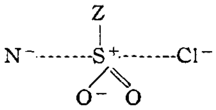
$SO_2Cl > C_6H_5SO_2Cl > m\text{-}NO_2C_6H_4SO_2Cl$. In each case electron supply assists the reaction. The slow rate for 1-chloroethanesulfonyl chloride cannot be attributed to a steric effect, because in the carbonyl chloride series the following S_N2 solvolytic rate sequence is observed[18]: $Cl_2CHCOCl > ClCH_2COCl > CH_3COCl$.

As noted above, the reactions of methanesulfonyl and benzenesulfonyl chlorides may proceed by a hydration mechanism. An intimation that this may be the case for the latter is obtained by plotting Hedlund's rate data[2] for substituted benzenesulfonyl chlorides against the Hammett σ-constants of the substituents (Fig. 3). The data for substituted benzoyl chlorides[1] are included for comparison. It can be seen that both plots fall into two parts. This behavior can be interpreted in terms of a duality of mechanisms.[6] Lines II and IV are considered to describe a region of reaction by direct displacement, while lines I and III describe a region where the hydration mechanism is dominant.

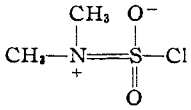
Negative Nucleophiles.—Here the reaction will be facilitated by strong coulombic attraction between N and S, as



Therefore, it is predicted that toward negative nucleophiles (hydroxide, phenoxide), methanesulfonyl chloride should be more reactive than benzenesulfonyl chloride. Again no data are available to test this prediction.

A similar point of view has been taken by Swain and Scott[3] in explaining the high reactivity of hydroxyl ion toward aromatic acid chlorides.

Ionization.—The high positive charge on sulfur may also be responsible for the S_N1 sequence, $(CH_3)_2NSO_2Cl < CH_3OSO_2Cl$. Since dimethylamino is much more effective than methoxyl at stabilizing a carbonylium ion, the observed sequence must mean that much of the stabilization by the former is already provided in the initial state by the resonance form:



$$CH_3-\overset{\displaystyle CH_3}{\underset{+}{N}}=\!=\!\overset{\displaystyle O^-}{\underset{\displaystyle \overset{\|}{O}}{S}}-Cl$$

Acknowledgments.—We are indebted to Dr. Paul W. Morgan for inspiration and encouragement and to Mr. Donald G. Preis for invaluable technical assistance.

WILMINGTON, DELAWARE

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[18] R. Leimu, *Ber.*, **70**, 1040 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Solvolysis and Base-catalyzed Dehydrohalogenation of 1,1- and 1,2-Dihalocyclohexanes[1]

BY HARLAN L. GOERING AND HERBERT H. ESPY[2]

RECEIVED SEPTEMBER 6, 1955

The relative rates of second-order dehydrohalogenation of 1,1- and *cis*- and *trans*-1,2-dihalocyclohexanes (dibromo-, dichloro- and bromochloro-) and cyclohexyl bromide and chloride in "80%" ethanol containing 0.1 *M* sodium hydroxide have been determined. Under the conditions of the kinetic experiments the reactions are second-order and E_2 elimination is not accompanied by S_N2 substitution. The solvolytic reactivities of a number of the compounds in "80%" ethanol were determined and show that under the conditions of the dehydrohalogenations, the E_2 reactions are essentially completely isolated from competing solvolysis except for the 1,1-dihalocyclohexanes. The order of reactivity for the E_2 dehydrohalogenation of the isomeric dihalides is: *cis*-1,2- $\gg$ 1,1- $>$ *trans*-1,2-. Under the conditions of the present experiments the 1,1- and *cis*-1,2-dihalocyclohexanes eliminate one molecule of hydrogen halide. The *trans*-1,2-dihalocyclohexanes give two molecules of hydrogen halide. The stoichiometry and relative reactivities indicate that a *trans*-elimination is involved. The relative reactivities, together with conformational considerations, provide information concerning the effects of α- and β-halogen atoms on the rate of dehydrohalogenation.

Introduction

In connection with other work[3] in this Laboratory pure samples of 1,1- and *cis*- and *trans*-1,2-dihalocyclohexanes (dibromo-, dichloro- and bromochloro-) were obtained. These compounds are suitable simple models for studying the stereochemistry of dehydrohalogenation and the effect of α- and β-halogen atoms on the rate of dehydrohalogenation. This paper describes the stoichiometry and relative rates of base-catalyzed dehydrohalogenation of these compounds and of cyclohexyl chloride and bromide in "80%" ethanol containing 0.1 *M* sodium hydroxide. With the isomeric 1,2-dihalocyclohexanes the orientation, and thus the stereochemistry, of the dehydrohalogenation can be determined readily from the stoichiometry, *i.e.*, the number of molecules of hydrogen halide eliminated. If the elimination product is 1-halocyclohexene only one molecule of hydrogen halide is eliminated. The initial formation of 3-halocyclohexene leads to the formation of two molecules of hydrogen halide since the allylic halide is rapidly dehydrohalogenated (or solvolyzed) under the conditions of the reaction.

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[1] This work was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command, and in part by the Research Committee of the Graduate School with funds given by the Wisconsin Alumni Research Foundation.

