitution were the dominant process in the system! We are unable to explain why this first preparation behaved so differently from all other samples of what was ostensibly the same material. It was not subjected to elementary analysis and might have been contaminated with undecomposed sulfonyl chloride, although the failure of the rotation to approach zero at long times implies a more complicated explanation.

Effects of Acid on Reactions. The allylic chloride slowly decomposed during a run, producing equivalent amounts of hydrogen and chloride ions. Potential interference of these products was suggested by polarimetric runs containing no initial TEACl. Whether or not $TEAClO_4$ was added, these runs exhibited an accelerating racemization that rapidly became faster than the chloride-catalyzed reactions discussed above.

A solution that was 0.019 *M* in HCl and 0.10 *M* in $TEAClO_4$ racemized dramatically faster, and the effect of 0.010 *M* H_2SO_4 was nearly the same as that of 0.019 *M* HCl. Both sodium acetate and pyridine greatly reduced the effect of added acid.

In view of the unequivocal evidence for acid-catalyzed racemization in these runs, it is remarkable that the polarimetric runs with added TEACl did not exhibit autocatalytic behavior. Such an effect was suggested in some runs, particularly with low concentrations of added chloride, but it appeared only at very long times when darkening of the solution made it difficult to measure the small residual angles.

The only isomerization run without added TEACl gave no evidence of autocatalysis. Effect of added acid was also tested by a run initially 0.0042 *M* in HCl and 0.0251 *M* in TEACl. The rate of isomerization in this run was actually *depressed* to that expected for 0.0196 *M* TEACl.

The effect of added acid on the rate of exchange was not studied. However, exchange runs generally required much shorter times than either isomerization or polarimetry, and effects of decomposition products should be less important.

These observations indicate that TEACl dramatically reduces the undesirable effects of acids. Kolthoff, *et al.*,[13] report that the p*K* of association of HCl_2^- in acetonitrile at 25° is −2. Evidently this ion does not promote the reactions of interest.

Decomposition Kinetics. Allylic chloride decomposes slowly to form HCl and diene IV. In solutions 0.10 *M* in tetraethylammonium salts, the rate indicated by chloride titrations was not autocatalytic.

Although the *net* rate of decomposition is slow, these observations do not rule out a faster elimination and readdition of HCl to diene. At the suggestion of Dr. A. J. Parker, a series of runs was made with 0.2 *M* 2,6-lutidine to prevent the possible readdition. These runs gave fairly good kinetics very comparable to rates observed in the absence of lutidine.

Let $^*k_{\text{dec}}$ be the first-order rate constant for decomposition of allylic chloride in the presence of lutidine. Values in min^{-1} could be represented well by

$$^*k_{\text{dec}} = 0.00006 + 0.0007[\text{TEACl}] \qquad (20)$$

The chloride-independent term is approximately one-quarter of the intercept in Figure 7, and the chloride-dependent term is about one-third of the standard deviation of the slope used to determine k_{rac}. All of the other processes of interest are very much faster than racemization, and decomposition rates are much less than probable errors in those quantities.

Discussion

Summary of Numerical Results. All of the kinetic parameters of mechanistic interest can be derived from five independently measured rate constants and one equilibrium constant. The values selected (in l./mole min for rate constants) are

$$\text{“}K\text{”} = 2.39 \pm 0.09$$

$$k_{\text{iso}} = 0.449 \pm 0.016$$

$$\text{“}k_{\text{cex}}\text{”} = 0.295 \pm 0.010$$

$$\text{“}k_{\text{tex}}\text{”} = 0.143 \pm 0.010$$

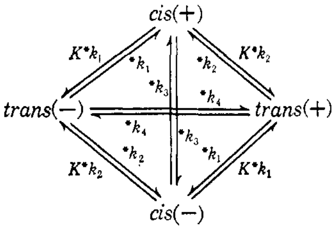
$$k_{\text{mut}} = 0.618 \pm 0.033$$

$$k_{\text{rac}} = 0.0243 \pm 0.0021$$

The indicated uncertainties are standard deviations to be expected for the indicated quantities on the basis of the deviations of individual points from the best least-squares fits. To the extent that errors are randomly distributed, chances are only a few per cent that any quantity is in error by more than twice its standard deviation and are negligible that any quantity is in error by more than three times this amount.

