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Kinetics of Dehydrochlorination of Chloroalkenes

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The kinetics of dehydrochlorination of five vinylic chlorides with sodium methoxide in methanol are reported. Energies and entropies of activation per mole are as follows: chloroethene (34.1 kcal., 9 e.u.), *cis*-1-chloropropene (34 kcal., 7 e.u.), *trans*-1-chloropropene (40.5 kcal., 10 e.u.), and 2-chloropropene (35 kcal., 8 e.u.) and *cis*-β-chlorocrotonate anion (28.6 kcal., 1 e.u.). Comparison of similar haloalkanes and -alkenes shows that their elimination rates are not too different. The present status of the elimination reaction (E2) with respect to structure-reactivity, mechanistic variations and medium effects is discussed briefly.

There is surprisingly little systematic information on bimolecular elimination (E2) reactions of vinylic halides.[1-4] Michael's useful stereochemical rule, that *trans*-located groups are eliminated more readily than *cis*-located groups,[5] has been used often.[6] However, the problems of multiple mechanisms, structure reactivity and medium effects have been recognized but have yet to be elucidated in detail. In this paper we report on the elimination reaction of five chloroalkenes in methanolic methoxide:

$$\mathrm{RCH{=}CR'Cl + CH_3O^-} \longrightarrow \mathrm{RC{\equiv}CR' + CH_3OH + Cl^-} \quad (1)$$

At the outset it is necessary to point out that we are here chiefly concerned with the structure-reactivity problem. It is understood that comparisons should be made for compounds undergoing elimination by well defined mechanisms. To rationalize the Michael rule, Cristol suggested that *trans* groups are eliminated in one step and that *cis* groups are eliminated in essentially a two step process involving a sterically labile carbanion.[4,7] Recently we have demonstrated that such eliminations show many mechanistic variations: They may be concerted or stepwise; the intermediate carbanion may or may not be sterically stable; the intermediate may lose halide in a *cis* or *trans* sense.[1,2] We have proposed a general elimination mechanism and derived a general rate law which embraces these possibilities. This rate law is necessarily complex, but in appropriate approximations appears to apply to real cases.[2] Therefore, since we are dealing with overall dehydrochlorination rates, our present data are useful more for gross structure-reactivity evaluation than for detailed insight into mechanism.

Apart from several elimination mechanisms, it is important to recognize other reactions of nucleophiles with vinylic halides.[8-10] For example, alkoxide substitution for halide may occur: 1) by elimination-addition through an alkyne intermediate, 2) by addition-elimination through a carbanion or substituted ethane, 3) by some other

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(1) S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 629 (1952).

(2) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

(3) S. J. Cristol and A. Begoon, *J. Am. Chem. Soc.*, **74**, 5025 (1952); E. Grunwald and S. J. Cristol, *J. Am. Chem. Soc.*, **77**, 2891 (1955).

(4) S. J. Cristol, A. Begoon, W. P. Norris, and P. S. Ramey, *J. Am. Chem. Soc.*, **76**, 4558 (1954); S. J. Cristol and W. P. Norris, *J. Am. Chem. Soc.*, **76**, 3005 (1954).

(5) A. Michael, *Ber.*, **34**, 4215 (1901); *J. prakt. Chem.*, **52**, 344 (1895).

(6) G. Huett and S. I. Miller, *J. Am. Chem. Soc.*, **83**, 408 (1961).

(7) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947); S. J. Cristol, N. L. Hause, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 674 (1951).

(8) S. I. Miller and P. K. Yonan, *J. Am. Chem. Soc.*, **79**, 5931 (1957).

(9) D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 2349 (1960).

(10) F. Montanari, *Boll. sci. fac. chim. ind. Bologna*, **16**, 31 (1958).