[2] Du Pont Summer Research Assistant, 1953, 1954.

[3] (a) H. L. Goering and L. L. Sims, THIS JOURNAL, **77**, 3465 (1955); (b) P. Bender, D. L. Flowers and H. L. Goering, *ibid.*, **77**, 3463 (1955); (c) H. L. Goering and H. H. Espy, *ibid.*, **77**, 5023 (1955).

TABLE I

RATES OF BASE-CATALYZED DEHYDROHALOGENATION OF HALO- AND DIHALOCYCLOHEXANES IN "80%" ETHANOL

Cyclohexane derivative	[NaOH] 10^2, M	[Organic halide] 10^2, M	Moles of[a] HX produced	$t \pm 0.02$, °C.	$10^4 k_2$, l. mole^{-1} sec.$^{-1}$	$\Delta H^{\ddagger} \pm 0.4$,[b] kcal.	$\Delta S^{\ddagger} \pm 1$,[b] e.u.
1,1-Dibromo-	10.74	2.37	1.001	79.75	28.9 ± 0.4	22.3	7
	10.74	2.37		49.80	1.34 ± .03		
	10.74	2.09		30.05	0.136 ± .001		
1-Bromo-1-chloro-	10.72	2.38	0.996	79.75	32.5 ± .3	21.9	−8
	10.72	2.38		49.80	1.62 ± .02		
	10.67	2.66		30.05	0.166 ± .002		
1,1-Dichloro-	10.66	2.38	1.002	99.80	5.32 ± .09	24.7	−8
	10.66	2.38		79.75	0.755 ± .008		
cis-1,2-Dibromo-	10.65	2.64	1.001	30.05	26.1 ± .2	19.1	−7
	10.65	2.19		20.03	8.50 ± .19		
cis-1-Bromo-2-chloro-	10.77	2.91	1.001	30.05	7.92 ± .06	19.3	−9
	10.66	2.20		20.03	2.56 ± .01		
cis-1,2-Dichloro-	10.72	2.86	1.007	79.75	28.3 ± .2	22.9	−6
	10.72	2.78		49.80	1.24 ± .01		
	10.72	2.78		30.05	0.116 ± .002		
trans-1,2-Dibromo-	10.74	2.29	2.004	79.75	13.6 ± .1	23.1	−7
	10.74	2.29		49.80	.587 ± .004		
trans-1-Bromo-2-chloro-	10.69	1.71	1.912[c]	99.80	19.7 ± .2	23.3	−9
	10.69			79.75	3.15 ± .08		
	10.66	1.51	1.860[c]	99.80	20.0 ± .4		
	10.66			79.75	3.12 ± .05		
trans-1,2-Dichloro-	10.66	2.01		99.80	0.721 ± .004[d]	26.3	−7
	10.66	2.01		79.75	.0910 ± .00002[d]		
Bromo-	10.69	2.17	0.997	79.75	17.0 ± .1	22.0	−9
	10.69	2.17		49.80	.842 ± .013		
Chloro-	10.67	2.10		99.80	2.22 ± .06	24.9[e]	−9[e]
	10.67	2.10		79.75	.311 ± .0094		

[a] Determined from initial concentrations and "infinity" titers. [b] These errors calculated from high and low values of k at the extreme temperatures, assuming an average deviation in $k \pm \leq 1.5\%$. [c] A value of 2.00 was assumed for calculating the rate constants. This compound contained a small amount of rapidly-reacting impurity which presumably is responsible for this low value. [d] Initial rate constant determined from plot of k *vs.* percentage reaction. [e] Estimated errors. ±0.8 kcal. in $\Delta H^{\ddagger}$; ±2 e.u. in $\Delta S^{\ddagger}$.

The rates of solvolysis of some of these compounds in 80% ethanol are also reported in this paper. These data were required to determine the extent to which solvolysis competes with the second-order dehydrohalogenations.

Results

The specific second-order rate constants (k_2) and activation parameters for the dehydrohalogenation of the dihalocyclohexanes in "80%" ethanol[4] containing 0.1 M sodium hydroxide are presented in Table I together with similar data for cyclohexyl bromide and chloride. The second-order constants were calculated from the rate and stoichiometry of the reaction by use of the appropriate integrated equation. The reported values are the averages and mean deviations of five to nine values determined during the reactions. The reactions were generally followed to over 80% completion and except for *trans*-1,2-dichlorocyclohexane, the observed values of k_2 did not show any significant trends. The downward trend in the apparent rate constant for the *trans*-dichloride, which is the least reactive compound investigated, is due to destruction of the base by reaction with the glass vessel (see below). Concentrations are reported for 25° and the second-order rate constants are corrected for thermal expansion of the solvent. The reported second-order rate constants for 1,1-dibromocyclohexane and 1-bromo-1-chlorocyclohexane have been corrected for competing solvolysis (see below).

The rates of dehydrohalogenation were determined from the observed rate of formation of halide ion, measured by periodically determining the halide ion concentration in aliquots of reaction mixture by the Volhard method. Early experiments showed that the unreacted organic halide is hydrolyzed during the Volhard titration, *i.e.*, in the presence of silver nitrate. This was prevented by extracting the unreacted organic halide from the acidified aliquot of reaction mixture, before adding the silver nitrate.

