97–99° (3.5 mm). The 3,5-dinitrobenzoate melted at 102–103°. *Anal.* Calcd for $C_{14}H_{14}O_7N_2$: C, 52.18; H, 4.38; N, 8.69. Found: C, 52.23; H, 4.50; N, 9.09.

Acknowledgments. We wish to thank the Whitehall Foundation who provided funds for the Perkin-Elmer 421 spectrophotometer upon which the spectral determinations were made. This research was supported in part by the National Institutes of Health, Grant No. A 107766, and the Petroleum Research Fund, administered by the American Chemical Society.

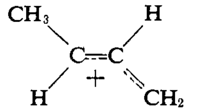
The Heat Capacity of Activation and Mechanism of the Hydrolysis of Methylallyl Chlorides

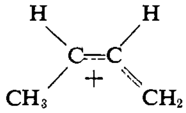
L. J. Brubacher,[1] L. Treindl,[1] and R. E. Robertson

Contribution No. 10294 from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. *Received January 11, 1968*

Abstract: Data from a careful study of the temperature dependence of the rate of hydrolysis in water of α-, β-, γ-*cis*-, and γ-*trans*-methylallyl chlorides are presented. The implications of these results together with the corresponding products are discussed in terms of the detailed mechanism.

The solvolysis of allylic types of halides has been widely studied and comprehensively reviewed by DeWolfe and Young.[2a] Various mechanisms have been postulated for the solvolysis of different allyl substrates in several solvent systems including normal bimolecular substitution (SN2), abnormal bimolecular substitution (SN2′), unimolecular substitution (SN1), and intramolecular isomerization *via* an ion-pair intermediate. In the silver ion assisted hydrolysis of α- and γ-methylallyl chlorides[2b] the reaction is presumed to proceed *via* a free carbonium ion in which the positive charge is delocalized over the allylic system. Since rotation about the partial double bond is unlikely, the carbonium ion can exist in either *cis* or *trans* geometry, depending on the geometry or conformation of the original substrate.


I (*trans*)


I (*cis*)

As a continuation of our studies on the temperature dependence of the enthalpy of activation of hydrolytic reactions in water, we have made a careful kinetic study of the hydrolysis of α-, β-, and γ-*cis*- and *trans*-methylallyl chlorides. We report here the thermodynamic activation parameters derived from this study and the products observed over the temperature range studied.

In previous publications we have concluded that the heat capacity of activation, $\Delta C_p^{\neq}$, is determined to an important degree by the temperature sensitivity of the structure of the solvation shell around the solute in the initial state.[3,4] The basic hypothesis is that this structure must be broken down in the activation process and the work so required makes a significant contribution to $\Delta F^{\neq}$.[4] As the temperature is raised the solvation shell around the solute becomes more mobile and the ground state becomes more like the transition state; thus $\Delta H^{\neq}$ decreases with rising temperature, and $d\Delta H^{\neq}/dT = (\Delta C_p^{\neq})$ is negative as observed. The actual value of $\Delta C_p^{\neq}$ will be related to the extent of solvent reorganization in the activation process, and empirically it would appear that $\Delta C_p^{\neq}$ may serve to distinguish between the SN1 and SN2 mechanisms for solvolysis in water[4] and in combination with $\Delta S^{\neq}$ in mixed solvents.[5] Thus $\Delta C_p^{\neq}$ generally has a value of −50 cal/mol deg for SN2 hydrolysis reactions of alkyl halides in water, and a corresponding value of −80 to −100 cal/mol deg for SN1 reactions. In this paper we show that this same generalization holds for the methyl-substituted allyl chlorides but must be applied with care if the reaction proceeds by two competing mechanisms.

Experimental Section

Materials. ***cis*-γ-Methylallyl Chloride.** 2-Butyn-1-ol was converted into *cis*-2-buten-1-ol according to the procedure of Georgoulous[6] modified to employ the Lindlar catalyst.[7] *cis*-γ-Methylallyl chloride (*cis*-crotyl chloride) was obtained by treatment of the latter alcohol with thionyl chloride.[2b] The chloride was finally purified by preparative gas chromatography using a 9 ft × 3/8 in. column of 15% β,β′-oxydipropionitrile on Chromosorb P (80–100 mesh), which is capable of separating the *cis* and *trans* isomers. A 6 ft × 0.25 in. column of the same material was used to check the purity of the final product on the F & M Model 700 gas chromatograph: injector, 100°; oven, 41°; detector, 197°; helium flow rate, 27 cc/min. The sample was found to contain none of the *trans* isomer within an estimated absolute experimental error of less than 0.3%. The purified compound was stored in a Parafilm-sealed flask at −20°.