TABLE I

Rate Constants of Elimination Reactions of Chloroalkenes with Methoxide Ion[a]

RCH=CR'Cl, Mole Liter^{-1}	CH$_3$ONa, Mole Liter^{-1}	124.95°	109.1°	108.65°	93.53°	93.15°
CH$_2$=CHCl						
0.08875	0.14297	158 × 10^{-4}		253 × 10^{-5}		392 × 10^{-6}
0.22179	0.07149	158		261		403
0.03940	0.04289	164	272 × 10^{-5}		415 × 10^{-6}	
0.00773	0.05719	175	265		432	
k (liter mole^{-1} min.$^{-1}$)		(164 ± 9) × 10^{-4}	(269 ± 10) × 10^{-5}	(257 ± 5) × 10^{-5}	(424 ± 12) × 10^{-6}	(398 ± 9) × 10^{-6}
k_{corr} (liter mole^{-1} sec.$^{-1}$)		(315 ± 15) × 10^{-6}	(50 ± 2) × 10^{-6}	(48 ± 1) × 10^{-6}	(77 ± 2) × 10^{-7}	(72 ± 2) × 10^{-7}
CH$_3$CCl=CH$_2$		125.15°		108.89°	93.6°	
0.07087	0.07210	595 × 10^{-5}		103 × 10^{-6}	165 × 10^{-6}	
0.04114	0.14419	587		104	135	
0.02702	0.02884	600		84	160	
0.00689	0.05768	—		84	167	
0.00713	0.25408	600		—	123	
k (liter mole^{-1} min.$^{-1}$)		(596 ± 4) × 10^{-5}		(94 ± 11) × 10^{-6}	(150 ± 17) × 10^{-6}	
k_{corr} (liter mole^{-1} sec.$^{-1}$)		(114 ± 1) × 10^{-6}		(17 ± 2) × 10^{-6}	(27 ± 3) × 10^{-7}	
cis-CH$_3$CH=CHCl[b]		125.35°	109.03°		93.85°	
0.08043	0.07622	658 × 10^{-5}	99 × 10^{-5}		163 × 10^{-6}	
0.11548	0.05082	655	104		166	
0.01283	0.25408	586	95.5		155	
0.05100	0.10163	601	98.5		163	
0.02053	0.12704	530[c]	85[c]		138[c]	
k (liter mole^{-1} min.$^{-1}$)		(625 ± 32) × 10^{-5}	(99.3 ± 3) × 10^{-5}		(161 ± 3) × 10^{-6}	
k_{corr} (liter mole^{-1} sec.$^{-1}$)		(120 ± 6) × 10^{-6}	(186 ± 3) × 10^{-7}		(293 ± 6) × 10^{-8}	
trans-CH$_3$CH=CHCl		149.8°	125.3°			
0.06916	0.14838	181 × 10^{-6}	118 × 10^{-7}			
0.02719	0.22257	206	96			
0.10518	0.14838	200	89			
0.07394	0.12704	182	100			
0.05576	0.25408	194	106			
0.10360	0.07622	183	102			
k (liter mole^{-1} min.$^{-1}$)		(191 ± 9) × 10^{-6}	(102 ± 7) × 10^{-7}			
k_{corr} (liter mole^{-1} sec.$^{-1}$)		(38 ± 2) × 10^{-7}	(196 ± 14) × 10^{-9}			
β-CH$_3$CCl=CHCOO$^-$		108.6°	91.9°	79.5°		
0.06260	0.06444	0.0859	—	—		
0.03330	0.16435	0.103	0.0203	0.00552		
0.02193	0.24160	0.114	0.0236	—		
0.06202	0.13563	0.102	0.0207	0.00556		
0.03294	0.03294	0.0751	0.0138	0.00361		
0.04392	0.08784	0.0887	0.0176	0.00471		
k_0 (liter mole^{-1} min.$^{-1}$)[d]		0.0658	0.0123	0.00306		
k_{corr} (liter mole^{-1} sec.$^{-1}$)[d]		(123 ± 2) × 10^{-5}	(223 ± 2) × 10^{-6}	(55 ± 4) × 10^{-6}		

[a] Uncertainty in the temperature is ±0.1° to ±0.3°. [b] The factor 0.86 was used to correct the concentration of *cis*-chloropropene. [c] This run was not used in obtaining k_{corr}. [d] Rate constant at zero ionic strength.

path. For the compounds of this study, the intermediacy of the alkyne according to 1 seems reasonably well established. Vinyl chloride yields ethyne[11]; the 1- and 2- chloropropenes yield propyne[9,12,13]; *cis*-*β*-chlorocrotonic acid yields methylpropiolic acid.[14,15] In several other cases we shall discuss, the choice of a reaction path is not so clear.[16,17]

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[11] J. A. Nieuwland and R. R. Vogt, *The Chemistry of Acetylene*, Reinhold, N. Y., 1945, p. 18.