In preliminary kinetic experiments, in which Pyrex ampoules were used, the specific second-order rate constants showed serious downward trends. This was found to be due to destruction of the alkali by reaction with the Pyrex glass. For this reason it was necessary to use Kimble and Corning "Alkali-Resistant" (No. 7280) glass ampoules for the kinetic experiments. The relative rates at which Pyrex, Kimble and Corning "Alkali-Resistant" glass are attacked by 0.1 M sodium hydroxide in "80%" ethanol are shown in Table II.

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(4) The solvent was prepared by mixing four volumes of pure ethanol and one volume of water at 25°.

TABLE II

REACTION OF 0.1 *M* SODIUM HYDROXIDE IN "80%" ETHANOL WITH VARIOUS GLASSES

Glass	Temp., °C.	Area, cm.^{2}	% Base destroyed in 24 hr.
Pyrex	80	18	88
Kimble	80	18	14
Kimble	100	18	40
Corning No. 7280	100	24	4

When Kimble glass vessels were used the isomeric dibromides, *cis*-1,2- and 1,1-bromochlorocyclohexane, *cis*-1,2-dichlorocyclohexane and cyclohexyl bromide gave steady second-order rate constants. Corning "alkali-resistant" ampoules were used for the least reactive compounds (*i.e.*, *trans*-1-bromo-2-chlorocyclohexane, 1,1- and *trans*-1,2-dichlorocyclohexane and cyclohexyl chloride). Steady rate constants were obtained for all of the compounds except *trans*-1,2-dichlorocyclohexane, for which the integral rate constants decreased during the reaction. The reported values of k_2 for this compound are initial rate constants and were obtained by extrapolation to zero time. This downward drift is clearly due, at least in part, to destruction of the alkali by reaction with the glass since the reaction is so slow that *ca.* 37% of the base is destroyed by this process during the time required for 30% reaction.

In order to determine whether second-order elimination is exclusive of second-order substitution the amounts of cyclohexene resulting from the reactions of cyclohexyl chloride and bromide were determined by titration of the reaction mixtures with a standard solution of bromine in carbon tetrachloride. These titrations showed that both cyclohexyl bromide and chloride give 1.00 ± 0.05 equivalent of cyclohexene under the conditions of the kinetic experiments. Thus k_2 corresponds to the E_2 reaction for these compounds. That an S_N2 reaction does not contribute to the second-order rate for the other compounds is apparent from the relative rates as well as from the products of reaction. For an S_N2 reaction the 1,1- and 1,2-dihalocyclohexanes would be much less reactive than the monohalides since α- and β-halogen substituents decrease the rate of S_N2-type displacements.[5,3c] As shown in Table I the *cis*-1,2- and 1,1-dihalocyclohexanes react faster than the corresponding monohalides. The *trans*-1,2-dihalides react slower than the monohalides but only by a factor of 5, a factor which is considerably smaller than would be expected for an S_N2 reaction.[3c] These observations indicate that the measured second-order constants are for the E_2 reactions without contributions from S_N2 reactions.

The number of molecules of hydrogen halide eliminated from the dihalides was determined from the "infinity" titers, *i.e.*, from the amount of halide ion released. These data, which are included in Table I, show that the *cis*-1,2- and 1,1-dihalocyclohexanes eliminate one molecule of hydrogen halide. *trans*-1,2-Dibromocyclohexane eliminates two molecules of hydrogen halide. The observed values for two carefully fractionated samples of *trans*-1-bromo-2-chlorocyclohexane were 1.912 and 1.860. Evidently a persistent unknown impurity is responsible for these low values. The impurity, which reacts faster than the *trans*-bromochloride, substantially disappears during the temperature equilibration of the kinetic experiments and thus does not interfere with the determination of the rate constants. The second-order rate constants reported in Table I for this compound (and for the other *trans*-1,2-dihalides) were obtained by assuming that exactly two moles of hydrogen halide is produced. The values of k_2 for the *trans*-1,2-dihalides are for the elimination of the first molecule of hydrogen halide which is the rate-determining step. *trans*-1,2-Dichlorocyclohexane and cyclohexyl chloride react so slowly that the base is destroyed by reaction with the glass ampoule before the reaction is complete. Thus the stoichiometry of the second-order reaction of these compounds could not be determined from the "infinity" titers.

The solvolyses of the more reactive dihalides and of cyclohexyl bromide in "80%" ethanol[4] were investigated to determine to what extent solvolysis competes with the second-order dehydrohalogenations. The results of these experiments are summarized in Table III. The first-order rate constants (k_1) were determined from the apparent "infinity" titer and rate of formation of acid by use of the integrated equation for a first-order reaction. Under the present conditions the solvolyses of the dihalides are complicated and the apparent rate-constants show significant trends. The percentage drift in k_1 during the first 50% reaction is shown in the last column of Table III. The values of k_1 in Table III are initial rate constants, determined by least-square extrapolations of the six to fourteen values of k_1 to zero time.