Comparison of Isomerization and Polarimetric Measurements. Interconversion of the four stereospecific types of allylic chloride molecules is represented in Scheme I.

Scheme I



The rotation of the system at any time is given by

$$\alpha = ([cis(+)] - [cis(-)])\alpha_{\text{C}} + ([trans(+)] - [trans(-)])\alpha_{\text{T}} \qquad (21)$$

where α_{C} and α_{T} are the rotations of completely resolved *cis* and *trans* isomers, respectively. The kinetic behavior can be described by four linear dif-

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[13] I. M. Kolthoff, S. Bruckenstein, and M. K. Chantooni, *J. Am. Chem. Soc.*, **83**, 3927 (1961).

ferential equations of the form

$$\frac{d[cis(+)]}{dt} = {}^*k_1[trans(-)] + {}^*k_2[trans(+)] + {}^*k_3[cis(-)] - (K{}^*k_1 + K{}^*k_2 + {}^*k_3)[cis(+)] \qquad (22)$$

Such a system of equations can be solved by standard methods;[14] the mathematical details are available elsewhere.[2] Although Scheme I involves four rate constants, the degeneracies of the system are such[2] that α can be expressed by a two-term equation of the form

$$\alpha = \alpha_A e^{-{}^*k_A t} + \alpha_B e^{-{}^*k_B t} \qquad (23)$$

where values of α_A and α_B are related to the initial conditions of a particular experiment. The rate constants of eq 23 can be related to those of Scheme I by

$$ {}^*k_A = {}^1/_2(P + Q) \qquad (24)$$

$$ {}^*k_B = {}^1/_2(P - Q) \qquad (25)$$

where

$$P = {}^*k_A + {}^*k_B = (1 + K)({}^*k_1 + {}^*k_2) + 2({}^*k_3 + {}^*k_4) \qquad (26)$$

$$Q = {}^*k_A - {}^*k_B = [P^2 - 8(2K{}^*k_1{}^*k_2 + ({}^*k_1 + {}^*k_2)({}^*k_3 + K{}^*k_4) + 2{}^*k_3{}^*k_4)]^{1/2} \qquad (27)$$

Since the experimental data have already been fitted to an equation of the form of (23), it is permissible to equate ${}^*k_A$ with ${}^*k_{mut}$ and ${}^*k_B$ with ${}^*k_{rac}$. Since all experimental rate constants are first order in TEACl, asterisks can be omitted in subsequent equations involving these quantities.

Since $k_{tis} = k_1 + k_2$, eq 5 becomes

$$k_{iso} = (1 + K)(k_1 + k_2) \qquad (28)$$

Then eq 26–28 can be rearranged to

$$k_{mut} + k_{rac} - k_{iso} = 2(k_3 + k_4) \qquad (29)$$

$$\frac{k_{mut}k_{rac}}{k_{iso}}(1 + K) + k_{iso} - k_{mut} - k_{rac} = \frac{4(Kk_1k_2 + k_3k_4)}{k_1 + k_2} + 2(K - 1)k_4 \qquad (30)$$

Rate constants on the left-hand sides of eq 28–30 are experimentally measurable; those on the right-hand sides are defined by Scheme I. To the extent that this scheme correctly identifies the over-all processes and provided that only one molecule of cyclohexenyl chloride participates in each rate-determining step, these equations are exact independent of detailed mechanism.

Of course measurements of the three quantities k_{iso}, k_{mut}, and k_{rac} are not sufficient to determine the four rate constants in Scheme I. However, the experimental observations permit four specific mechanistic conclusions to be made with somewhat decreasing certainty.

As is shown in Figure 3, for runs starting with *cis* isomer the sign of the angle of rotation is reversed before the final racemization occurs. This observation requires the unequivocal conclusion that (1) *in more than half of the cis–trans isomerization events, the reactant and product molecules have rotations of opposite sign.* It follows that

$$k_1 > k_2 \qquad (31)$$

Because negative rate constants are impossible, the right-hand side of eq 29 must be positive or zero. The experimental values in the summary indicate that the left-hand side of this equality is not zero unless the reported value of k_{iso} is 12 standard deviations too small or the reported value of k_{mut} is six standard deviations too large. We conclude with considerable confidence that k_3 and k_4 are not both zero. Hence, (2) *at least a significant fraction of the events contributing to racemization are not accompanied by cis–trans isomerization.*

Since $K > 1$, the right-hand side of eq 30 must also be positive or zero. If it is zero and if eq 31 is also satisfied, both k_2 and k_4 must be zero. Since (as is shown later) k_1 is by far the largest of the rate constants, small positive values of k_2 will cause the value of eq 30 to deviate from zero more than will the same values of k_4.