[12] J. Wislicenus, *Ann.*, **248**, 281 (1888); C. Friedel, *Ann.*, **134**, 262 (1865).

[13] A. Favorsky, *J. prakt. Chem.*, **37**, 382, 531 (1888).

TABLE II

KINETIC DATA FOR DEHYDROCHLORINATION OF CHLOROALKENES.[a] *Trans* ELIMINATIONS

Compound	$E_{exp.}$,[b] Kcal./Mole	$\Delta S\ddagger$,[b] Cal./Mole Deg.	$k_{100°}$, L. Mole^{-1} Sec.$^{-1}$	Medium[c]	Reference
$CH_2{=}CHCl$	34.1 ± 0.5	9 ± 2	5×10^{-5}	CH_3OH	[d]
$CHCl{=}CHCl$	35.1 ± 0.3	22 ± 1	1.25×10^{-2}	CH_3OH	1
	34 ± 1	24	1.5×10^{-1}	C_2H_5OH	18
	31	−0.4	3.4×10^{-5}	C_2H_5OH—KOH	18
$CH_3CH{=}CHCl$	34 ± 1	7 ± 3	1.86×10^{-5}	CH_3OH	[d]
$CH_3CCl{=}CH_2$	35 ± 1.5	8 ± 4	1.74×10^{-5}	CH_3OH	[d]
$CH_3CCl{=}CHCl$	31.9	15	2.3×10^{-2}	C_2H_5OH	17
$CH_3CH{=}CCl_2$	40.6	31	1.0×10^{-3}	C_2H_5OH	17
$^{-}OOCCCl{=}CHCOO^{-}$	23.1 ± 0.7	$-12 + 3$	3.3×10^{-3}	54% C_2H_5OH—NaOH	3
	21.0 ± 0.7	-16 ± 3	6.8×10^{-3}	H_2O	3
$CH_3CCl{=}CHCOO^{-}$	21.3	−12	3.5×10^{-2}	H_2O	[a], 16
$CH_3CCl{=}CHCOOC_2H_5$	19.2	−4	26	C_2H_5OH	[a], 9
		cis Eliminations			
$CHCl{=}CHCl$	29	−12	1.44×10^{-6}	CH_3OH	1
	20	−38	3.9×10^{-7}	C_2H_5OH—KOH	18
$CH_3CH{=}CHCl$	40.5 ± 1.5	10 ± 4	2.3×10^{-8}	CH_3OH	[d]
$CH_3CCl{=}CHCl$	31.5	7	9×10^{-4}	C_2H_5OH	17
$^{-}OOCCCl{=}CHCOO^{-}$	24.0 ± 0.7	-14 ± 3	3.6×10^{-4}	54% C_2H_5OH—NaOH	3
	24.9 ± 0.7	-9 ± 3	1.4×10^{-3}	H_2O	3
$CH_3CCl{=}CHCOO^{-}$	28.6 ± 0.6	1 ± 2	1.24×10^{-3}	CH_3OH	[d]
$CH_3CCl{=}CHCOO^{-}$	21.3	−12	3.8×10^{-2}	H_2O	[a], 16
$CH_3CCl{=}CHCOOC_2H_5$	17.6	−7	54	C_2H_5OH	[a], 9

[a] Note that the elimination path may be in doubt; remarks in this paper or in the citation bear on this matter. [b] The uncertainty in the activation parameters is that estimated in the referenced work. [c] Unless otherwise indicated, the conjugate base is used—*e.g.*, methanol-methoxide, water-hydroxide, etc. [d] This study.

In this work the overall rate of chloride production was followed in methanolic sodium methoxide. A second order rate law was used to treat the data. The rate data are given in Table I; representative plots are given in Figs. 1 and 2. The activation parameters are given in Table II. In the latter table are included previously reported elimination data on vinyl chlorides; for convenience these are grouped as *trans* or *cis* eliminations.[19] The data for the compounds of this study now make possible a preliminary survey of the field.

