Experimental

Twenty-five ml. of a standardized solution of selenious acid was pipetted into a 35-cc. platinum crucible. With the fluorine cell operating, the platinum delivery tube was introduced into the solution through a hole in the cover. The solution was maintained at steam-bath temperature. Following fluorination, aliquots were analyzed for unoxidized selenious acid.

Table I shows the results of trials on solutions of 0.393 equivalent of selenious acid per 25 ml.

TABLE I

Equiv. F_2	X-fold excess F_2	Conversion to H_2SeO_4, %
1.2	3	46.6
2.8	7	58.0
3.0	7.5	59.8
4.5	11.5	70.8
7.8	19.8	69.8

During the fluorination the volume of the solution was reduced considerably due to evaporation and to reaction between water and fluorine. In all concentration ranges studied, a maximum conversion limit was approached beyond which further fluorination had no effect.

The progressive addition of water during fluorination, such that the volume of solution was held constant, resulted in virtually complete conversion to selenic acid. In all cases a few tenths of a per cent. of unoxidized selenious acid was detected, as has been reported using hydrogen peroxide as oxidizing agent.[1] The X-fold excess fluorine needed to attain $99^{+}\%$ conversion did not vary significantly with the original concentration of selenious acid.

[1] L. I. Gilbertson and G. B. King, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 137.

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Acetolysis Rates of the *cis*- and *trans*-2-Chloro- and 2-Bromocyclohexyl *p*-Bromobenzenesulfonates

BY ERNEST GRUNWALD[1]

In the previous work on the acetolysis of various substituted cyclohexyl *p*-bromobenzenesulfonates,[2] it was important to know the driving forces due to the nucleophilic participation of the neighboring 2-substituents. To evaluate these driving forces, we compared the observed acetolysis rates k with the rates k_C predicted for a mechanism of the carbonium type. Whenever k significantly exceeded the estimate of k_C, a nucleophilic driving force due to the neighboring group was indicated.

In the case of the monatomic or structurally simple neighboring groups such as halogen or OH, values of k_C were calculated[2] from the extra electrostatic work[3] W needed to generate the C–O dipole M_1 of the partly ionized *p*-bromobenzenesulfoxy group in the transition state against the dipole of the neighboring group. In the case of the complex neighboring groups such as acetoxy and *p*-bromobenzenesulfoxy, *a priori* calculation of the carbonium rates was not readily feasible. It turned out[2] that the *cis*- and *trans*-cyclohexane 1,2-di-*p*-bromobenzenesulfonates reacted at slow and nearly equal rates. The *cis*-2-acetoxycyclohexyl *p*-bromobenzenesulfonate also reacted slowly, but the *trans*-ester was several thousand times faster. This contrasting behavior suggested[2] that the *trans*-2-acetoxy group was furnishing a driving force which the *cis*-group, due to its geometry, could not provide. To estimate this driving force, it was assumed that the carbonium rate k_C for the *trans*-compound was nearly equal to the observed rate for the *cis*-compound. Although this assumption seemed reasonable in view of the reactivities of the cyclohexane 1,2-di-*p*-bromobenzenesulfonates further evidence is desirable.

The *cis*- and *trans*-2-chloro- and 2-bromocyclohexyl *p*-bromobenzenesulfonates are excellent models for further study of these points.[4] The neighboring halo-groups are simple enough to permit *a priori* calculation of the carbonium rates k_C with some certainty even for the *cis*-isomers. Thus, some insight may be gained into the acetolysis mechanism of the *cis*-compounds.

The pertinent first-order acetolysis rate constants at 74.9° are summarized in Table I. The new rate constants[5] corroborate our previous conclusions[2] based on data for the *cis*- and *trans*-2-acetoxy- and 2-bromobenzenesulfoxycyclohexyl compounds. In the case of *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate where the previous evidence[2,6] had suggested a mechanism of the carbonium type, the rate agrees with that of the *cis* isomer within a factor of 4 (Table I). On the other hand, the *trans*-2-bromo ester reacts 800 times faster than the *cis*-2-bromo ester. This is again consistent with our previous judgment that the *trans*-2-bromine atom is furnishing a nucleophilic driving force.[2,6] The rates of the *cis*-2-chloro- and *cis*-2-bromocyclohexyl esters are nearly equal, consistent with the nearly equal inductive effects of these two atoms.

Beyond their low rates, little is known about the solvolytic reactions of the 2-halocyclohexyl esters. We have calculated the extra electrostatic work W, assuming a mechanism of the carbonium type, on the same basis as before.[2,3] The results, summarized in Table II, predict values of k_C $^1/_{14}$ of the observed rate for the *cis*-2-chloro ester and $^1/_5$ of the observed rate for the *cis*-2-bromo ester. These factors are large enough to make it appear unlikely that mechanisms of the carbonium type

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[1] Visiting Associate Chemist, Brookhaven National Laboratory, June–September, 1950; Department of Chemistry, Florida State University.