The reported values of k_{iso}, k_{mut}, k_{rac}, and "K" lead to a negative value of the left side of eq 30 in spite of the absolute mathematical proscription of such a contingency. If the reported values of k_{iso}, k_{rac}, and "K" are increased and that of k_{mut} is decreased such that all changes are 1.64 standard deviations, the value will be zero. Alternatively, the value will be zero if k_{mut} is decreased 2.9 standard deviations while the other values remain unchanged. Theories of statistics suggest a discouragingly small but not completely implausible probability that errors of this magnitude might be due to random fluctuations, but the experimental data argue moderately strongly for a negligibly small value of k_2 and somewhat less strongly for a small value of k_4. The mechanistic conclusions based on these experimental values are that (3) *virtually no racemization events involve simultaneous cis–trans isomerization*, and (4) *the rate constant for racemization of cis molecules is probably considerably greater than that for the racemization of trans molecules.*

If indeed $k_2 = k_4 = 0$, the most satisfactory fit to the data gives

$$k_3 = 0.056 \text{ l./mole min} \qquad (32)$$

Comparison of Isomerization and Exchange Measurements. Equations 11 and 15 indicate the equality

$$\text{“}k_{eqi}\text{”} = k_{eqe} \qquad (33)$$

The agreement is to within about half a per cent between quantities having standard deviations of 4% or less.

It follows that (5) *if K = "K," then in any system at isomeric equilibrium the rate at which molecules exchange is equal to the rate at which they undergo cis–trans isomerization.* The further mechanistic conclusions that can be drawn are influenced by which of three additional assumptions is adopted.

Assumption A is that the isomeric allylic chlorides are correctly assigned by the designations in quotation marks in Figure 1 and that all use of quotation marks in the above discussion has been superfluous. If this assumption is correct, eq 9, 10, 12, and 13 indicate that the equality of eq 33 is fortuitous and that systems rich in *trans* isomer undergo exchange more rapidly than isomerization while systems rich in *cis* undergo isomerization more rapidly than exchange. The sub-

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[14] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, p 173.

sequent discussion will reveal some of the mechanistic difficulties of chloride ion catalyzed *cis–trans* isomerization unaccompanied by exchange. These difficulties are sufficient to render assumption A very doubtful.

Assumption B is that molecules isomerize and exchange at equal rates in all systems whether at isomeric equilibrium or not. Such an assumption requires that $k_{\text{cis}} = k_{\text{cex}}$ and $k_{\text{tis}} = k_{\text{tex}}$. If eq 5, 8, 12, and 13 are solved simultaneously with the additional relation

$$K = \frac{(1 - \tau)``K" + \gamma}{1 - \gamma + \tau``K"} \tag{34}$$

derivable from eq 1 and 2, the solution gives

$$K = 2.36 \tag{35}$$

$$k_{\text{cis}} = k_{\text{cex}} = 0.315 \text{ l./mole min} \tag{36}$$

$$k_{\text{tis}} = k_{\text{tex}} = 0.134 \text{ l./mole min} \tag{37}$$

$$\gamma = 0.111 \tag{38}$$

$$\tau = 0.051 \tag{39}$$

Assumption B thus permits an internally consistent combination of isomerization and exchange results that requires only trivial change in the kinetic isomerization conclusions based on the assignments designated by quotation marks in Figure 1.

Application of these γ and τ values to the absorbance data gives $\epsilon_{1282}{}^{cis} = 46.24$, $\epsilon_{1282}{}^{trans} = 13.18$, $\epsilon_{1258}{}^{cis} = 8.18$, and $\epsilon_{1258}{}^{trans} = 35.62$. These points represent the ends of the line in Figure 1 and are designated *cis*(B) and *trans*(B).