Within the chloroalkenes, there are large variations in reactivity, *ca.* 10^5 in the compounds given; undoubtedly the spread can be increased with other substituents. Speaking generally, vinyl chlorides are known for their low reactivity with nucleophiles.[8] Applied to dehydrohalogenation, this statement becomes misleading. For, if related ethanes and ethenes are compared, the relative dehydrochlorination rate (E2) for 2-chloropropane[28] and 2-chloropropene is *ca.* 20 at 109° and for 1,2-dichlorosuccinate[29] and chlorofumarate[3] it is *ca.*

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(14) A. Michael and O. Schulthess, *J. prakt. Chem.*, **46**, 236 (1892); R. Friedrick, *Ann.*, **219**, 322 (1883).

(15) In the case of 2-chloropropene, the formation of propadiene followed by rearrangement to propyne cannot be completely excluded[18]; in the case of chlorocrotonic acid, addition-elimination may become competitive under some conditions.[14,16]

(16) I. T. A. Kudryavtseva and N. M. Chirkov, *Zhur. Fiz. Khim.*, **32**, 2236 (1958); **33**, 255 (1959); *Chem. Abstr.*, **53**, 10917 (1959).

(17) W. H. King and H. A. Smith, *J. Am. Chem. Soc.*, **72**, 95, 3459 (1950). These workers were studying substitution by ethoxide. For the *cis-* and *trans*-1,2-dichloropropenes they favor an elimination path; whether this is 1,2- or 2,3-dehydrohalogenation is unclear. For 1,1-dichloropropene there is evidence for 1,2-elimination—V. Valentin, *Ber.*, **28**, 2661 (1895).

(18) W. E. Truce, M. M. Boudakian, R. F. Heine, and R. J. McManimie, *J. Am. Chem. Soc.*, **78**, 2743 (1956); F. Martin and A. Bruylants, *Bull. soc. chim., Belge*, **60**, 259 (1951).

(19) Omitted are examples for which the kinetic data are incomplete or qualitative. In these cases structural assignments have been made or verified by the Michael rule; they include the 1-chloro-1-butenes,[20] 2-chloro-2-butenes,[20] 1-chloro-3-hydroxy-1-propenes,[21] 2-chloro-4-hydroxy-2-butenes,[22] α-chlorocinnamates,[23] β-chlorocinnamates,[24] α-chlorocrotonates,[12] several substituted 1-arylsulfonyl-2-chloroethenes,[25] and several 1-arylmercapto-2-chloroethenes.[26,10] Also omitted are bromo- and iodoalkenes for which some data have been listed elsewhere.[4,27]

(20) L. Navez, *Bull. soc. chim. Belg.*, **39**, 435 (1930).

(21) L. J. Andrews and R. E. Kepner, *J. Am. Chem. Soc.*, **69**, 2230 (1947).

(22) L. F. Hatch and P. S. Hudson, *J. Am. Chem. Soc.*, **72**, 2505 (1950).

(23) J. J. Sudborough and T. C. James, *J. Chem. Soc.*, **89**, 105 (1906).

(24) T. C. James, *J. Chem. Soc.*, **99**, 1620 (1911).

(25) L. Maioli and G. Modena, *Gazz. chim. ital.*, **89**, 854 (1959).

(26) E. Angeletti, F. Montanari, and A. Negrini, *Gazz. chim. ital.*, **87**, 1086 (1957).

(27) S. I. Miller, Doctoral dissertation, 1951, Library, Columbia University, New York 27, N. Y.

(28) E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937).

(29) H. V. W. Robinson and D. T. Lewis, *J. Chem. Soc.*, 1260 (1933).