It is difficult to assess the accuracy of the solvolytic rate constants determined by the above method because of several complications. In the first place the stoichiometry of the solvolysis, which is required for calculating the rate constants, cannot be predicted for the dihalides since this depends on the reactivity of the initial solvolysis products. The stoichiometry cannot be determined accurately from the apparent "infinity" titer because part of the hydrogen halide is consumed by reaction with the solvent. Moreover, the stoichiometry, and thus the infinity titer, are probably temperature dependent, and could not be determined at the lower temperatures because the reactions are too slow. The reaction of hydrogen halide with aqueous ethanol has been observed in previous kinetic studies[6] and appears to be complicated. At 100°, the titer of a 0.045 *M* solution of hydrogen bromide in "80%" ethanol decreased to 93.6% of the original value in 22 hours; after 3000 hours (the time required for some of the "infinity" titers) the titer had increased to *ca.* 98.5% of the original value.[7] Because of this behavior no attempt was made to correct the observed "infinity" titers. The ob-

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(5) J. Hine, C. H. Thomas and S. J. Ehrenson, THIS JOURNAL, **77**, 3886 (1955); J. Hine and W. H. Brader, Jr., *ibid.*, **77**, 361 (1955); **75**, 3964 (1953).

(6) (a) E. D. Hughes and U. G. Shapiro, *J. Chem. Soc.*, 1177 (1937); (b) M. L. Bird, E. D. Hughes and C. K. Ingold, *ibid.*, 255 (1943); V. R. Stimson and E. J. Watson, *ibid.*, 2848 (1954).

(7) Similar behavior occurs at 140°; an initial decrease in titer (to a lower value than at 100°) is followed by an apparent increase.

TABLE III

RATES OF SOLVOLYSIS OF HALO- AND DIHALOCYCLOHEXANES IN "80%" ETHANOL

Cyclohexane derivative	[Organic halide] 10^2, M	Moles of HX produced	$t \pm 0.02$, °C.	$10^6 k_1$,[a] sec.$^{-1}$	$\Delta H^{\ddagger} \pm 0.5$,[b] kcal.	$\Delta S^{\ddagger} \pm 1$,[b] e.u.	Drift in k_1[c]
1,1-Dibromo-	2.43	1.052	99.80	75.9 ± 2.5	25.1	−10	+ 9.4
	2.43		79.99	10.71 ± 0.06			+ 9.6
	2.26		79.99	12.0 ± .1[d]			None
1-Bromo-1-chloro-	2.70	1.089	79.99	24.7 ± .2	25.4	− 8	+ 7.2
	2.70		50.00	.787 ± .007			+ 9.1
cis-1,2-Dibromo-	2.66	1.24	99.80	0.79 ± .04	32	− 1	∼−10
	5.33		79.99	0.067 ± .002			None
cis-1-Bromo-2-chloro-	2.73	1.00[e]	99.80	∼0.7			∼−50
trans-1,2-Dibromo-	2.68	1.96	99.80	1.055 ± .071	27	−15	+34
	2.66		79.99	.132 ± .007			None
			99.80	.11 ± .02[f]			None
trans-1-Bromo-2-chloro-	2.84	2.00[e]	99.80	<1.2[g]			−>90
Bromo-	2.98	1.00[e]	99.80	23.1 ± .14	24.3	−15	None
	2.98		79.99	3.45 ± .05			None

[a] Where drifts are indicated, rate constants are initial values. [b] Estimated errors calculated from high and low values of *k* at the two temperatures used, assuming an average deviation ± ≤2% in each *k*, except where noted. [c] Percentage change in k_1 during first 50% reaction. [d] Solvent contained 0.106 *M* lithium perchlorate. [e] The stoichiometry was not measured. This value was assumed for calculating the rate constants. [f] The solvent for this run was 99% methanol (by weight). [g] Since the serious downward drift in *k* may be due in part to a reactive impurity, this value is an extreme upper limit.

served values for the highest temperature at which each compound was investigated were used to calculate the constants at the lower temperatures. The "infinity" titers for *cis*- and *trans*-1-bromo-2-chlorocyclohexane were not determined and the rate constants were calculated by assuming that these compounds give one and two molecules of hydrogen halide, respectively.

As shown in Table III all of the dihalides for which the stoichiometry ("infinity" titer) was determined give more than one equivalent of hydrogen halide. Since it has been shown[8] that the solvolysis of cyclohexyl chloride in 50% aqueous ethanol at 95° gives 57% elimination and 43% substitution it seems likely that the dihalocyclohexanes also give elimination and substitution products. Thus the possible initial products from the 1,2-dihalocyclohexanes are: 1-halocyclohexene, 3-halocyclohexene and 2-halocyclohexyl alcohol and ethyl ether (presumably the *trans* isomer). The possible initial products from the 1,1-dihalocyclohexanes are 1-halocyclohexene and 1-halocyclohexyl alcohol and ethyl ether. All of these initial products except 1-halocyclohexene would be expected to solvolyze under the present conditions to give a second molecule of hydrogen halide. The rate constants were calculated by assuming that the formation of the first equivalent of hydrogen halide, from the fraction of dihalide which gives two equivalents, is the rate-determining step. In other words it is assumed that the initial products which are subsequently solvolyzed are more reactive than the dihalides. This will likely be the case except for the fraction of the reaction that gives *trans*-2-halocyclohexyl ethyl ether. For example, if the solvolysis of the *trans*-1,2-dibromocyclohexane gives *trans*-2-bromocyclohexyl ethyl ether, this initial product will solvolyze somewhat slower[9] than the dihalide and the kinetics will thus be complicated.

