Anal. Calcd. for $C_{16}H_{19}N_3O_2Si$: Si, 8.96. Found: Si, 9.18.

A sample of this aldehyde gave, after exposure to air and working up in a manner similar to the *p*-isomer, *o*-trimethylsilylbenzoic acid, m.p. 98–99.5°.

***p*-Trimethylsilylbenzyl Acetate.**—To a mixture of 34.76 g. (0.143 mole) of *p*-trimethylsilylbenzyl bromide and 22.49 g. (0.274 mole) of anhydrous sodium acetate was added 37.55 g. (0.625 mole) of glacial acetic acid. The reaction mixture became quite viscous and heat was evolved during the addition. The reaction mixture was then refluxed gently with stirring for 13 hr. Approximately 30 ml. of acetic acid was then distilled from the reaction mixture, the residue was cooled and 95 ml. of water was added. The resulting mixture was extracted with ether and the ether solution was dried over Drierite. The ether was then removed by distillation and the residue was distilled through a short Vigreux column. This gave 27.9 g. (87.8%) of *p*-trimethylsilylbenzyl acetate, b.p. 145° (15.5 mm.), $n^{20}D$ 1.4960, d^{20}_4 0.9837; *MR* (calcd.)[7] 65.76, *MR* (found) 66.02.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: Si, 12.62. Found: Si, 12.61.

***m*-Trimethylsilylbenzyl acetate** was prepared from 32.3 g. (0.133 mole) of *m*-trimethylsilylbenzyl bromide, 22.5 g. (0.274 mole) of sodium acetate and 37.55 g. (0.625 mole) of glacial acetic acid following the directions given for the *p*-isomer. There was obtained 22.1 g. (74.6%) of *m*-trimethylsilylbenzyl acetate, b.p. 139° (15.5 mm.), $n^{20}D$ 1.4955, d^{20}_4 0.9832; *MR* (calcd.)[7] 65.76, *MR* (found) 66.00.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: Si, 12.62. Found: Si, 12.99.

***o*-Trimethylsilylbenzyl Acetate.**—From 32.4 g. (0.133 mole) of *o*-trimethylsilylbenzyl bromide, 22.5 g. (0.274 mole) of sodium acetate and 37.55 g. (0.625 mole) of glacial acetic acid, following the directions given for the *p*-isomer, there was obtained 24.18 g. (81.8%) of *o*-trimethylsilylbenzyl acetate, b.p. 139.5° (15.5 mm.), $n^{20}D$ 1.5045, d^{20}_4 1.0025; *MR* (calcd.)[7] 65.76, *MR* (found) 65.72.

Anal. Calcd. for $C_{12}H_{18}O_2Si$: Si, 12.62. Found: Si, 12.98.

***p*-Trimethylsilylbenzyl Alcohol.**—A solution of 13.3 g. (0.06 mole) of *p*-trimethylsilylbenzyl acetate in 40 ml. of hot methanol was thoroughly mixed with 28 g. of 15% aqueous sodium hydroxide. The reaction mixture was heated with stirring for 10 min. and then poured onto approximately 350 ml. of an ice-water mixture. This aqueous mixture was extracted with ether. The ether solution was dried over Drierite and the ether was removed by distillation. The residue was distilled through a small Vigreux column giving 8.44 g. (78%) of *p*-trimethylsilylbenzyl alcohol, b.p. 139° (16 mm.), $n^{20}D$ 1.5140, d^{20}_4 0.9605; *MR* (calcd.)[7] 56.28, *MR* (found) 56.51.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.56. Found: Si, 15.78.

***m*-Trimethylsilylbenzyl Alcohol.**—From 15.2 g. (0.068 mole) of *m*-trimethylsilylbenzyl acetate, following the procedure given for the *p*-isomer, there was obtained 8.72 g. (71%) of *m*-trimethylsilylbenzyl alcohol, b.p. 137° (16 mm.), $n^{20}D$ 1.5150, d^{20}_4 0.9648; *MR* (calcd.)[7] 56.28, *MR* (found) 56.35.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.56. Found: Si, 15.88.

***o*-Trimethylsilylbenzyl Alcohol.**—From 15.1 g. (0.068 mole) of *o*-trimethylsilylbenzyl acetate, following the procedure given for the *p*-isomer, there was obtained 10.62 g. (88%) of *o*-trimethylsilylbenzyl alcohol, b.p. 134° (16 mm.), $n^{20}D$ 1.5265, d^{20}_4 0.9887; *MR* (calcd.)[7] 56.28, *MR* (found) 56.02.