A further argument for the reasonableness of this interpretation is provided by the numerical values. Apparently some isomerization occurs during conversion of allylic alcohol to chloride. If the isomerization path involves a transition state equilibrated with allylic chloride, then microscopic reversibility requires that $\gamma/\tau = K$. For the above results, $\gamma/\tau = 2.19$ in good agreement with this prediction.

Most physical organic chemists regard equality in the rates of two processes as evidence for simultaneity of occurrence. Then assumption B leads to the conclusion (6) *isotopic exchange is almost invariably accompanied by cis–trans isomerization and vice versa.*

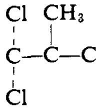
Assumption C is that the equality of eq 33 is fortuitous and that k_{eqe} is really greater than k_{eqi} with the rate of exchange generally greater than that of isomerization. This assumption requires that the assignment in quotation marks in Figure 1 is incorrect and that $\gamma/\tau > K$.

Although a small inequality corresponding to this assumption cannot be ruled out, the mechanistic conclusions reached below must be valid unless the difference between isomerization and exchange rates is great enough that all of the racemization can be explained by SN2′ type processes. Then $k_{\text{cex}} - k_{\text{cis}} = k_3 = 0.056$ l./mole min if conclusions 3 and 4 are accepted. Solution of the simultaneous equations with this restriction gives $K = 2.83$, $k_{\text{eqi}} = 0.173$, $k_{\text{cis}} = 0.332$, $k_{\text{cex}} = 0.388$, $\gamma = 0.343$, and $\tau = 0.095$.

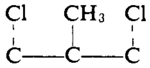
This set of figures requires that when a sample of allylic chloride was prepared from a pure *cis* or *trans* alcohol, the material went over 40% of the way to isomeric equilibrium during the first few minutes of the preparation, underwent this large amount of isomerization reproducibly in several preparations, went a greater fraction of the way to equilibrium in preparations starting with *cis* alcohol than with *trans* alcohol, and did not undergo further isomerization during the distillation and work-up of the product chloride. These values of γ and τ also lead to a *negative* value for $\epsilon_{1258}{}^{cis}$! We believe these implausible requirements and the resulting impossible interpretation of the absorbance data require assumption C to be rejected as a method for interpreting the observations.

Symmetry suggests a fourth assumption that k_{eqe} is really smaller than k_{eqi}. Such an assumption requires that the rate of chloride-catalyzed isomerization is generally faster than that of exchange, and we have not been able to devise any mechanistic explanation of such a possibility.

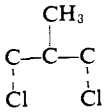
Mechanistic Consequences of Rate Comparisons. The possible transition states can be represented by projection in a plane perpendicular to that of the three allylic carbons and containing the outermost of those carbons. The four conventional nucleophilic substitution mechanisms are illustrated by structures a–d.



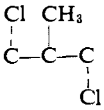
a SN2



b *cis*-SN2′(*cis*)



c *cis*-SN2′(*trans*)



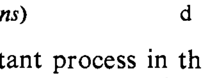
d *trans*-SN2′

The most important process in the system obviously involves simultaneous *cis–trans* isomerization and exchange with reversal of the sign of rotation. Goering, Nevitt, and Silversmith[3,8] have demonstrated that *cis* and *trans* chlorides attached to the same carbon have opposite signs of rotation. Therefore (7) *the conventional SN2 process (structure a) is the most common reaction in the system.*

Conclusion 3 above requires that (8) *the trans-SN2′ process (structure d) is unimportant.* This conclusion is consistent with the observations of Stork and White[15] on SN2′ reactions in a very different system.

Assumption C permits the racemization to be explained by *cis*-SN2′ reactions (structures b and c). However, the above discussion has shown that assumption B is a much more plausible explanation of equality 33. If this assumption is accepted, (9) *the cis-SN2′ processes (structures b and c) are also unimportant.*

Another conceivable structure in this system is the "platter" designated e. It is clearly racemic and will result in exchange half of the times in which it is formed.



e platter

It could explain the consequence of assumption A that the *cis* chloride must undergo isomerization more rapidly than exchange, but it could do so only if structure e is not a transition state but an intermediate that is more apt to produce *trans* product than *cis*. Even though structure e can account for isomerization with-

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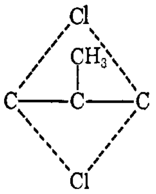
(15) G. Stork and W. N. White *J. Am. Chem. Soc.*, 78, 4609 (1956).

out exchange, it frequently results in racemization with simultaneous *cis–trans* isomerization in violation of conclusion 3 above. It therefore seems permissible to reject both assumption A and structure e.