In spite of the complicated kinetics it seems clear that the solvolysis constants are sufficiently accurate for their intended purpose. These data show that solvolysis competes to a small extent with the second-order dehydrohalogenation of the 1,1-dihalides but is unimportant in the dehydrohalogenations of the other compounds. The values of k_2 in Table I for 80, 50 and 30° have been lowered by 4.2, 2.8 and 2.0%, respectively, for the 1,1-dibromide, and 8.3, 4.9 and 3.3% for the 1,1-bromochloride. These percentages represent the fraction of compound undergoing first-order solvolysis under the initial conditions of reaction, *i.e.*, at a base concentration of 0.1 *N*. Presumably solvolysis competes with the second-order dehydrohalogenation of 1,1-dichlorocyclohexane; however, these constants were not corrected because the rate of solvolysis was not determined.

Discussion

The orientation and relative rates of second-order dehydrohalogenation indicate that a concerted *trans* dehydrohalogenation[10] (E_2 elimination) is involved as illustrated below for the 1,1(I)-, *cis*-1,2(II)- and *trans*-1,2(III)-dihalocyclohexanes. It has been pointed out previously[11,12] that for cyclohexyl halide only one of the two chair conformations has the required geometry for a concerted *trans* dehydrohalogenation. In the illustrations below the reactive conformations are shown for each of the

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(8) J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951).

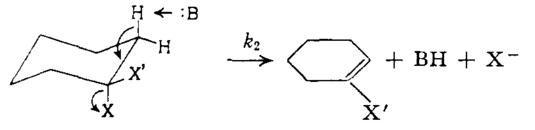
(9) This assumption is based on the observation of S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948), that *trans*-2-methoxycyclohexyl *p*-toluenesulfonate undergoes acetolysis approximately one-half as fast as *trans*-2-bromocyclohexyl *p*-toluenesulfonate.

(10) S. J. Cristol, N. L. Hause and J. S. Meek, THIS JOURNAL, **73**, 674 (1951), and references therein.

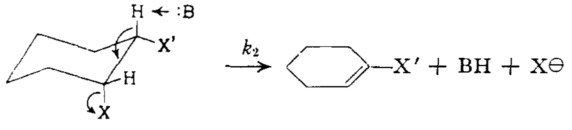
(11) H. D. Orloff, *Chem. Revs.*, **54**, 347 (1954).

(12) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 466.

dihalides. Since hydrogen bromide is eliminated more readily than hydrogen chloride[6a,13] (*cf.* bromides with corresponding chlorides, Table I) it seems likely that the bromochlorides eliminate hydrogen bromide almost exclusively. Thus in the illustrations below, X = Br, and X′ = Cl for the bromochlorides.



I



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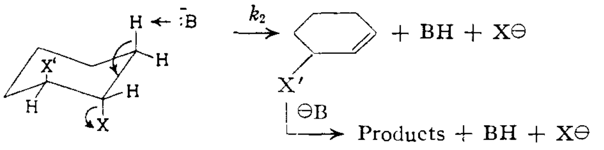

III

The 1,1- and *cis*-1,2-dihalocyclohexanes give one equivalent of halide ion which shows that 1-halocyclohexene is the exclusive product. This is consistent with the previous reports that the dehydrohalogenation of *cis*-1,2-dibromocyclohexane[14,15] and *cis*-1-bromo-2-chlorocyclohexane[2b] give good yields of 1-bromocyclohexene and 1-chlorocyclohexene, respectively. The formation of as little as 1% of 3-halocyclohexene could be detected by the present method since this product would react rapidly under the conditions of the reaction to give a second equivalent of halide ion. Thus, in the *cis*-1,2-dihalides the equatorial β-halogen atom activates the axial hydrogen atom sufficiently so that only one of the two possible *trans*-elimination products is formed. These data also provide additional evidence[3] that the *cis* isomers are configurationally homogeneous—*trans* isomers give two equivalents of halide ion—and that substitution does not compete with dehydrohalogenation; under the conditions of the reactions the expected substitution products would react to give a second equivalent of halide ion.

The second-order dehydrohalogenation of *trans*-1,2-dibromocyclohexane (and presumably *trans*-1,2-dichloro- and *trans*-1-bromo-2-chlorocylohexane) gives two equivalents of halide ion. The elimination of the first molecule of hydrogen bromide is the rate-determining step. These data clearly show that 3-bromocyclohexene, the *trans*-elimination product, is the exclusive[16] initial product as would be expected from previous observations that *trans* dehydrohalogenation is considerably faster than *cis* dehydrohalogenation in similar systems.[17] In connection with the exclusive *trans* dehydrohalogenation observed in the present case it is interesting to note that dehydrobromination of *trans*-1,2-dibromocyclohexane in refluxing quinoline gives *ca.* 10% of the *cis*-elimination product, 1-bromocyclohexene.[14,18] Similarly *trans*-1,2-dichlorocyclohexane gives approximately equimolar amounts of 1,3-cyclohexadiene (*trans* elimination) and 1-chlorocyclohexene (*cis* elimination) when dehydrohalogenated in refluxing quinoline.[19,20]