***trans*-γ-Methylallyl Chloride (*trans*-Crotyl Chloride).** Material purchased as crotyl chloride from Columbia Organic Chemicals Co. was purified in the same way as the *cis* isomer. The final product contained 0.3% of the *cis* isomer and 0.04% α-methylallyl chloride.

α-Methylallyl Chloride. Material purchased as 3-chloro-1-butene from Columbia Organic Chemicals Co. was also purified by preparative gas chromatography. Since this compound isomerized readily to *trans*-γ-methylallyl chloride in the hot injector of the gas

---

[1] National Research Council of Canada Postdoctorate Fellow.

[2] (a) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, **56**, 753 (1956); (b) W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 1376 (1960).

[3] R. E. Robertson, *Suomen Kemistilehti*, *A*, 33, 63 (1960).

[4] R. E. Robertson, *Progr. Phys. Org. Chem.*, **4**, 213 (1967).

[5] G. Kohnstam, *Advan. Phys. Org. Chem.*, **5** (1967).

[6] C. Georgoulous, *Ann. Chim.* (Paris), **6**, 5 (1961).

[7] H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

Table I. Empirical Constants[a] for Rate Equation 1

Chloride	A	B	C	Exptl temp range, °C	n[b]
Allyl[c]	−8,312.903	−23.9642	81.2515	34–84	48
β-Methylallyl	−8,006.314	−23.3589	79.3662	47–87	35
α-Methylallyl	−10,989.75	−45.10898	145.42829	1–26	51
trans-γ-Methylallyl	−10,375.23	−40.08963	130.86891	6–28	59
cis-γ-Methylallyl	−9,173.300	−32.16028	106.67233	12–40	48

[a] For use with decadic logarithms. [b] Number of rate constants included in the calculation. [c] Reference 9b.

chromatograph, an injector temperature of only 55° was used in checking the purity. The purified compound contained 0.2% *trans*-γ-methylallyl chloride as the only impurity.

β-Methylallyl Chloride. Material was purchased as 3-chloro-2-methylpropene (practical grade) as distilled and passed through alumina. Kinetic purity was confirmed by rate studies.

Methods. Kinetic Measurements. Reaction mixtures were prepared by shaking approximately 12 μl of halide with 100 ml of deionized distilled water (containing up to 0.0002 *M* HCl as backing electrolyte) and filtering to remove undissolved solute. Four Kohlrausch cells were filled with this solution so that replicate determinations could be made at each temperature. Reaction rates were followed by a conductance method and the constant-temperature water bath was controlled to ±0.002° as described earlier.[4] By means of a computer program the conductance data were converted into concentration, using the Onsager equation, and fitted by a least-squares procedure to the integrated form of the first-order rate equation. The relative standard deviation of the experimental points from the calculated first-order curve was usually less than 0.01% and the scatter was random, indicating that the chlorides were indeed kinetically pure. (The *cis*-γ-methylallyl chloride was allowed to react for one half-life before measurements were begun in order to reduce the last traces of the faster reacting *trans* isomer.) The average of the three or four rate constants determined at each temperature usually showed a relative standard deviation of approximately 0.1% and never more than 0.2%.

Rate of Isomerization of α-Methylallyl Chloride to *trans*-γ-Methylallyl Chloride in Water. α-Methylallyl chloride (40 μl) was shaken with 1.6 ml of distilled water at 25.0° to form a temporary emulsion. This heterogeneous mixture was stirred continuously and shaken vigorously every 2–3 min until the reaction was interrupted by adding 2.0 ml of spectrograde methylene chloride which extracts the unreacted chlorides. To analyze for chlorides 50 μl of the methylene chloride layer was injected into the gas chromatograph equipped with the same column used to check substrate purity.

Product Analysis. To 2.00 ml of distilled water equilibrated to the desired temperature was added 50 μl of the desired chloride. The mixture was stirred until reaction was complete, then extracted twelve times with 0.8-ml aliquots of spectrograde methylene chloride. The combined extracts were analyzed for the product alcohols by gas chromatography using a 9 ft × 1/8 in. glass column packed with neopentyl glycol sebacate on Chromosorb: injector, 90°; oven, 40°; detector, 215°; helium flow rate, 60 cc/min. Control experiments showed that the extraction by methylene chloride was complete and that there was no significant rearrangement of the product alcohols in either water or methylene chloride during the times involved.