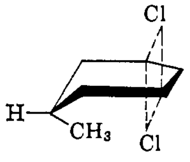
The argument leads by the method of Holmes[16] to the "sandwich" designated f. This type of structure has been proposed previously to explain anion-catalyzed rearrangements in phenylallyl systems[17] and iodine atom reactions with allyl iodide.[18]



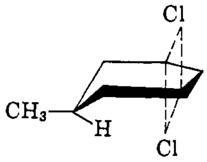
f sandwich

Structure f is clearly racemic, but the two chlorines are not equivalent. If the chlorine that adds during its formation is different from the one that ultimately dissociates, the consequences would frequently be similar to those of the *trans*-SN2′ process that has already been rejected; hence the formation of structure f is controlled by kinetic rather than thermodynamic considerations. This fact and conclusion 4 indicate that (10) *structure f is usually formed from cis allylic chloride and usually reverts to the same isomer.*

This conclusion can be rationalized by examining the steric influence of the methyl group. Five of the ring carbons in structure f are virtually coplanar. Structures g and h illustrate the isomeric possibilities for the carbon containing the methyl group. The methyl group and the chlorine *cis* to it are so crowded in structure g that this structure is not apt to exist. Even in structure h, the chlorine *trans* to the methyl is crowded by the hydrogen on the extraplanar carbon and is apt to be less strongly held. Hence structure h is most apt to form from and the revert to the *cis* allylicc hloride.



g



h

The above rationalization is related to the interesting observation of Goering and Josephson[4] that the acid-catalyzed racemization of *trans*-5-methyl-2-cyclohexenol is usually accompanied by exchange of oxygen with the solvent, while racemization of the *cis* alcohol usually takes place intramolecularly without oxygen exchange. These authors also recognized that five of the six ring carbons were virtually coplanar in the carbonium ion or transition state and proposed that the sixth carbon was on the same side of the plane as the alcohol oxygen. If the sixth carbon is instead on the opposite side of that plane, the *trans* alcohol would have to racemize with exchange by a *cis*-SN2′ mechanism, while the *cis* alcohol could racemize intramolecularly without exchange by a mechanism similar to structure h. In such a mechanism, either one or two water molecules could solvate the opposite side of the allylic system while the alcohol oxygen migrated.

Then the final mechanistic conclusion for the chloride reactions is that (11) *the transition-state structures a and f–h must be invoked to account for the experimental observations. These two structures are sufficient to account for all of these observations, although it is not possible to reject small contributions from paths passing through others of the proposed structures.*

Summary of Mechanistic Argument. Although the detailed argument is necessarily involved, the basic reasoning can be summarized very briefly.

The most important reaction involves simultaneous *cis–trans* isomerization and exchange with reversal of sign of rotation; it is SN2 substitution with entering and leaving chlorines on the same carbon atom.

The sum of the rates of mutarotation and racemization is over 40% more than that of *cis–trans* isomerization. The analysis based on Scheme I shows this difference requires that most reactions leading to racemization are not accompanied by isomerization and that *trans*-SN2′ processes are hence unimportant.

Although *cis*-SN2′ processes lead to racemization without isomerization, they require exchange at a greater rate than isomerization. Since the two latter rates seem to be equal, these processes also appear to be unimportant.

The sandwich structure satisfies the necessary requirement of a mechanism leading to racemization without either isomerization or exchange, and subtle quantitative arguments of somewhat less certain validity suggest that *cis* isomers react preferentially by this structure.

Implications for Other Systems. This study was undertaken in order to measure lifetimes of different types of ion pairs. The specific system was chosen because these allylic compounds were well known[4] to undergo unimolecular ion-pair processes in polar protic solvents. If the keen insights of Parker[19] had been available at that time, we might have anticipated our subsequent discovery that bimolecular processes predominate in this polar aprotic solvent.

The racemization plot of Figure 7 does suggest a small intercept consistent with a unimolecular process. When this intercept is corrected for the chloride-independent contribution to decomposition, the remainder is almost exactly one standard deviation. Hence chances are slightly better than even but very unconvincing that some unimolecular racemization has been observed. There is no evidence whatsoever for a unimolecular contribution to the *cis–trans* isomerization.