The relative rates of second-order dehydrohalogenation at 30 and 100° are shown in Table IV together with the relative rates of solvolysis at these same temperatures. Some of the members of the present series of compounds, *e.g.*, the 1,1- and *cis*-1,2-dichlorides and dibromides, exist entirely in the reactive conformation. With these compounds the relative effects of α- and β-equatorial halogen atoms on the rate of second-order dehydrohalogenation can be determined. *cis*-1,2-Dibromocyclohexane reacts 194 times faster at 30° and 70 times faster at 100° than 1,1-dibromocyclohexane.[21] Similarly *cis*-1,2-dichlorocyclohexane reacts 61 times faster at 30° and 33 times faster at 100° than the 1,1-isomer. The bromochlorides are similar to the dichlorides in that the 1,1-isomer is less reactive than the *cis*-1,2-isomer by a factor of 48 at 30° and 21 at 100°. Although the bromochlorides, unlike the dichlorides and dibromides, are not conformationally homogeneous it seems likely that both isomers exist in the reactive conformation (a-Br; e-Cl) to about the same extent (somewhat less than 50%). Thus these isomers can be compared without complications which result if the conformational composition varies.[22] Since the 1,1-isomers dehydrohalogenate in two equivalent directions whereas the *cis*-1,2-isomers eliminate in one direction the above factors should be multiplied by two to obtain the relative effects of α- and β-halogen atoms on the rate of dehydrohalogenation. These data show that (a) the rate of dehydrohalogenation is greater with a β- than with an α-halogen substituent (equatorial in each case), (b) the difference between the two positions is greater with bromine than with chlorine and (c) the difference is similar for dehydrochlorin-

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[13] H. C. Brown and I. Moritani, THIS JOURNAL, **76**, 455 (1954).

[14] H. L. Goering, P. I. Abell and B. F. Aycock, *ibid.*, **74**, 3588 (1952).

[15] R. Cornubert, *et al.*, *Bull. soc. chim. France*, 46, 60 (1955).

[16] The formation of as little as 1% of 1-bromocyclohexene could be detected by the present method.

[17] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947); S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953); E. D. Hughes, C. K. Ingold and R. Pasternak, *J. Chem. Soc.*, 3832 (1953).

[18] N. Zelinsky and A. Gorski, *Ber.*, **44**, 2312 (1911).

[19] H. C. Stevens and O. Grummitt, THIS JOURNAL, **74**, 4876 (1952).

[20] In this connection it is interesting that Mr. King Howe of this Laboratory has observed that the elimination of *p*-toluenesulfonic acid from *trans*-2-methylcyclopentyl *p*-toluenesulfonate in refluxing pyridine gives a mixture of 1- and 3-methylcyclopentenes containing *ca.* 90% of 1-methylcyclopentene, the *cis*-elimination product. Elimination in refluxing ethanol containing 2.86 *N* sodium ethoxide gives a mixture of methylcyclopentenes containing 86% 3-methylcyclopentene (*trans*-elimination) and 14% 1-methylcyclopentene (*cis*-elimination). Presumably, in the latter case, the second-order reaction is not isolated from competing solvolysis.

[21] This difference in reactivity is similar to that observed by S. C. J. Olivier and A. P. Weber, *Rec. trav. chim.*, **53**, 1087 (1934) for 1,1- and 1,2-dibromoethane. The 1,2-isomer undergoes base-catalyzed dehydrobromination 200 times faster than the 1,1-isomer in 25% aqueous acetone at 30°.

[22] It can be shown readily that for a stereospecific reaction in which only one of two (or more) rapidly interconvertible conformations has the required geometry for reaction the rate will be proportional to the fraction of substrate in the reactive conformation.

ation and dehydrobromination (*cf.* the isomeric dichlorides and bromochlorides).

The data in Table I show that the difference in reactivity of the 1,1- and *cis*-1,2-isomers is due to a lower heat of activation for the *cis*-1,2-isomers; $\Delta\Delta H^{\ddagger}$ is 3.2 kcal. for the dibromides, 2.6 kcal. for the bromochlorides and 1.8 kcal. for the dichlorides. As Ingold has pointed out[23] the greater reactivity with a β- than with an α-halogen substituent can be attributed to the inductive effect of the halogen atom. In the β-position this effect weakens the carbon–hydrogen bond and thus facilitates the concerted elimination.