Anal. Calcd. for $C_{10}H_{16}OSi$: Si, 15.56. Found: Si, 15.87.

GRAND FORKS, NORTH DAKOTA

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

The Solvolysis of *cis*- and *trans*-2-Chlorocycloalkyl Aryl Sulfides in 80% Aqueous Ethanol[1]

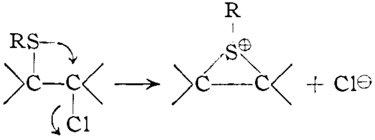
BY HARLAN L. GOERING AND KING L. HOWE[2]

RECEIVED AUGUST 19, 1957

The rates of solvolysis of *cis*-(Ia) and *trans*-2-chlorocyclohexyl phenyl sulfide (IIa) and *cis*-(IIIa) and *trans*-2-chlorocyclopentyl phenyl sulfide (IVa) and *p*-substituted derivatives of these β-chlorosulfides in 80% aqueous ethanol have been determined. In both the cyclohexyl and cyclopentyl systems the *trans* isomers, in which the neighboring sulfide group can participate in the ionization step, are more reactive than the corresponding *cis* isomers by factors of 10^5 to 10^6. Electron-withdrawing substituents retard the rate of solvolysis of the *trans*-2-chlorocycloalkyl phenyl sulfides (II and IV) but do not affect the reactivity of the *cis* isomers (I and III). At 118° the *cis*-2-chlorocyclohexyl aryl sulfides (I) are one-sixth as reactive as cyclohexyl chloride and the *cis*-2-chlorocyclopentyl aryl sulfides are one-fifteenth as reactive as cyclopentyl chloride. Similar values of ρ and k_{trans}/k_{cis} for the cyclohexyl and cyclopentyl chlorosulfides show that sulfur participates about equally well in the two systems.

Introduction

As has been pointed out previously[3,4] it is clear from the high solvolytic reactivities of β-chlorosulfides, *e.g.*, β,β′-bis-chloroethyl sulfide,[4,5] that the sulfide group participates in the rate-determining ionization step.



Such participation is also indicated by the effect of substituents on the rates of solvolysis of substituted phenyl β-chloroethyl sulfides in 50% aqueous acetone.[6] The sign and magnitude of ρ (-1.671^7) for this reaction is consistent with a process involving participation by the neighboring sulfide group. In the absence of such participation the effect of substituents would be expected to be negligible.

In order to obtain quantitative information concerning the rate enhancement (anchimeric assistance[8]) resulting from participation by a neighboring sulfide group we have measured the rates of solvolysis of several *cis*- (I) and *trans*-2-chlorocyclohexyl aryl sulfides (II) and *cis*- (III) and

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(1) This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)-1037.

(2) Socony-Mobil Fellow, 1955–1956.

(3) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

(4) P. D. Bartlett and C. G. Swain, *ibid.*, **71**, 1406 (1949).

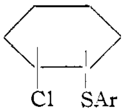
(5) A. G. Ogston, E. R. Holiday, J. S. L. Philpot and L. A. Stocken, *Trans. Faraday Soc.*, **44**, 45 (1948).

(6) G. M. Bennett and W. A. Berry, *J. Chem. Soc.*, 1676 (1927); G. Baddely and G. M. Bennett, *ibid.*, 261 (1933).

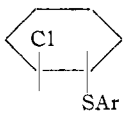
(7) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(8) S. Winstein, C. R. Lindegren, H. Marshall and L. L. Ingraham, THIS JOURNAL, **75**, 147 (1953).