Results

The series of rate constant–temperature data[8] were fitted to an equation equivalent to

$$\ln k' = A' + \frac{B'}{T} + C \ln T$$

using the methodology given in the paper by Clarke and Glew.[9] The assumption in the above formulation is that $d\Delta C_p^{\ddagger}/dT = 0$, an assumption without theoretical justification but imposed by the practical limitations of experimental accuracy presently available and the limited temperature range studied. The reduced rate, k', was related to the measured rate as

$$k' = \frac{k_{\text{obsd}}}{Tk/h}$$

The values of the constants used were $k = 1.38034 \times 10^{-6}$ erg/°K, $h = 6256 \times 10^{-27}$ erg/sec, and $R = 1.9872$ cal/deg mol. Then for the case where $d\Delta C_p^{\ddagger}/dT = 0$, $RA' = (1/T)(\Delta H_T^{\ddagger} - \Delta F_T^{\ddagger}) - \Delta C_p^{\ddagger}(1 + \ln T)$, $RB' = (TC_p^{\ddagger} - \Delta H_T^{\ddagger})$, $RC' = \Delta C_p^{\ddagger}$, and the relation between A', B', C' and the constants given in Table I is given in the following equations: $A = B'/\ln 10$; $B = C' + 1$; $C = (A' + \ln k/h)/\ln 10$. These values may differ by small amounts from those published elsewhere[6] due to rounding approximations and constants, but these differences are negligible. The values of $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta C_p^{\ddagger}$ together with errors for a series of temperatures are given in Table II, and illustrate the increase in the error of derived constants when $(T - \phi)$ increases, where ϕ is the mid-temperature of the experimental range used in the Clarke–Glew transformation.

Rearrangement of Substrate Prior to Hydrolysis. Previous work has shown that, of the compounds under study, α-methylallyl chloride is most susceptible to intramolecular rearrangement, forming either *cis*- or *trans*-γ-methylallyl chloride.[2b] The kinetic results for this compound showed very good first-order behavior; therefore, α-methylallyl chloride does not isomerize to *cis*-γ-methylallyl chloride since the latter is fourfold less reactive than the former. However, this criterion cannot rule out the possibility of rearrangement to *trans*-γ-methylallyl chloride which hydrolyzes at five-sixths the rate of α-methylallyl chloride. In fact, the analysis of reacting mixtures of α-methylallyl chloride showed that *trans*-γ-methylallyl chloride was slowly formed. These experiments were performed on two-phase mixtures in which about 85% of the initially added α-methylallyl chloride was undissolved. Since the mixture was continuously agitated, and since *trans*-γ-methylallyl chloride is less soluble in water than the parent chloride, it is reasonable to assume that the *trans* isomer was extracted into the organic layer as it was formed. The ratio of rearrangement rate to hydrolysis rate for α-methylallyl chloride is then calculated to be 0.022. Knowing this value and the rate of hydrolysis of *trans*-γ-methylallyl chloride, and taking the observed hydrolysis rate for α-methylallyl chloride as a good approximation of the true rate, it is possible to calculate that the expected deviation from first-order behavior lies within experimental error as observed. Furthermore it may be calculated that the observed rate is 99.7% of the true rate at low temperatures and 99.5% of the true rate at the highest temperatures. This change with temperature arises because at the highest temperatures data were collected between the

---

(8) A complete record of the individual rates have been filed with the Depository of Unpublished Data, National Science Library, National Research Council, Ottawa, Canada.

(9) (a) E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 62, 539 (1966); (b) L. Treindl, R. E. Robertson, and S. E. Sugamori, in preparation.

Table II. Derived Thermodynamic Parameters for the Hydrolysis of Allylic Chlorides