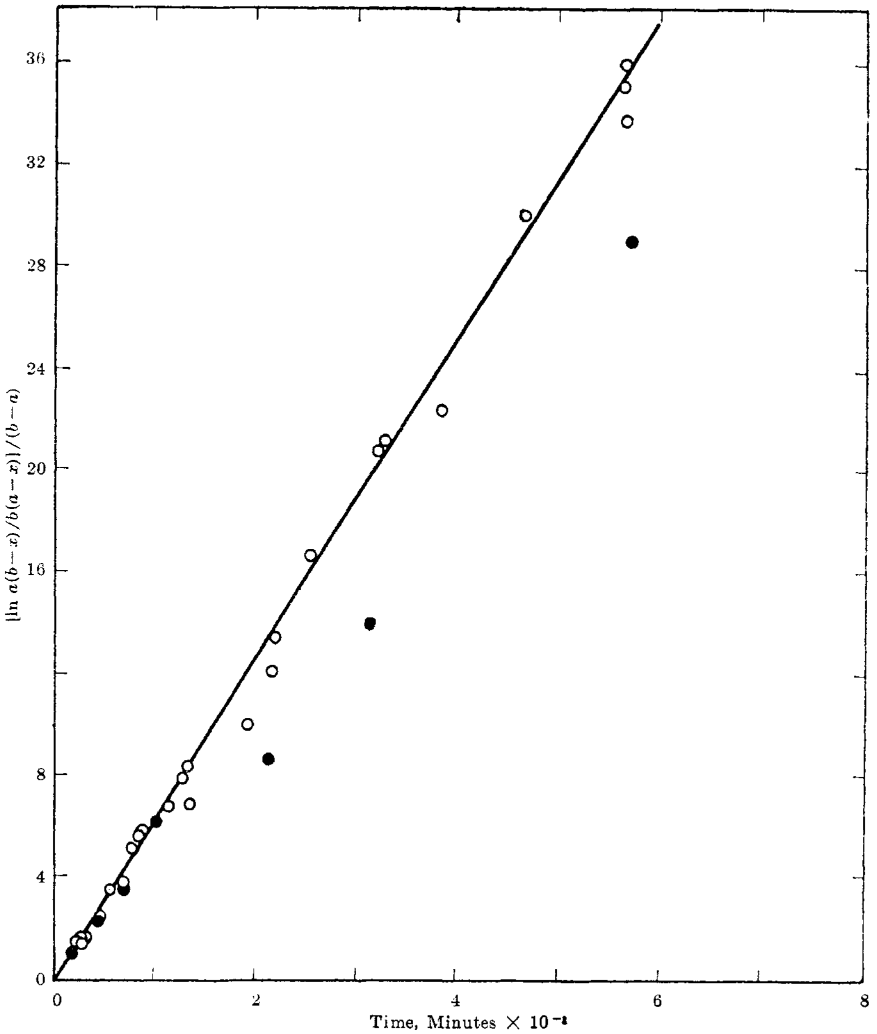

Fig. 1. Reaction of *cis*-1-chloropropene at 125.40 with methanolic-methoxide—four runs. To correct for an unreactive impurity the factor 0.86 has been used to correct the *cis* concentration. One run, solid circles, has not been used in obtaining *k*

1 at 25°. Confirmation of this observation was sought in other systems. The zinc debromination of 1,1,2,2,-tetrabromoethanes is somewhat faster than that of 1,2-dibromoethenes.[30] But the dehydrobromination rate of *cis*-β-bromostyrene[4] is actually *ca.* 10^2–10^3 times that of 1-phenyl-2-bromoethane[31] at 55°. We conclude that the reactivity of haloalkanes and haloalkenes in *trans* eliminations (E2) may be very similar. In passing, it is of interest that the *cis* elimination, sodium hydroxide with chlorobenzene,[32] is much slower than corresponding *cis* eliminations of chloroalkenes.

The Michael rule of favored *trans* elimination (E2) holds by factors of 10–10^4 over *cis* eliminations for chloroalkenes; larger or smaller factors have been reported for other haloalkenes.[19] From Table II it is clear that this stereochemical reactivity difference must be ascribed to both energy and entropy factors which themselves are composite for complex mechanisms.[2] The suggestion[7] that *cis* eliminations invariably have higher energies of activation than *trans* eliminations and that the difference can be estimated fairly simply appears to be invalid.

Let us examine the reactivity order of Table II. For any group of haloalkenes RCH=CClR′ one might predict that electron withdrawing groups R and R′ will render the proton more acidic but at the same time strengthen the C-Cl bond. Using the Hammett σ constants as a measure of electron-withdrawing ability,[33] it would appear that for the *trans* eliminations, the reactivity order for R is $CH_3 < H < COO^- < Cl$, that is, in order of increasing σ. Apparently the effect here is on proton lability. For R′ the order of rate enhancement is roughly the reverse of that for R:Cl < COO^- <

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[30] W. G. Lee and S. I. Miller, *J. Am. Chem. Soc.*, **82**, 2463 (1960); J. Wislicenus and P. Schmidt, *Ann.*, **313**, 210 (1900).