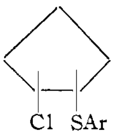
trans-2-chlorocyclopentyl aryl sulfides (IV) in 80% aqueous ethanol.[9] These compounds were prepared in connection with a study[10] of the stereochemistry of the radical addition of thiophenol and substituted thiophenols to 1-chlorocycloalkenes. In these cyclic systems the neighboring sulfide group can participate in the *trans* but not in the *cis* isomers. Thus the ratio of the rate constant for a *trans* isomer (k_{trans}) to that for the corresponding *cis* isomer (k_{cis}) is a measure of the rate enhancement resulting from participation of the neighboring sulfide group.[11] The compounds available for the present investigation enable comparison of anchimeric assistance in the cyclohexyl and cyclopentyl systems as well as comparison of the sulfide group with neighboring groups that have been investigated previously.[11]



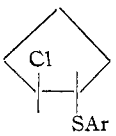
Ia, Ar = p-$C_6H_4CH_3$
Ib, Ar = C_6H_5
Ic, Ar = p-C_6H_4Cl



IIa, Ar = p-$C_6H_4CH_3$
IIb, Ar = C_6H_5
IIc, Ar = p-C_6H_4Cl
IId, Ar = p-$C_6H_4NO_2$



IIIa, Ar = p-$C_6H_4CH_3$
IIIb, Ar = C_6H_5
IIIc, Ar = p-C_6H_4Cl



IVa, Ar = p-$C_6H_4CH_3$
IVb, Ar = C_6H_5
IVc, Ar = p-C_6H_4Cl
IVd, Ar = p-$C_6H_4NO_2$

The *cis*-2-cycloalkyl aryl sulfides I and III were prepared by the radical addition of thiophenol and substituted thiophenols to 1-chlorocyclohexene and 1-chlorocyclopentene.[10,12] The *trans*-chlorosulfides II and IV were prepared by the addition of the corresponding aryl sulfenyl chloride to cyclohexene and cyclopentene.[12] The method of preparation, kinetic studies of the base-promoted dehydrohalogenation of the corresponding sulfones[12] and rates of solvolysis reported in the present paper establish the structures of the chlorosulfides beyond all reasonable doubt.

The *trans*-chlorosulfides II and IV solvolyze rapidly in 80% ethanol at low temperatures, *e.g.*, at 30° the half-life for the most reactive *trans*-chlorosulfide, IVa, is 10 minutes. On the other hand, the *cis* isomers are relatively unreactive; the most reactive *cis*-chlorosulfide has a half-life of 39 hr. at 118°.

Solvolyses of the *trans*-chlorosulfides at 20 and 30° were followed by intermittent titration of the entire reaction mixture[4] with a standard solution of sodium hydroxide in 80% ethanol. With initial concentrations of 0.02 M chlorosulfide the specific first-order rate constants for the *trans*-2-chlorocyclopentyl aryl sulfides IV showed appreciable downward drifts. That this was largely or completely due to external ion return[13] (reversal of ionization) was shown by comparison of the depression of the initial rate resulting from the addition of 0.087 M sodium chloride with that resulting from accumulation of chloride ion during solvolysis.[14] The fact that at this concentration the observed infinity titers for all of the *trans*-2-chlorocyclopentyl aryl sulfides agreed within 2% of the calculated values shows that external ion return gives the *trans*-chlorosulfides exclusively since any unreactive *cis*-chlorosulfide produced in this way would survive under these conditions.

Complications arising from external ion return were largely eliminated by lowering the initial concentration of substrate to 10^{-3} molar. In order to avoid possible complications resulting from changes in ionic strength during solvolysis, the ionic strength was maintained at a constant level by using 80% ethanol containing 0.0504 M lithium perchlorate as the solvent. The results of these rate studies are presented in Table I.

The first-order constants for the *trans*-chlorosulfides obtained by the present method were quite satisfactory; some showed no trends whatsoever and in only one case (solvolysis of IIb, expt. 16) did the drift exceed 5% at 50% reaction. In this experiment the integrated rate constant at 91% reaction was 81% of its initial value. The values reported in Table I are average values and mean deviations of a large number of determinations during the run except in cases where consistent downward trends were observed. For these experiments initial rate constants, determined by extrapolation to zero time, are reported together with the average deviations of the points from the least square plots. The data presented in Table I show that the rate constants are reproducible to within 2%. Two batches of solvent were used, however; several chlorosulfides were solvolyzed in both batches and in every case the rate constants agreed within the combined mean deviations. Comparison of experiments 2 and 3 and experiments 6 and 7 show that the positive salt effect on the rate of solvolysis is small. When reactions were carried out under acidic conditions, *i.e.*, acid was allowed to accumulate and carefully titrated periodically, the rate was the same as when the solution was kept basic. Indeed, in one experiment (8) an amount of base sufficient to neutralize 80% of the acid formed in the solvolysis was added at the outset. The rate constant for this experiment was within experimental error of that for experiment 6 in which acid was allowed to accumulate. This clearly shows that the first-order rate of solvolysis is not affected by intermittent titration of the reaction mixture.