		Allyl Chloride[a]		
Temp, °C	25	40	50	70
$\Delta F^{\ddagger}$, cal/mol	25531 ± 2	25665 ± 0.8	25774 ± 0.6	26037 ± 0.5
$\Delta H^{\ddagger}$, cal/mol	23239 ± 42	22495 ± 25	21999 ± 14	21007 ± 15
$\Delta S^{\ddagger}$, cal/mol deg	−7.69 ± 0.13	−10.12 ± 0.08	−11.68 ± 0.04	−14.66 ± 0.4
$\Delta C_p^{\ddagger}$, cal/mol deg	−50 ± 1.2			
k_1 (calcd), $\sec^{-1} \times 10^6$	1.180	7.883	24.6	184.3
		3-Chloro-2-methylpropene		
Temp, °C	40	50	60	80
$\Delta F^{\ddagger}$, cal/mol	25128 ± 4.5	25253 ± 1.92	25392 ± 1.2	25546 ± 1.2
$\Delta H^{\ddagger}$, cal/mol	21469 ± 121	20985 ± 78	2050 ± 39	20017 ± 30
$\Delta S^{\ddagger}$, cal/mol deg	−11.69 ± 0.37	−13.21 ± 0.24	−14.68 ± 0.12	−17.50 ± 0.19
$\Delta C_p^{\ddagger}$, cal/mol deg	−49 ± 4.5			
k_1, $\sec^{-1} \times 10^5$	6.431	9.404	25.98	80.06
		α-Methylallyl Chloride		
Temp, °C	**5**	**15**	**25**	40
$\Delta F^{\ddagger}$, cal/mol	21760.1 ± 0.4	21667.7 ± 0.4	21606.6 ± 0.7	21572 ± 0.4
$\Delta H^{\ddagger}$, cal/mol	24791 ± 27	23874 ± 12	22959 ± 39	21585 ± 85
$\Delta S^{\ddagger}$, cal/mol deg	10.89 ± 0.1	7.66 ± 0.04	4.53 ± 0.13	0.04 ± 0.28
$\Delta C_p^{\ddagger}$, cal/mol deg	−92 ± 3.1			
k_1, $\sec^{-1} \times 10^4$	0.4563	2.198	8.897	56.6
		trans-γ-Methylallyl Chloride		
Temp, °C	5	15	25	30
$\Delta F^{\ddagger}$, cal/mol	21863 ± 0.7	21774 ± 0.3	21713 ± 0.4	21693 ± 0.9
$\Delta H^{\ddagger}$, cal/mol	24753 ± 42	23937 ± 12	23121 ± 28	22712 ± 44
$\Delta S^{\ddagger}$, cal/mol deg	10.39 ± 0.14	7.51 ± 0.04	4.72 ± 0.09	3.36 ± 0.14
$\Delta C_p^{\ddagger}$, cal/mol deg	−82 ± 3.3			
k, $\sec^{-1} \times 10^4$	0.3783	1.808	7.43	14.30
		cis-γ-Methylallyl Chloride		
Temp, °C	5	15	25	40
$\Delta F^{\ddagger}$, cal/mol	22489 ± 0.9	22460 ± 0.3	22453 ± 0.2	22484 ± 0.4
$\Delta H^{\ddagger}$, cal/mol	23637 ± 29	22978 ± 16	22319 ± 5	21331 ± 21
$\Delta S^{\ddagger}$, cal/mol deg	4.12 ± 0.1	1.799 ± 0.05	−0.448 ± 0.02	−3.682 ± 0.068
$\Delta C_p^{\ddagger}$, cal/mol deg	−66 ± 1.4			
k_1, $\sec^{-1} \times 10^4$	0.1213	0.5408	2.138	3.995

[a] Reference 9b.

second and sixth half-life of the reaction since the first two half-lives were required for temperature equilibration of the reaction cells, whereas at low temperatures temperature equilibration required only a small fraction of the first half-life and data were collected over approximately the first four half-lives. Thus more of the rearranged isomer had collected to perturb the observed rate at high temperatures than at low temperatures. This small temperature-dependent change in the ratio of observed rate to true rate imposes a small negative component on $\Delta C_p^{\ddagger}$. However, it is so small an effect that it may be neglected, especially since it is partially cancelled by the small positive component imposed by the *trans*-γ-methylallyl chloride impurity which has a less negative $\Delta C_p^{\ddagger}$.

No intramolecular rearrangement of *trans*-γ-methylallyl chloride was detected by the same experimental method discussed above.

Hydrolysis Products. In Table III are summarized the product data for the chlorides in this study. Rearranged alcohols as well as normal alcohols were observed. These results are in good agreement with the available literature data.[2] In the case of β-methylallyl chloride, detection of rearrangement would require carbon labeling experiments. This was not done. The percentages shown in Table III are relative yields. Actual product recovery accounted for about 90% of the theoretical yield at low temperature and somewhat less at higher temperatures. Loss of reactant by evaporation from the two-phase mixture probably explains the incomplete recovery. No attempt was made to detect the possible elimination product, butadiene; if it is formed at all, it would account for less than 10% of the total products. An important generalization from Table III is that the amount of rearranged product from *cis*- and *trans*-γ-methylallyl chlorides increases with increasing temperature but is temperature independent for α-methylallyl chloride.

Table III. Reaction Products in the Hydrolysis of Methylallyl Chloride

Chloride	Temp, °C	% substituted allyl alcohol[a] α-Me	 *trans*-γ-Me	 *cis*-γ-Me	 β-Me
α-Methylallyl	2	67.0	33.0		
	15	66.6	33.5		
	28	66.0	34.0		
	40	67.0	33.0		
trans-γ-Methylallyl	2	46.4	53.6		
	15	49.0	51.0		
	25	49.0	51.0		
	28	53.4	46.6		
	40	55.5	44.5		
cis-γ-Methylallyl	15	34.9	2.5	62.7	
	25	34.6	3.1	62.4	
	28	39.3	3.5	57.2	
	40	44.7	1.0	54.3	
β-Methylallyl	68				90[b]

[a] Estimated absolute error is ±1.5%. [b] Besides the β-methylallyl alcohol a product component which constituted about 10% of total products was observed. It was shown not to be β-methyl-, *trans*-γ-methyl-, or *cis*-γ-methylallyl alcohol, but was otherwise unidentified.