[31] E. D. Hughes, C. K. Ingold, S. Masterman, and J. McNulty, *J. Chem. Soc.*, 899 (1940).

[32] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1458 (1957).

[33] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

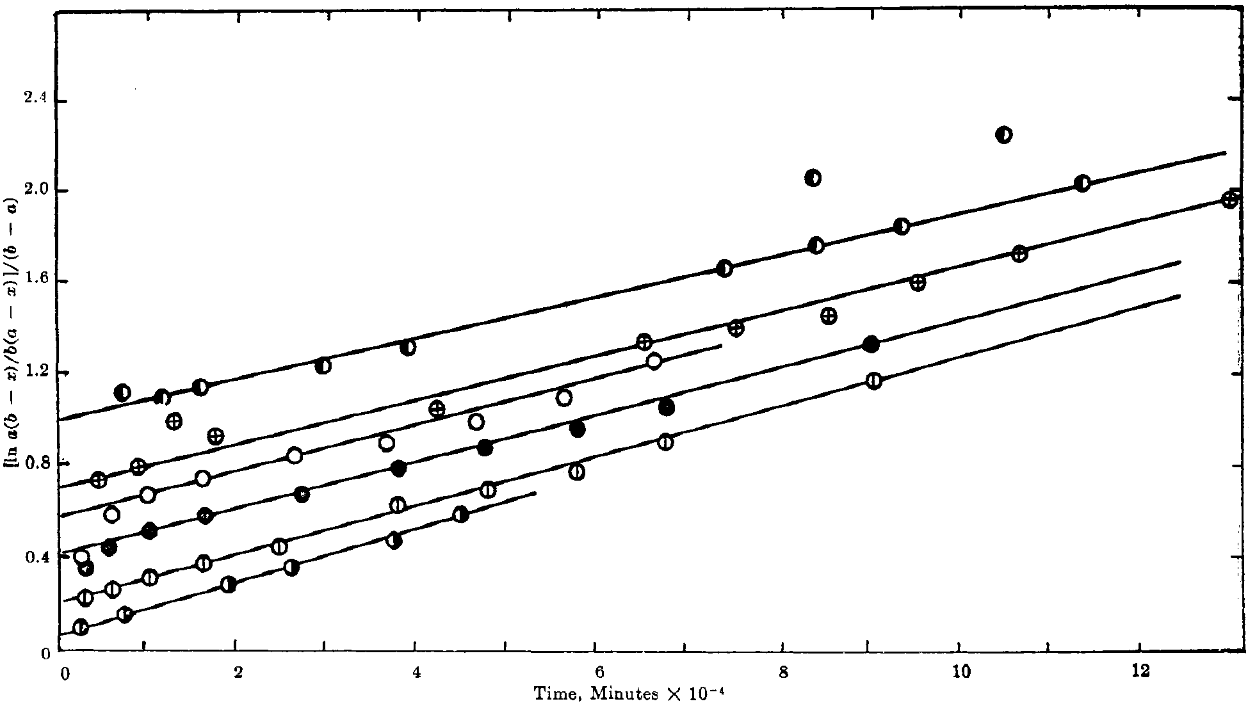

Fig. 2. Reaction of *trans*-1-chloropropene at 125.3° with methanolic methoxide

$CH_3 < H$. Bond strengthening of the C—Cl bond by the electron-withdrawing substituent is indicated. These remarks must be both tentative and qualitative because of the nature of the available data.

Fairly large solvent and ionic strength effects have been noted in elimination reactions of haloalkenes.[1,3,4] In this study the rate constant for methoxide with β-chlorocrotonate, an ion-ion reaction, increases as the ionic strength increases (see Table I); with methoxide and *trans*-1,2-dichloroethene, an ion-molecule reaction, the rate constant also increases with ionic strength.[1] The solvent effects are large and sometimes puzzling. Not only does solvent change affect the activation parameters, but it may affect them differently in related *cis*- and *trans*-isomers. For example, the rate at 129° of *cis*-1-chloropropene changes from our 1.7×10^{-4} in methanol-methoxide to 3.4×10^{-4} l. $mole^{-1}$ sec^{-1} in ethanol-ethoxide.[9] The relative *trans/cis* elimination rate of the 1,2-dichloroethenes changes from *ca.* 10^4 in methanol-methoxide to *ca.* 10^2 in potassium hydroxide–ethanol at 109°.[1,18] While it seems important to underline these large medium effects and possibly rationalize them, a complete discussion must await further careful experimental work.