The rates of solvolysis of the *cis*-chlorosulfides I and III in 80% ethanol at 118.2° were determined from the rates of formation of chloride ion which were measured by Volhard titration of aliquots of reaction mixtures. These rates were so slow that

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[9] The solvent composition is based on volumes of the pure components at 25° before mixing.

[10] H. L. Goering, D. I. Relyea and D. W. Larsen, THIS JOURNAL, **78**, 348 (1956); K. L. Howe and D. I. Relyea, unpublished results.

[11] (a) S. Winstein, E. Grunwald and L. L. Ingraham, *ibid.*, **70**, 821 (1948); (b) E. Grunwald, *ibid.*, **73**, 5458 (1951).

[12] H. L. Goering, D. I. Relyea and K. L. Howe, *ibid.*, **79**, 2502 (1957).

[13] S. Winstein, E. Clippinger, A. Fainberg, R. Heck and G. Robinson, *ibid.*, **78**, 328 (1956).

[14] It has previously been observed that the rate of solvolysis of β-chloro-β'-hydroxyethyl sulfide is depressed by accumulation or addition of chloride ion (ref. 4).

TABLE I

FIRST-ORDER RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE SOLVOLYSIS OF 10^{-3} M *trans*-2-CHLOROCYCLOPENTYL AND *trans*-2-CHLOROCYCLOHEXYL ARYL SULFIDES IN 80% ETHANOL CONTAINING 0.0504 M LITHIUM PERCHLORATE

Expt.	Compound	Temp., °C.	$10^6 k_{trans}$, sec.$^{-1}$	E_a,[a] kcal.
	trans-2-Chlorocyclopentyl sulfide (IV)			
1	*p*-Tolyl (IVa)	30.05	1180 ± 10	19.8
2		30.05	1158 ± 14	
3		30.05	1030 ± 10[b]	
4		20.05	384 ± 2	
5		20.05	377 ± 2	
6	Phenyl (IVb)	30.05	656 ± 2[c]	19.2
7		30.05	675 ± 5[d]	
8		30.05	660 ± 7[e]	
9		20.05	221 ± 1[f]	
10	*p*-Chlorophenyl (IVc)	30.05	284 ± 4[c]	19.8
11		20.05	91.4 ± 0.3[f]	
12	*p*-Nitrophenyl (IVd)	30.05	24.0 ± .4	22.5
13		20.05	6.70 ± .06	
	trans-2-Chlorocyclohexyl sulfide II			
14	*p*-Tolyl (IIa)	30.05	329 ± 1[f]	21.1
15		20.05	99.8 ± 0.3[f]	
16	Phenyl (IIb)	30.05	172 ± 1[f]	20.7
17		20.05	53.3 ± 0.1[f]	
18	*p*-Chlorophenyl (IIc)	30.05	73.3 ± .2[f]	21.9
19		20.05	21.2 ± .2	
20	*p*-Nitrophenyl (IId)	30.05	5.84 ± .09	23.9
		20.05	1.51 ± .01	

[a] The estimated uncertainty in E_a is 0.5 kcal. [b] No $LiClO_4$ added, *i.e.*, the initial ionic strength was zero. [c] Average value and mean deviation of two independent kinetic experiments. [d] In this experiment the ionic strength was 0.1. [e] In this experiment an amount of base sufficient to neutralize 80% of the total amount of acid produced in the solvolysis was added at zero time. [f] Determined by least square extrapolation of plot k *versus* time to zero time.

TABLE II

COMPARISON OF RATES OF SOLVOLYSIS OF *cis*- AND *trans*-2-CHLOROCYCLOALKYL ARYL SULFIDES IN 80% ETHANOL IN 118.2°

Compound	k_{trans},[a] sec.$^{-1}$	$10^7 k_{cis}$,[b] sec.$^{-1}$	k_{trans}/k_{cis}
2-Chlorocyclopentyl *p*-tolyl sulfide	1.96	50 ± 6	3.9×10^5
2-Chlorocyclopentyl phenyl sulfide	0.845	49 ± 3[c]	1.7×10^5
2-Chlorocyclopentyl *p*-chlorophenyl sulfide	.454	47 ± 6	9.7×10^4
2-Chlorocyclohexyl *p*-tolyl sulfide	.868	8.9 ± 0.2	9.7×10^5
2-Chlorocyclohexyl phenyl sulfide	.394	8.7 ± 0.3	4.5×10^5
2-Chlorocyclohexyl *p*-chlorophenyl sulfide	.265	10.8 ± 0.5	2.4×10^5
Cyclopentyl chloride		730 ± 10	
Cyclohexyl chloride		55 ± 1	