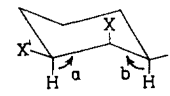
TABLE IV

RELATIVE RATES OF BASE-CATALYZED DEHYDROHALOGENATION AND SOLVOLYSIS OF HALO- AND DIHALOCYCLOHEXANES IN "80%" ETHANOL

Cyclohexane derivative	Base-catalyzed dehydrohalogenation 100°	30°	Solvolysis 100°	30°
1,1-Dibromo-	1.7	1.6	3.3	2.6
1-Bromo-1-chloro-	1.9	2.0	7.7	5.7
1,1-Dichloro-	0.055	0.023		
cis-1,2-Dibromo-	120	310	0.034	0.002
cis-1-Bromo-2-chloro-	39	95	0.03	
cis-1,2-Dichloro-	1.8	1.4		
trans-1,2-Dibromo-	0.86	0.63	0.046	
trans-1-Bromo-2-chloro-	0.20	0.14		
trans-1,2-Dichloro-	0.0074	0.0020		
Bromo-	1	1	1	1
Chloro-	0.023	0.012		

cis-1,2-Dibromocyclohexane undergoes dehydrobromination faster than *cis*-1-bromo-2-chlorocyclohexane by a factor of *ca.* 3 and this factor remains substantially constant with a 70° change in temperature. As mentioned above, somewhat less than 50% of the bromochloride is in the reactive conformation; steric factors should slightly favor the unreactive conformation with bromine in equatorial position. Thus if the reactive conformation of the bromochloride is as reactive as the dibromide we would expect the dibromide to be a little over twice as reactive as the bromochloride.[22] That this is indeed the case shows that bromine and chlorine atoms in the β-equatorial position have very similar effects on the rate of dehydrobromination. This might be expected, since there is other evidence that the inductive effects of bromine and chlorine are very similar, *e.g.*, the similar dissociation constants for bromo and chloroacetic acid[24] and the similar carbon–halogen bond moments for bromine and chlorine.[3b]

The effect of replacing α- or β-equatorial hydrogen atoms by halogen on the rate of dehydrohalogenation cannot be determined quantitatively from the present data. Comparison of the mono- and dihalocyclohexanes does not provide this information since the conformational composition of the monohalides is unknown and differs from that of the dihalides.[22] It is clear, however, that replacing a β-equatorial hydrogen atom by halogen results in a considerable increase in rate. The fact that the *cis*-1,2-dihalides give >99% 1-halocyclohexene shows that process *a* is >100 times as fast as process *b*.



Evidently the replacement of an α-equatorial hydrogen atom by halogen results in a decrease in the rate of dehydrohalogenation. Cyclohexyl bromide (or chloride) reacts one-half as fast as the 1,1-dibromide (or dichloride). Since the monohalide exists primarily in the unreactive equatorial conformation[11] it is clear that the reactive axial conformation of the monohalide is more reactive than the 1,1-dihalide. Comparison of the 1,1-dibromide with the 1,1-bromochloride shows that an α-equatorial bromine atom decreases the rate more than an α-chlorine atom. Although the bromochloride is less than 50% in the reactive conformation it reacts slightly faster than the dibromide which indicates that, *ceteris paribus*, dehydrobromination is two to three times as fast with an α-chlorine substituent as with an α-bromine substituent. Evidently the inductive effect of a halogen atom in the α-position retards elimination and the smaller effect with chlorine than with bromine can be attributed to the somewhat larger compensating electromeric effect of the chlorine atom.[25]

Comparison of the data in Table I for the compounds which undergo dehydrobromination with the corresponding compounds which undergo dehydrochlorination shows that the activation enthalpy for E_2 dehydrobromination is 2.8 to 3.6 kcal. less than for the dehydrochlorination. This agrees well with the previous observation[26] that the energy of activation is 2.2 kcal. less for dehydrobromination of isopropyl bromide than for dehydrochlorination of isopropyl chloride in 80% ethanol. In every case the activation parameters for the bromochlorides are within the combined experimental errors of those for the corresponding dibromides.

Experimental

Materials.—The dihalocyclohexanes[27] were prepared and purified by previously described methods. Physical properties of some of the organic halides used in this work are listed in Table V, with references to their methods of preparation and/or purification. Halides not mentioned in Table V have been described in a previous paper.[3c]

Solvents were prepared from absolute methanol or absolute ethanol[28] and conductivity water. "Eighty per cent." ethanol was prepared by mixing 4 volumes of dry ethanol and 1 volume of water at 25°. The solvent used in dehydrohalogenations was an approximately 0.1 M solution of reagent grade sodium hydroxide in "80%" ethanol, standardized against potassium acid sulfate.

Kinetic Experiments.—All concentrations are reported at 25°. For runs at temperatures over 30°, the sealed ampoule technique was used and the reactions were quenched by immersing the ampoules in an ice-bath. Solutions were made up volumetrically and aliquots were measured at 25° with calibrated pipets. For dehydrohalogenation

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[23] Ref. 12, p. 446.

[24] D. J. G. Ives and J. H. Pryor, *J. Chem. Soc.*, 2104 (1955).

[25] Ref. 12, p. 75.

[26] K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. MacNulty, *J. Chem. Soc.*, 2049 (1948).

[27] We are indebted to Dr. L. L. Sims of these laboratories for providing samples of *cis*-1,2-dibromocyclohexane, *cis*- and *trans*-1-bromo-2-chlorocyclohexane and 1-bromocyclohexene.

[28] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, 1941, 2nd ed., pp. 359–360.