Discussion

The results of this research indicate that the substituted methylallyl chlorides appear to hydrolyze in water by mechanisms similar to those in other solvents,[1] and arguments will be presented that these compounds exhibit a spectrum of mechanisms in water also ranging from SN1 (for α-methylallyl chloride) through mixed SN1, SN2 (for *cis*- and *trans*-γ-methylallyl chloride) to SN2 (for β-methylallyl chloride). For simplicity in the discussion of mixed SN1, SN2 reactions the assumption will be made that some hydrolytic events are pure SN1 and others pure SN2. However, a single mechanism which is intermediate between these extremes is also consistent with the data presented here.

α-Methylallyl Chloride. There is considerable experimental support for the view that α-methylallyl chloride hydrolyzes in aqueous solvent mixtures *via* the SN1 mechanism: (1) in aqueous ethanol the rate of hydrolysis is practically, independent of the concentration of hydroxide ion;[10] (2) in aqueous ethanol, aqueous acetone, and aqueous formic acid the *m* value[11] lies between 0.9 and 1.0;[12] (3) the solvolysis rate in 50% aqueous ethanol is much greater than in absolute ethanol.[13] Since water is a better ionizing solvent than aqueous ethanol there is little doubt that α-methylallyl chloride hydrolyzes also in pure water *via* the SN1 mechanism. Furthermore, under conditions where α-methylallyl chloride is known to react by an SN2 mechanism (with KI in acetone and sodium ethoxide in ethanol) it reacts about 100-fold slower than the γ-methylallyl chlorides.[14] Since the α- and γ-methylallyl chlorides react with nearly the same rate in water (see Table II), either or both of the isomers probably react by a mechanism other than SN2.

The large negative $\Delta C_p^{\neq}$ value of −92 cal/mol deg for α-methylallyl chloride (see Table II) is consistent with the SN1 mechanism. Other compounds which react by the SN1 mechanism such as *t*-butyl chloride[15] and cyclobutyl chloride[16] have similar values of $\Delta C_p^{\neq}$ (−83 and −107 cal/mol deg, respectively), in contrast with reactions that proceed by the SN2 mechanism where $\Delta C_p^{\neq}$ values of about −50 cal/mol deg are usual.[4] The hydrolysis products from α-methylallyl chloride are also consistent with the SN1 mechanism involving the fully developed carbonium ion, I, either at or subsequent to the transition state.

Rearranged and unrearranged alcohols result from attack at the primary and secondary carbons, respectively. The absence of *cis*-γ-methylallyl alcohol as a product supports the conclusion (see Results) that α-methylallyl chloride does not isomerize to *cis*-γ-methylallyl chloride during the reaction, and also indicates that the reaction proceeds exclusively *via* the *trans* carbonium ion intermediate I (*trans*), a rather surprising observation.

***trans*-γ-Methylallyl Chloride.** Since *trans*-γ-methylallyl chloride does not give the same ratio of products as α-methylallyl chloride, it may proceed in part by the SN2 mechanism.[2a] An alternative explanation that the products arise from competing SN2 and SN2′ mechanisms may be ruled out since the SN2′ mechanism is not likely to occur with a primary halide having a γ substituent and with water as the nucleophile.[1] The hypothesis of concurrent SN1 and SN2 mechanisms explains the temperature dependence of the ratio of rearranged to unrearranged alcohol product, if one assumes that the SN2 mechanism has a lower enthalpy of activation than the SN1 mechanism. That part of *trans*-γ-methylallyl chloride which reacts *via* the SN1 mechanism should give rise to the same product ratio that is found for α-methylallyl chloride since the reaction proceeds *via* the same intermediate, I (*trans*). On this basis it is possible to calculate that 70% of the reaction proceeds *via* SN1 at 2° and 83% at 40°. Thus the SN1 mechanism is dominant over the temperature range studied, and the observed $\Delta C_p^{\neq}$ should reflect this. However, the SN2 mechanism, with its less negative $\Delta C_p^{\neq}$, will impose a positive component on $d\Delta H^{\neq}/dT$. The observed value of $\Delta C_p^{\neq}$ of −82 cal/mol deg for *trans*-γ-methylallyl chloride is indeed slightly less negative than the value for α-methylallyl chloride and is consistent with the hypothesis of concurrent SN1 and SN2 mechanisms, but does not necessarily require mixed kinetics.