Apparently aliphatic allylic systems do not lend themselves to studies of ion-pair processes in aprotic solvents. The more labile phenylallyl systems do undergo some unimolecular rearrangement in aprotic solvents,[17] but bimolecular processes are apt to be major competitors.[20]

The highly reactive triarylmethyl species in aprotic solvents certainly undergo unimolecular dissociations to ions or ion pairs,[21] but we are not aware of trapping experiments indicating reaction with solute species could compete with collapse of an ion pair. Thus,

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(16) Apparently the first chemical reference to this method is R. E. Dickerson, P. J. Wheatley, P. A. Howell, W. N. Lipscomb, and R. Schaeffer, *J. Chem. Phys.*, **25**, 606 (1956).

(17) D. J. Rawlinson and R. M. Noyes, *J. Chem. Soc.*, 1793 (1963).

(18) W. P. Cain and R. M. Noyes, *J. Am. Chem. Soc.*, **81**, 2031 (1959).

(19) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(20) J. K. Addy and R. M. Noyes, *J. Chem. Soc.*, 2473 (1964).

(21) U. Miotti and A. Fava, *J. Am. Chem. Soc.*, **88**, 4274 (1966).

data of Fava[22] on exchange in acetonitrile of tri(*p*-nitrophenyl)methyl chloride, $(O_2NC_6H_4)_3CCl$, with up to 0.10 M TEACl give no evidence that the apparent second-order component might be competition of chloride exchange with the collapse of a short-lived intermediate. Since the rate constant for such chloride exchange would presumably be of the order of 10^{10} l./mole sec, any ion pairs in this medium collapse in considerably less than 1 nsec.

Competition of this type in a partially protic solvent was recently claimed by Sneen and Larsen.[23] They studied the reaction of 2-octyl mesylate with sodium azide in aqueous dioxane. If k_{-1} is the first-order rate constant for collapse of an ion pair, and if k_N is the second-order rate constant for substitution of mesylate by azide in the ion pair, they find $k_{-1}/k_N = 0.27$ mole/l. in 75 vol. % water at 36.2°. It is not certain that the reaction of azide ion with the 2-octyl mesylate ion pair is diffusion controlled, but if it is then k_{-1} is about 3×10^9 sec^{-1}. In 25 vol. % water, 2-octyl brosylate and azide ion react with clean second-order kinetics indicating that $k_{-1} \gg k_N[N_3^-]$. The results suggest that ion-pair lifetimes decrease as solvents become more aprotic and that competitive techniques may be unsuitable for estimating lifetimes in such solvents, but more information is needed before mechanistic conclusions can be drawn with any confidence.

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Mass Spectrometry in Structural and Stereochemical Problems. CXLIX.[1] The Question of Ring Expansion in the Fragmentation of ^{13}C-Labeled Nitrogen Heterocycles[2]

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Abstract: The mass spectra of 1-^{13}C-methylisoquinoline, 1-methyl-^{13}C-isoquinoline, 2-^{13}C-methylindole, 2-methyl-^{13}C-indole, N-methyl-^{13}C-pyrrole, and N-methyl-^{13}C-indole were examined. In each case a large degree of skeletal rearrangement involving migration of the exocyclic methyl group was found to accompany the fragmentation leading to an [M − (H + HCN)] ion. The data are consistent with the intermediacy of azatropylium, quinolinium, pyridinium, or other ring-expanded ions along this fragmentation pathway. In the case of the C-methylated compounds, a marked preference for carbon–carbon *vs.* carbon–nitrogen migration was observed.

One of the more intriguing problems in mass spectrometry concerns the determination of the actual structures of fragment ions produced by electron impact. In the fragmentation of alkyl aromatic compounds, the question of ring expansion to tropylium ions has been of particular interest. Following the classic studies[4] of Meyerson and coworkers demonstrating that the fragment of mass 91 in the spectrum of toluene is best represented as a tropylium ion, similar ring-expansion processes have been proposed, generally on an intuitive basis, for the fragmentations of various alkylated heteroaromatic systems:[5] *e.g.*, furans[6] and benzofurans[7] → pyrylium ions, pyrroles[8] and indoles[9] →

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[3] Postdoctoral Fellow, 1966–1967.

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