EXPERIMENTAL

The procedure for preparing runs for kinetic studies has been described.[1] The ampule technique was used. Volatile compounds were usually distilled or sucked into tared thin-walled bulbs. Stock solutions of chloroalkene and standard sodium methoxide were made up to 250 ml. which was then aliquoted into ampules. In all runs two or three aliquots were treated with concentrated methoxide, heated to obtain an "infinity" value and titrated with standard silver nitrate. The concentration of haloalkene obtained in this way was used to calculate the rate constants.

Temperatures recorded are to ±0.1° to ±0.15°, except for the very slowest reactions, *e.g.*, *trans*-1-chloropropene in which the uncertainty may be ±0.3°. The rate constants are defined by

$$(b - a)kt = \ln a(b - x)/b(a - x) \qquad (2)$$

where a = initial concentration of haloalkene in mole $liter^{-1}$, b = initial concentration of sodium methoxide in mole $liter^{-1}$, x = concentration of chloride in mole liter at time t. The rate constants were calculated from kt *versus* t plots as well as by averaging results of the runs. They were then corrected for the expansion of solvent to give k_{corr} from which activation parameters were calculated.

The uncertainties in k are usually average deviations. For the activation parameters somewhat liberal estimates of the precision are given. As will be pointed out below, there were certain experimental problems in obtaining the kinetic data. Among these the volatility of some of the compounds and the long reaction times were notable. Other specific points relevant to each system will be given below.

Commercial vinyl chloride was distilled from a tank into cooled methanol and the solution was made up for kinetic runs as described. Occasionally white insoluble material, probably polymer, was deposited in the heated ampules. Flushing with nitrogen above the solution just before sealing the ampule removed this difficulty.

2-Chloropropene was prepared from acetone and phosphorus pentachloride.[34] The head fractions from three different preparations, all boiling below 27°, were combined and redistilled at b.p. 23.5° at 750 mm. (lit.,[17] b.p. 22.6–23.0° at 739 mm.) Infrared spectra of these head fractions showed them to be free of a high-boiling component, possibly 2,2-dichloropropane as well as the other chloropropenes. For the kinetic runs, "infinity" chloride titrations appeared to be more reliable than weighed amounts in giving final concentrations. This is attributed to the volatility of 2-

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(34) A. L. Henne and M. W. Renoll, *J. Am. Chem. Soc.*, 59, 2434 (1937).

chloropropene. There was also scatter and there were both positive and negative intercepts in the *kt versus t* plots. Therefore, the rate constants were calculated from the slopes of these plots.

The *cis*- and *trans*-1-chloropropenes were obtained from commercial chloropropene. The foreshot materials boiling under 28° were discarded. The fractions 28–37° were distilled and *cis*- and *trans*- rich cuts were redistilled. The cuts used were *cis*, b.p. 29.5–31.2° at 760 mm. (lit.[17] b.p. 30.8° at 738 mm.) and *trans*, b.p. 36.4° at 761 mm. (lit.[17] 37° at 738 mm.) Infrared spectra indicated intercontamination. For the kinetic runs "infinity" chloride values as well as the initial weights of the 1-chloropropenes were obtained.

Consistent with the presence of an unreactive impurity, the apparent rate constants of the *cis* isomer fell with time. If f is the fraction of *cis*-1-chloropropene actually present, then the following modification of 2 should be used to calculate k.

$$kt(b - fa) = 2.303 \log a(b - x)/b(a - x/f) \qquad (3)$$

For $b \gg fa$ and $f \simeq 1$, the initial points should give fair values of k. These k's can be used at large t's to evaluate f. This was done and it was found that $f = 0.86$ removed most of the curvature from the kt versus t plots and gave consistent k's independent of initial reactant concentrations (see Fig. 1). One "bad" run not used in the calculation of the final k is given for comparison.