***cis*-γ-Methylallyl Chloride.** The same arguments used above for *trans*-γ-methylallyl chloride may be used for the *cis* isomer as well. Assuming that the *cis* carbonium ion I (*cis*) partitions in the same way as the *trans* carbonium ion, the product data in Table III imply that 67% of the reaction proceeds *via* the SN1 mechanism at 40° and 52% at 15°. Assuming that both the SN1 and SN2 mechanisms operate concurrently in the hydrolysis of *cis*-γ-methylallyl chloride, an attempt was made to reproduce the observed rates, activation parameters, and amount of rearranged product. Since the extent of solvent reorganization for the SN1 reaction of *cis*-γ-methylallyl chloride should be approximately the same as for α-methylallyl chloride, a $\Delta C_p^{\neq}$ value of −92 cal/mole deg was taken as a fixed parameter for the SN1 part of the calculation. The additional values shown in the footnote to Table IV were chosen by trial and error so as to give results in close agreement with the observed data. Using these parameters, values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated at several temperatures for both mechanisms so that the corresponding rate constants could be determined. At each temperature the rate constants for both mechanisms were added together to give the total rate constant. These synthetic rate constants were fitted to eq 1 ($\delta = 0.0002$; *cf.* Table I), and, from the empirical constants so obtained, values of k, $\Delta H^{\neq}$, and $\Delta S^{\neq}$ were calculated for several temperatures. The results are listed as calculated values in Table IV and are compared with the corresponding experimentally observed values which were determined from the empirical constants for *cis*-γ-methylallyl chloride shown in Table I. The agreement between calculated and observed values in Table IV, which could probably be improved slightly if the starting parameters were chosen with more care, is satisfactory. A similar calculation for *trans*-γ-methylallyl chloride gives equally good agreement between calculated and observed values. Thus the hy-

---

[10] W. G. Young and L. J. Andrews, *J. Amer. Chem. Soc.*, **66**, 421 (1944).

[11] S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951).

[12] Reference 2a, 790.

[13] C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

[14] Reference 2a, p 765.

[15] E. A. Moelwyn-Hughes, R. E. Robertson, and S. Sugamori, *J. Chem. Soc.*, 1965 (1965).

[16] C. Y. Wu and R. E. Robertson, *J. Amer. Chem. Soc.*, **88**, 2666 (1966).

Table IV. Comparison of Calculated and Experimental Data for *cis*-γ-Methylallyl Chloride Assuming Concurrent SN1 and SN2 Mechanisms[a]

T, °C	% rearranged product Calcd	% rearranged product Obsd	$k \times 10^4$, sec^{-1} Calcd	$k \times 10^4$, sec^{-1} Obsd	$\Delta H^{\neq}$, cal/mol Calcd	$\Delta H^{\neq}$, cal/mol Obsd	$\Delta S^{\neq}$, cal/mol deg Calcd	$\Delta S^{\neq}$, cal/mol deg Obsd	$\Delta C_p^{\neq}$, cal mol deg Calcd	$\Delta C_p^{\neq}$, cal mol deg Obsd
10			0.2629	0.2630	23277	23317	2.81	2.96	−62	−66
15	35.3	34.9	0.5459	0.5466	22968	22988	1.73	1.80		
20			1.095	1.097	22658	22658	0.66	0.67		
25	38.5	34.6	2.130	2.133	22348	22329	−0.38	−0.45		
28	39.2	39.3	3.127	3.130	22162	22131	−1.00	−1.11		
30			4.017	4.019	22038	21999	−1.41	−1.54		
35			7.361	7.355	21729	21669	−2.43	−2.62		
40	43.4	44.7	13.13	13.09	21419	21340	−3.43	−3.68		

[a] For the calculated data the values used for $\Delta H^{\neq}$ (10°), $\Delta C_p^{\neq}$, and k (10°) were 25,160 cal/mol, −92 cal/mol deg, and 1.350×10^{-5} sec^{-1}, respectively, for the SN1 mechanism, and 21,180 cal/mol, −60 cal/mol deg, and 1.280×10^{-5} sec^{-1}, respectively, for the SN2 mechanism.

pothesis of two competing mechanisms can be made consistent with the experimental data for both *cis*- and *trans*-γ-methylallyl chlorides.