TABLE V

PHYSICAL PROPERTIES OF HALO- AND DIHALOCYCLOHEXANES

Cyclohexane derivative	B.p., °C.	$n^{25}D$	Ref.
1,1-Dibromo-	76-77 (8.5 mm.)	1.5406	*a*
1-Bromo-1-chloro-	77.5 (17 mm.)	1.5093	*a*
1,1-Dichloro-	161–170 (739 mm.)	1.4788	*b*
cis-1,2-Dibromo-	107–108 (10.5 mm.)	1.5516	*a*
trans-1-Bromo-2-	76 (9 mm.)	1.5173	*a*
chloro-	82.4 (13.5 mm.)	1.5168	*a*
Bromo-	83.0-83.5 (57 mm.)	1.4936	*c*
Chloro-	139 (735 mm.)	1.4604	*c*
1-Bromocyclohexene	62–63 (20 mm.)	1.5105	*d*

[a] Ref. 3a. [b] B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, THIS JOURNAL, **73**, 5382 (1951). [c] Eastman Kodak Co. "White Label" product, purified by fractionation. [d] Ref. 18.

runs at 20 or 30°, dihalide was dissolved in an approximately known amount of previously thermostated solvent. Aliquots were measured at the temperature of reaction and delivered into dilute acid to quench the reaction. The exact initial concentrations of organic dihalide were determined from the "infinity" titers and the known stoichiometry of reaction. The stoichiometry was determined from a run using a volumetrically prepared solution of dihalide.

Dehydrohalogenation reactions were followed by adding 5-ml. aliquots of reaction mixture to 18 ml. of 1.5 *M* nitric acid in a 60-ml. separatory funnel, and extracting unreacted organic halide with two 8-ml. portions of carbon tetrachloride. The halide ion concentration was determined by the Volhard method, using 0.06 *M* silver nitrate and 0.07 *M* potassium thiocyanate. The titer changed about 1.5-3.0 ml. during the course of reaction; individual titrations were reproducible to ±0.005 ml.

Rates of solvolysis were followed by titration of 5-ml. aliquots of reaction mixture with 0.03 *M* sodium methoxide to the brom thymol blue end-point. Titrations were reproducible to ±0.01 ml.

Cyclohexene was determined as follows: a 5-ml. aliquot of dehydrohalogenation mixture was acidified with 2 drops of concentrated hydrochloric acid and titrated to the appearance of a pale yellow color with a 0.033 *M* solution of bromine in carbon tetrachloride. The bromine solution was standardized against sodium thiosulfate. The blank for the titration, determined using acidified "80%" ethanol, was 0.1 ml. There was no disappearance of the color in 0.5 hour, indicating a negligible reaction of bromine with ethanol. This method, tested with a 0.0197 *M* solution of pure cyclohexene, b.p. 81.7-82.0° (73.5 mm.), in "80%" ethanol, gave reproducible results which were 8% low. All titration values, after blank corrections, were therefore multiplied by 1.09. The estimated accuracy of this method is ±5%.

Specific second-order dehalogenation rate constants, k_2, were calculated from equation 1, in which a is the initial concentration of organic halide, b is the initial base concentration, x is the concentration of halide ion (*i.e.*, the concentration of reacted base and organic halide) and n is the number of equivalents of HX produced per mole of organic halide.

$$k_2 = \frac{1}{t[(b/n) - a]} \ln \left[\frac{a(b - x)}{b[a - (x/n)]}\right] \qquad (1)$$

Values of k_2 at temperatures of 50° or over were corrected for solvent expansion by multiplying by d_{25}/d_t, in which d_t = density of "80%" ethanol at t°. This ratio was determined by sealing 4.486 ml. of "80%" ethanol (at 25°) into a calibrated tube (an "Exax" 5-ml. microburet with the stopcock removed) and reading the liquid height at various temperatures.[29] The corrected values of d_{25}/d_t are: 1.000 (25°), 1.026 (50°), 1.064 (80°) and 1.092 (100°). All dehydrohalogenation rate constants (k_2) are average values except for those of the *trans*-1,2-dichloride. These are initial values, determined by extrapolating plots of k_2 *vs.* percentage reaction to zero per cent. reaction by the method of least squares.

First-order solvolysis rate constants (k_1) were calculated from equation 2 in which the symbols have the same meaning as in equation 1.

$$k_1 = \frac{1}{t} \ln \left[\frac{a}{a - (x/n)}\right] \qquad (2)$$

Constants for cyclohexyl bromide and the *cis*-1,2-dibromide are average values. The constants for the *cis*- and *trans*-1-bromo-2-chlorides result from rough graphical extrapolation of k_1 *vs.* t to $t = 0$; titration values for the former compound were quite erratic.

Second-order dehydrohalogenation rate constants were corrected where necessary, for the presence of simultaneous first-order solvolysis by equation 3, in which k_2 is the corrected second-order rate constant, "k_2" is the average

$$k_2 = \frac{\text{"}k_2\text{"}[\text{NaOH}]_0 - k_1}{[\text{NaOH}]_0} \qquad (3)$$

apparent second-order rate constant (corrected for solvent expansion) from equation 1 and k_1 is the independently measured solvolysis rate constant.

Activation parameters were calculated from the Eyring equation.[30]

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[29] The observed changes in volume were corrected for expansion of the glass by the method described by I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Organic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., p. 505.

[30] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 96-97.