[a] These values were obtained by extrapolation of data given in Table I. [b] To obtain steady constants it is necessary to correct for the reaction of hydrogen chloride with the solvent (see Experimental section). The initial concentration of alkyl chloride was 0.025 to 0.030 M. [c] The method used to compute the rate constants for the *cis*-chlorosulfides and for cyclohexyl and cyclopentyl chloride is illustrated for this experiment in the Experimental section.

the measurements were complicated by reaction of the hydrochloric acid produced during the reaction with the solvent to form ethyl chloride. The rate of reaction of hydrogen chloride with the solvent was determined so that the apparent first-order rate of solvolysis could be corrected for the subsequent reaction. In this way reasonably steady first-order constants were obtained. A typical kinetic experiment is included in the Experimental section. The results are summarized in Table II along with values of k_{trans} for 118.2° (obtained by extrapolation of the data in Table I) and the ratio of reactivities for pairs of isomers (k_{trans}/k_{cis}). For comparison purposes, the rates of solvolysis of cyclohexyl and cyclopentyl chloride at 118.2° in 80% ethanol were determined and are included in Table II.

The data presented in Tables I and II show that the rates of solvolysis of the *trans*-chlorosulfides II and IV are increased by electron-donating substituents and decreased by electron-withdrawing substituents. On the other hand, the rates of solvolysis of the *cis*-chlorosulfides I and III are essentially unaffected by *p*-substituents in the benzene ring. The data in Table I give an excellent fit with the Hammett equation.[15] The calculated[7] values of ρ were found to be -1.388 at 30.05° and -1.453 at 20.05° for the *trans*-2-chlorocyclopentyl aryl sulfides (IV) and -1.431 at 30.05° and -1.495 at 20.05° for the *trans*-2-chlorocyclohexyl aryl sulfides (II).

Discussion

The axial conformation of the *trans*-2-chlorocyclohexyl aryl sulfides has a favorable geometry for participation by sulfur; however, such participation is geometrically precluded in the *cis* isomers. The data presented in Tables I and II clearly show that such participation (illustrated by V) results in a large rate enhancement. If it is assumed that solvolysis of the *cis* isomers involves ionization and that in the absence of participation *cis* and *trans* isomers would react at comparable rates, the values of k_{trans}/k_{cis} given in the last column of Table II represent a quantitative measure of the anchimeric acceleration.[11] Actually, the observed rate of solvolysis for a *cis* isomer would be expected to exceed the rate of unassisted ionization for the corresponding *trans* isomer. Solvent participation may well be involved in the solvolysis of the unreactive *cis*-chlorosulfides and, furthermore, the *cis* isomers have a more favorable conformational equilibrium than the *trans* isomers for unassisted ionization,[16] *i.e.*, a larger fraction with chlorine in an axial position. Thus the observed values for k_{trans}/k_{cis} are lower limits for the increase in rate of ionization due to participation by the neighboring sulfide group. In view of the small effect of 0.05 M lithium perchlorate on the rate of solvolysis of the *trans*-chlorosulfides, *cf.* expts. 2 and 3, no corrections were made for the difference in the ionic strengths of the solvents used for the *cis* and *trans* isomers.

It is seen from the data in Table II that at 118° the *cis*-2-chlorocyclohexyl aryl sulfides (I) are

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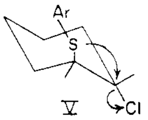
(15) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

(16) S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).

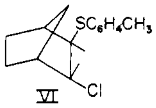
one-sixth as reactive as cyclohexyl chloride and the *cis*-2-chlorocyclopentyl aryl sulfides (III) are one-fifteenth as reactive as cyclopentyl chloride. Presumably the *cis*-β-sulfide group reduces the rate because of its electron-withdrawing inductive effect. The somewhat larger retarding effect on the rate in the cyclopentyl system than in the cyclohexyl system may be due to the fact that in the latter the inductive effect is partially offset by a favorable shift in the conformational equilibrium, *i.e.*, there is a greater population of the conformation with axial chlorine than if the *cis* substituent were not present.