Rationalization of the values chosen for $\Delta C_p^{\neq}$ and $\Delta H^{\neq}$ for the SN2 part of the reaction of *cis*-γ-methylallyl chloride is in order. The value of −60 cal/mol deg chosen for $\Delta C_p^{\neq}$ is somewhat more negative than the value of −50 cal/mol deg usually observed for the SN2 mechanism with primary alkyl halides.[4] In the SN2 reactions of alkyl halides the negative contribution to $\Delta C_p^{\neq}$ by solvent reorganization in going from the ground state to the transition state is believed to arise largely from the developing anion part of the molecule with a small positive contribution to $\Delta C_p^{\neq}$ from interaction between the nucleophile and the reacting center.[4] However, in *cis*-γ-methylallyl chloride the methylvinyl group, which can delocalize either negative or positive charge, facilitates SN2 reactions.[17] This long-range electronic readjustment in the molecule should have some effect on the solvent structure surrounding the alkenyl part of the molecule with a consequent negative contribution to $\Delta C_p^{\neq}$ in addition to that which arises from solvent reorganization about the developing anion. Furthermore, the small positive component of $\Delta C_p^{\neq}$ arising from interaction of the nucleophile with reactant will be correspondingly diminished. Thus a value of −60 for $\Delta C_p^{\neq}$ is not unreasonable for the SN2 reactions of the γ-methylallyl chlorides. There is no suggestion here that the coincidence so achieved necessarily implies that mixed kinetics exists, but it does show that the existence of mixed kinetics need not result in uncharacteristic values of $\Delta C_p^{\neq}$ such as an extreme example would imply. This permits a reasonable rationalization of the source of the products.

The choice of $\Delta H^{\neq}$ (10°) = 21,180 cal/mol for the postulated SN2 reaction of *cis*-γ-methylallyl chloride leads to a value of 20,280 cal/mol for $\Delta H^{\neq}$ at 25° which may seem unreasonably small when compared to the value of 23,260 cal/mole for the SN2 reaction of allyl chloride (see Table II). However, since the postulated SN2 part of the reaction of *cis*-γ-methylallyl chloride is 74-fold faster than allyl chloride at 25°, and since this rate enhancement by the γ-methyl group is an electronic effect rather than a steric effect, it is reasonable that the $\Delta H^{\neq}$ value for *cis*-γ-methylallyl chloride should be smaller than for allyl chloride. Furthermore, one would expect the $\Delta S^{\neq}$ values for the two compounds reacting by the same mechanism to be similar. This is indeed the case. For allyl chloride, $\Delta S^{\neq}$ (25°) = −7.7 cal/mole deg; for the postulated SN2 reaction of *cis*-γ-methylallyl chloride, $\Delta S^{\neq}$ (25°) = −9.1 cal/mol deg. The latter value is a mathematical consequence of the original choice of parameters in the calculation. Thus we feel that the value of $\Delta H^{\neq}$ chosen for the SN2 reaction of *cis*-γ-methylallyl chloride is reasonable (1) in the light of the rate enhancement argument and (2) because it gives rise to a reasonable value of $\Delta S^{\neq}$.

The small amount of *trans*-γ-methylallyl alcohol produced in the hydrolysis of *cis*-γ-methylallyl chloride has been ignored in the preceding considerations for the sake of simplicity. Since the *relative* error in determining this product for this particular case is large, no meaningful trend as a function of temperature can be detected. However, *trans*-γ-methylallyl alcohol is a real, though minor, product of the reaction. Its presence may be attributed to a slow (relative to product formation) isomerization of the *cis*-γ-methylallyl carbonium ion, I (*cis*), to the corresponding *trans* carbonium ion, I (*trans*). The intermediate I (*cis*) is probably more unstable than I (*trans*) because of steric hindrance between the methyl group and the *cis* hydrogen atom. Thus the conversion of I (*cis*) to I (*trans*) should be faster than the reverse reaction. This can account for the observed production of some *trans* alcohol from *cis* chloride and no *cis* alcohol from *trans* chloride within experimental error, providing that the difference between the free energies of the two ions is somewhat greater than the difference between the free energies of activation for the reaction of the two ions with water.

β-Methylallyl Chloride. The reaction of β-methylallyl chloride undoubtedly occurs *via* the SN2 mechanism; in aqueous ethanol this reaction is quite sensitive to the presence of added alkali;[18] the solvolysis rates in absolute ethanol and 50% aqueous ethanol are essentially identical.[14] Furthermore, in formic acid, where the reaction is probably SN1, β-methylallyl chloride is 5670-fold less reactive than α-methylallyl chloride,[17] whereas in water (see Table II) β-methylallyl chloride is only 300-fold less reactive than α-methylallyl chloride. Thus the reaction is probably SN2 in water. The observed value of $\Delta C_p^{\neq}$, −48 cal/mol deg, is consistent with this mechanism.

Finally, the entropies of activation shown in Table II are in agreement with previous results: positive values

---

[17] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1959, p 282.

[18] C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

for SN1 reactions (α-methylallyl chloride) and negative values for SN2 reactions (β-methylallyl chloride).

Effect of Reaction Impurities on the Heat Capacity of Activation. Some preliminary work done on unpurified samples of the allylic halides studied in this research points up the effect which certain impurities can have on derived thermodynamic parameters, particularly on the heat capacity of activation. In the present study this is most apparent in results obtained using a sample of *trans*-γ-methylallyl chloride which was later found to contain 6% of the *cis* isomer as an impurity. This has the effect of making the observed value of $\Delta H^{\neq}$ decrease more rapidly with increasing temperature than the true value does. Thus an erroneous value of $\Delta C_p^{\neq}$ of -170 cal/mol deg was obtained from these data.