Consistent with the presence of a reactive impurity in the *trans*-1-chloropropene, *kt versus t* plots showed positive intercepts in the *kt* axis. These plots were essentially parallel. It can be shown that if this impurity was the *cis*-isomer and its consumption by methoxide was relatively fast, the slopes of the *kt versus t* plots would give the true rate constant for *trans*-1-chloropropene (see Fig. 2). As different *trans* fractions were used, no single factor could be found to correct the concentrations—fortunately this was unnecessary. One other difficulty should be mentioned. Because the elimination was slow, it would have been desirable to make runs above 150°; however, the vapor pressure of the methanol at 150° was already dangerously high and occasional explosions of the Pyrex ampules did occur.

cis-β-Chlorocrotonic acid, m.p. 59–61° (lit.,[9] m.p. 60.3–60.6°) and sodium methoxide solutions were diluted with methanol (in this isomer the carboxylate and methyl groups are *cis*). The concentration of sodium methoxide is that remaining after the acid has been neutralized. Although the *kt versus t* plots appeared to be adequate, there appeared to be an ionic strength effect on k: log k appeared to increase linearly with $(a + b)$, that is, with the sodium chlorocrotonate plus the sodium methoxide concentrations (plots of k *versus* $(a + b)$ or log k *versus* $(a + b)^{1/2}$ showed somewhat more scatter). From plots of log k *versus* $(a + b)$, extrapolated values, k_0, were calculated which were then corrected for solvent expansion.

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CHICAGO 16, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Influence of Steric Hindrance on the Reaction of Acid Chlorides with Alcohols

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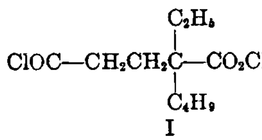
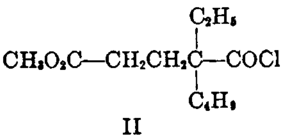
The reaction of α-butyl-α-ethyl-γ-carbomethoxybutyryl chloride (II) with alcohols is highly sensitive to traces of moisture. With carefully dried methanol at 0°, at least one fourth the yield was half ester. The unhindered acid chloride, I, is not subject to facile reaction with traces of water. At high temperature (180°), isomer II is no longer subject to preferential reaction with water. These results are correlated on the basis of dual reaction paths for the acid chloride (ionic and bimolecular displacement). Behavior of the hindered acid chloride under various conditions is consistent with the dual reaction path. There is described a high temperature method involving a continuous reactor for quantitative conversion of ester acid chloride II to dimethyl α-butyl-α-ethylglutarate.

In connection with an investigation[1] which required substantial quantities of the ester acid chloride, I, dimethyl α-butyl-α-ethylglutarate was required as an intermediate for synthesis of the ester acid chloride. Since direct esterification of the hindered carboxyl proceeds slowly and in poor yield,[2] and large amounts of diazomethane were regarded as undesirable, the diester was prepared by reaction of the ester acid chloride, II, with methanol. About one third the yield in this reaction, carried out at 0°, proved to be the half ester that would result from hydrolysis of II, even when there was used methanol that had been dried with magnesium. Although it was initially assumed that this half ester resulted from anhydride present as an impurity in II, this has proved not to be the case. Furthermore, isomer I or the ester acid chloride of glutaric acid reacts with undried commercial methanol, under the same conditions as used for isomer II, to give a quantitative yield of diester.



$$\mathrm{ClOC{-}CH_2CH_2\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle C_4H_9}{|}}{C}}{-}CO_2CH_3}$$

I



$$\mathrm{CH_3O_2C{-}CH_2CH_2\overset{\overset{\displaystyle C_2H_5}{|}}{\underset{\underset{\displaystyle C_4H_9}{|}}{C}}{-}COCl}$$

II

When acid chloride II was allowed to react with undried *n*-butyl alcohol, there was again obtained about 25% yield of half ester; however, butanol dried over magnesium gave only 10% yield of half ester. When the butanol, as well as the apparatus, was dried by azeotropic distillation the yield of half ester could be reduced to 5%, but this small amount persisted. The evidence suggests that the highly hindered acid chloride reacts with water

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[1] J. Cason and K. W. Kraus, *J. Org. Chem.*, **26**, 1772 (1961).

[2] J. Cason, *J. Org. Chem.*, **13**, 227 (1948).