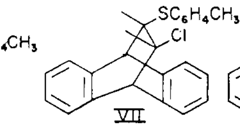
V

The large values of k_{trans}/k_{cis} for the cyclohexyl system and the cyclopentyl system show that in both systems the *trans* isomers solvolyze exclusively by the anchimerically assisted process. This is also indicated by similar values of ρ for the two *trans* series. The sign and magnitude of ρ (-1.388 for the cyclopentyl system and -1.431 for the cyclohexyl system) are consistent with the process in which sulfur participates in the rate-determining ionization step. The observation that ρ is zero for the two *cis* series shows that unassisted ionization is insensitive to the nature of substituents so far removed from the reaction center.

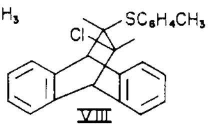
The present work shows that the increase in rate resulting from participation by the neighboring *trans*-sulfide group is nearly as large in the cyclopentyl system as in the cyclohexyl system. For corresponding pairs of isomers values of k_{trans}/k_{cis} are only 2.5 times larger for the cyclohexyl system than for the cyclopentyl system. This is especially interesting in view of recent evidence[17] that participation by a β-sulfide group is largely or completely precluded if the *trans*-carbon–chlorine and carbon–sulfur bonds cannot become coplanar. The rates of solvolysis of VI, VII and VIII in 85% ethanol at 116° are reported[17] to be 27, 1.4 and 5.6×10^{-6} sec.$^{-1}$, respectively. Thus the *trans*-chlorosulfide VI reacts at a rate comparable to that observed in the present work for cyclopentyl chloride. The reason for lack of participation in this system is not clear. It may be due to the fact that the rigidity of the system prevents coplanarity of the adjacent *trans* bonds[17] or perhaps the C_7-hydrogen interferes with participation. It is clear that participation is not involved to any appreciable extent in VIII. This *trans*-chlorosulfide is only 4 times more reactive than the *cis* isomer VII and reacts at about the same rate as cyclohexyl chloride. In this case lack of participation is likely due to the fact that the carbon–sulfur and carbon–chlorine bonds cannot become coplanar in this rigid system.[17] If this interpretation is correct the large anchimeric acceleration observed in the present work supports the previous suggestion[18] that not much strain is required for cyclopentane to assume a conformation in which adjacent *trans* bonds are coplanar.



VI



VII



VIII

It is interesting to compare the anchimeric acceleration for a sulfide group with that for an alkoxyl group in the cyclohexyl system. From the relative rates of acetolysis of *trans*-2-methoxycyclohexyl brosylate and cyclohexyl brosylate it has been estimated[11a] that in the former, ionization with participation of the neighboring methoxyl group is only about 4 times faster than unassisted ionization. In fact, anchimeric acceleration is so small that it does not offset the retarding inductive (and conformational) effect of the *trans*-methoxyl group; at 75° the *trans*-methoxy brosylate is one-eighteenth as reactive as cyclohexyl brosylate. As shown in Table II the phenyl sulfide group accelerates the rate of solvolysis of IIb by a factor of over 10^5. Since the solvolytic reactivity of ethyl β-chloroethyl sulfide is about 30 times greater than that of phenyl β-chloroethyl sulfide in aqueous dioxane[19] the expected value of k_{trans}/k_{cis} for methyl sulfide would be somewhat greater than that observed for phenyl sulfide. The much greater acceleration by sulfide than by alkoxyl is consistent with the well known superiority of sulfur over oxygen in second-order displacement processes.[20]

Experimental

2-Chlorocycloalkyl Aryl Sulfides.—The preparation and properties of the samples of *cis*- (I) and *trans*-2-chlorocyclohexyl (II) and *trans*-2-chlorocyclopentyl aryl sulfides (IV) used in the present work have been described in an earlier paper.[12,21] Preparations of the *cis*-2-chlorocyclopentyl aryl sulfides (III) also have been described[12]; however, in the earlier work these sulfides were not purified. Pure samples were obtained by chromatography following the procedure[12] used to purify the *cis*-2-chlorocyclohexyl aryl sulfides. The properties of the *cis*-2-chlorocyclopentyl aryl sulfides (III) are shown in Table III.