The preceding case is one in which it was quite apparent from an inspection of the kinetic data that the results were in error. In general this will be the case if a significant impurity is at least twofold slower reacting or twofold faster reacting than the compound of interest.

A situation in which the presence of an impurity is less easily detected kinetically occurs when the impurity reacts at nearly the same rate as the compound of interest. This situation was encountered in preliminary work on the hydrolysis of a sample of α-methylallyl chloride which was later found to contain a 10% impurity of *trans*-γ-methylallyl chloride. The experimental results were observed to deviate noticeably from the first-order rate law at the high end of the temperature range, but to a much lesser extent than in the preceding case. Even so, the effect on the derived value of $\Delta C_p^{\neq}$ was considerable; a value of -125 cal/mol deg was obtained from these data compared to the value of -92 cal/mol deg (see Table II) obtained on a purified sample.

In summary we make the following suggestions for examining kinetic data in order to detect the presence of kinetically significant impurities. (1) The first-order plot should be examined for indications of nonrandom deviations from true first-order behavior. Clearly deviations are more likely to be apparent in the later part of the main reaction (*i.e.*, beyond 3–4 half-lives). (2) Where a conductance bridge accurate to $^1/_{5000}$ is used and $\Delta t^0 = 0.002°$, relative standard deviations for pure compounds are usually <0.01% provided adsorption of ions on the cell walls is minimized.

Mechanism of Electron Transfer Oxidation of Alkyl Radicals by Copper(II) Complexes

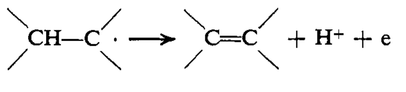
J. K. Kochi, A. Bemis, and C. L. Jenkins

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received February 1, 1968*

Abstract: The rates of oxidation of *n*-butyl, isopropyl, and neopentyl radicals by carboxylatocopper(II) complexes have been determined in acetonitrile–acetic acid solutions. The neopentyl radical is oxidized significantly slower than other alkyl radicals. Polar substituents have large effects on the relative rates of oxidative elimination and substitution of β-arylethyl radicals. Thus, the ratio of second-order rate constants k_e/k_s for oxidative elimination and oxidative substitution for a series of substituted β-phenethyl radicals varies from 50 for *m*-methoxy, 33 for hydrogen, 1.3 for *p*-methyl to 0.014 for *p*-methoxy. The rate of oxidative substitution is enhanced by electron-releasing substituents, but oxidative elimination is retarded by these polar groups. The *total rate* of oxidation (k_e/k_s) of these β-arylethyl radicals, however, is remarkably constant. We conclude that the rate-limiting step for oxidation of alkyl radicals by Cu^{II} precedes and is separate from the product-determining step. An alkylcopper intermediate which is reversibly formed is postulated. Oxidative substitution results from heterolysis of this organocopper species to Cu^I and a carbonium ion. (The β-arylethyl acetates isolated from the oxidation of β-phenethyl-β,β-d_2 and β-anisylethyl-α,α-d_2 radicals show complete equilibration of the α- and β-carbon atoms.) Oxidative elimination as a competing process also proceeds from the alkylcopper intermediate. Carbonium ions, as such, are not relevant to oxidative eliminations, since the styrenes which accompany the β-arylethyl acetates are not rearranged. The β-deuterium kinetic isotope effect in oxidative elimination of β-phenethyl radical is 2.8–2.9. We conclude that electron transfer to Cu^{II} has proceeded further than heterolysis of the β-proton in the transition state for oxidative elimination.

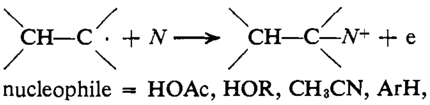
The electron-transfer oxidation of alkyl radicals by a variety of metal oxidants in solution generates alkenes and alkyl derivatives as the two principal types of products.[1–3] The standard (half-cell) reactions for oxidation of alkyl radicals can be represented by eq 1 and 2. The associated reduction of the metal oxidant

Oxidative elimination



(1)

Oxidative substitution



(2)

N = nucleophile = HOAc, HOR, CH_3CN, ArH, etc.

---

[1] J. Kochi and A. Bemis, *J. Amer. Chem. Soc.*, **90**, 4038 (1968).

[2] J. Kochi, J. Bacha, and T. Bethea, *ibid.*, **89**, 6538 (1967).

[3] J. Bacha and J. Kochi, *J. Org. Chem.*, **33**, 83 (1968).