Kinetic Experiments.—All concentrations are reported for 25°. The rates of solvolysis of the *trans*-2-chlorocycloalkyl aryl sulfides were determined by intermittent titration of thermostated reaction mixtures with 0.0235 *M* sodium hydroxide in 80% ethanol.[9] The procedure used was essentially that described by Bartlett and Swain[4] except that no provision was made for maintaining an atmosphere of nitrogen and no corrections for disturbances arising from heat of neutralization appeared necessary. The indicator used was a 2:3 mixture of 0.1% methyl red in 80% ethanol containing 0.1 *M* lithium perchlorate and 0.1% brom cresol green in the same solvent. In 80% ethanol, the mixed indicator had a greenish-blue color. Upon addition of 10^{-4} mole of chlorosulfide to 100 ml. of thermostated solvent containing 0.5 ml. of indicator, the color gradually changed to orange. A timer was started when the color of the reaction mixture matched the intermediate shade of a reference cell. Base was added intermittently and the times at which the color matched that of the reference cell were recorded. "Infinity" titers were obtained after 10 half-lives. For the less reactive chlorides the "infinity" titers were obtained by heating the reaction mixtures to 70° for 5–9 hr. A typical kinetic experiment is summarized in Table IV.

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[17] S. J. Cristol and Robert P. Arganbright, Abstracts of Papers Presented at Atlantic City, N. J., Sept. 16–21, 1956, p. 24-O.

[18] J. Weinstock, S. N. Lewis and F. G. Bordwell, THIS JOURNAL, **78**, 6072 (1956).

[19] H. Bohme and K. Sell, *Ber.*, **81**, 123 (1948).

[20] See A. Streitwieser, *Chem. Revs.*, **56**, 571 (1956), for references.

[21] We are indebted to Dr. D. I. Relyea for providing pure samples of the *cis*- and *trans*-2-chlorocyclohexyl aryl sulfides.

TABLE III

PHYSICAL PROPERTIES AND ANALYTICAL DATA FOR *cis*-2-CHLOROCYCLOPENTYL ARYL SULFIDES

2-Chlorocyclopentyl sulfide	B.p.[a] °C.	Mm.	n^{25}D	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
p-Tolyl (IIIa)	136–139	0.25	1.5758	$C_{12}H_{15}ClS$	63.56	63.40	6.67	6.68
Phenyl (IIIb)	119–123	.1	1.5858	$C_{11}H_{13}ClS$	62.10	62.49	6.16	6.16
p-Chloro (IIIc)	150–153	.08	1.5932	$C_{11}H_{12}Cl_2S$	53.45	53.61	4.90	5.03

[a] Boiling points of samples prior to chromatography.

TABLE IV

RATE OF SOLVOLYSIS OF *trans*-2-CHLOROCYCLOPENTYL *p*-TOLYL SULFIDE IN 80% ETHANOL AT 30.05

Time, sec.	Vol. of 0.0235 *M* NaOH, ml.	10^3k, sec.$^{-1}$
0	0	
81	0.399	1.153
172	.820	1.177
239	.992	1.188
304	1.346	1.185
418	1.739	1.177
497	1.972	1.170
573	2.180	1.166
656	2.389	1.164
736	2.579	1.167
839	2.786	1.162
924	2.939	1.158
1019	3.092	1.153
1089	3.199	1.153
1184	3.329	1.151
1364	3.538	1.147
1521	3.685	1.141
1639	3.784	1.141
1782	3.889	1.142
1935	3.979	1.138
2138	4.079	1.135
2399	4.182	1.147
6470	4.474	
	Mean	1.158 ± 0.014

TABLE V

SOLVOLYSIS OF *cis*-2-CHLOROCYCLOPENTYL PHENYL SULFIDE IN "80%" ETHANOL AT 118.2°

Time, sec.	Apparent % reaction	$10^6k'_{cis}$,[a] sec.$^{-1}$	Corrected % reaction	10^6k_{cis},[b] sec.$^{-1}$
0	0	5.3[c]		
8,092	3.8	4.84	4.2	5.27
19,692	7.9	4.20	9.5	5.09
28,052	10.4	3.92	13.3	5.08
36,152	11.1	3.27	15.4	4.63
45,092	13.3	3.17	19.2	4.73
84,652	19.6	2.57	32.8	4.70
			Mean	4.9

[a] Apparent first-order constants. [b] Rate constants corrected for the reversible reaction of hydrogen chloride with solvent. [c] Value obtained by extrapolation to zero time.

For the solvolysis of the *cis*-chlorosulfides at 118° the sealed ampule technique was used and reactions were quenched by chilling the ampules in ice-water. Five-ml. aliquots were measured at 25° into a separatory funnel containing 5 ml. of carbon tetrachloride, 5 ml. of water and 10 drops of 6 *N* nitric acid. After two extractions with carbon tetrachloride the amount of chloride ion in the aqueous solution was determined by the Volhard method using 0.02 *N* silver nitrate and potassium thiocyanate. During the measured portion of the reactions the titers changed about 1–2 ml. and individual titrations were reproducible to within 0.01 ml. Initial concentrations of substrate (and "infinity" titers) were calculated from the weights of the samples.

These rate measurements were complicated by the reversible reaction of hydrogen chloride with the solvent (eq. 1) which resulted in a serious downward drift in the apparent first-order rate constants (k'_{cis}). A typical kinetic experiment is shown in Table V.

$$C_2H_5OH + HCl \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_2H_5Cl + H_2O \qquad (1)$$

The apparent first-order constants (k'_{cis}) and the rate constant for zero time (obtained by extrapolation) for the solvolysis of *cis*-2-chlorocyclopentyl phenyl sulfide (IIIb) are shown in the third column.

That the downward trend in the apparent rate constant is due to the reversible reaction shown by equation 1 was determined as follows. The reaction of 0.03030 *M* HCl with 80% ethanol at 118° was followed to equilibrium by titration of 5-ml. aliquots with 0.05 *N* NaOH. At equilibrium the concentration of HCl was 0.01594 *M*; $K_{eq} = 0.901$ under these conditions. The value of k_1 (eq. 1) was determined by use of equation 2 which is the integrated equation for the reversible process shown by equation 1.

$$-\ln([C_2H_5Cl]_{eq} - [C_2H_5Cl]_t)/[C_2H_5Cl]_{eq} = k_1t[HCl]_0/[C_2H_5Cl]_{eq} \qquad (2)$$

As predicted by equation 2, a plot of $-\ln([C_2H_5Cl]_{eq} - [C_2H_5Cl]_t)$ against time (t) was linear and k_1 was found from the slope to be 2.03×10^{-5} sec.$^{-1}$. From this value and that for K_{eq} (0.901) the value of k_2 was found to be 2.26×10^{-5} sec.$^{-1}$.

If the situation that prevails during solvolysis is summarized by equation (3) the amount of C_2H_5Cl at any time can be determined from the relationship shown by equation (4)[22] provided values for the constants are available. As indicated above k_1 and k_2 can be measured independently; k_{cis} can be approximated from the initial rate, *e.g.*, for the solvolysis of IIIb the value of 5.3×10^{-6} sec.$^{-1}$ was used for k_{cis}.

$$RCl \xrightarrow{k_{cis}} HCl \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_2H_5Cl \qquad (3)$$

$$[C_2H_5Cl] = \frac{k_1[RCl]_0}{k_1 + k_2}\left(1 + \frac{k_{cis}}{k_1 + k_2 - k_{cis}}e^{-(k_1 + k_2)t}\right) - \frac{k_1[RCl]_0}{k_1 + k_2 - k_{cis}}e^{-k_{cis}t} \qquad (4)$$

Since k_{cis} (eq. 3) is the rate constant for the formation of the sum $HCl + C_2H_5Cl$, and since the concentration of each of these can be determined (the former by direct measurement and the latter by use of equation 4) the first-order constant for the disappearance of the substrate (RCl) can be calculated. These values are given in the last column in Table V. The mean value of these corrected constants is probably not a more accurate measure of k_{cis} than that obtained by extrapolation of the apparent rate constants to zero time. However, the observation that the present treatment compensates for most of the downward drift, *cf.* columns 3 and 5, indicates that the drift in the apparent constants is indeed due to the reversible reaction shown by equation 1 superimposed on the solvolysis. The values for k_{cis} reported in Table II are mean values for the corrected constants.

MADISON, WISCONSIN

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[22] This relationship is a modification of the equation[23] for the scheme

$$A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} A_3$$

taking into account that in the present scheme (eq. 3) k_{-1} is zero.

[23] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 162.