[2] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

[3] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

[4] The author is grateful to Dr. R. B. Loftfield of the Massachusetts General Hospital for providing him with pure samples of these compounds.

[5] The rate constants listed in Table I measure the acetolysis of the *p*-bromobenzenesulfonate group, not of the less reactive halogen atoms which may also solvolyze. The solvolysis rates of the halogen atoms may be estimated from the relative reactivities, cyclohexyl *p*-bromobenzenesulfonate:cyclohexyl bromide:cyclohexyl chloride $\approx 1:3 \times 10^{-3}:1 \times 10^{-4}$; and k/k_H for a *cis*- or *trans*-2-*p*-bromobenzenesulfoxy substituent $\approx 7 \times 10^{-5}$ (ref. 2). Thus one would expect reaction rates 1/10,000 of the observed rates if the *cis*-chlorine atom was sovolyzing, and 1/500 of the observed rates if the *cis*-bromine atom was solvolyzing.

[6] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).

are the major reaction paths in the acetolysis of the *cis*-2-halocyclohexyl *p*-bromobenzenesulfonates.

TABLE I

FIRST-ORDER ACETOLYSIS RATE CONSTANTS OF 2-SUBSTITUTED CYCLOHEXYL *p*-BROMOBENZENESULFONATES, 74.9°

2-Substituent	$ROSO_2C_6H_4Br$ *m*	$KOC_8H_5O_3$[a] *m*	10^8 *k*, sec.$^{-1}$
trans-Cl	0.0393	....	5.97[b]
	.0736	....	5.94
	.0434	0.0168	6.3[c]
cis-Cl	.0392	....	1.58
	.0778	....	1.58
	.0470	.0168	2.32
cis-Br	.0446	....	1.51
	.0723	....	1.58
	.0481	.0167	2.58
trans-Br[d]	.05	....	1250

[a] $KOC_8H_5O_3$, potassium acid phthalate. [b] Previous value[2] 5.64. [c] Extrapolated value at zero time. [d] Data taken from reference 2.

Experimental

Materials.—*cis*-2-Chlorocyclohexyl *p*-bromobenzenesulfonate, m.p. 93–94°, *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate, m.p. 79–80°, and *cis*-2-bromocyclohexyl *p*-bromobenzenesulfonate, m.p. 95.4–95.6°, were prepared and furnished by Dr. R. B. Loftfield. The syntheses will be described by him elsewhere.

Glacial acetic acid, acetic anhydride, and potassium acid phthalate were reagent grade chemicals.

Rate Measurements.—The sealed ampoule technique of rate measurement described previously[2] was used. Titrations were done with perchloric acid or potassium acid phthalate in glacial acetic acid to brom phenol blue[2] or tropaolin 00 indicator. Rates were followed to about 10% reaction, and over this range the kinetics was first order within the experimental error of 5% for the *cis*-2-haloesters. For the acetolysis of *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate in the absence of potassium acid phthalate, first-order kinetics was observed within the experimental error of 5%, but the end-points of the titration were not very sharp and reaction mixtures to which a slight excess of potassium acid phthalate was added turned neutral in a few minutes due to some secondary reaction. Acetolysis of *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate in the presence of 0.017 *m* potassium acid phthalate proceeded with complicated kinetics. Calculated first-order rate constants increased during the reaction, as is illustrated in Table III, again presumably due to a consecutive reaction involving acetate. The specific rate listed in Table I was obtained by extrapolation to zero time.

TABLE II

PREDICTED VALUES OF k_C FOR THE 2-HALOCYCLOHEXYL *p*-BROMOBENZENESULFONATES, 74.9°

2-Substituent	*W*, kcal./mole[a]	$k_C \times 10^8$, sec.$^{-1}$	$k \times 10^8$, sec.$^{-1}$
trans-Cl	(5.30)[a]	(5.9)	5.9
cis-Cl	8.03	0.11	1.58
trans-Br	4.90	10.4	1250
cis-Br	7.36	0.30	1.55

[a] The value of the parameter M_1/D_E was obtained from the data for *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate. $W = RT \ln (k_H/k_C)$, as in reference 2.

TABLE III

ACETOLYSIS OF *trans*-2-CHLOROCYCLOHEXYL *p*-BROMOBENZENESULFONATE IN THE PRESENCE OF 0.0168 *m* POTASSIUM ACID PHTHALATE, 74.9°

Time, hr.	$ROSOOC_6H_4Br$, *m*	$KOC_8H_5O_3$, *m*	10^8 *K*,[a] sec.$^{-1}$
0.0	0.04345	0.01676	(6.3)
89.5	.04255	.01586	6.49
267.5	.04068	.01399	6.84
476.0	.03838	.01169	7.24
767.7	.03464	.00795	8.20
976.3	.03234	.00565	8.40

[a] $K = [\ln a/(a - x)]/t$.

Calculation of *W*.—Study of Fisher–Taylor–Hirshfelder models revealed that electron attracting *trans*-1,2-cyclohexane substituents choose only the polar-*trans* positions of the chair form of cyclohexane[7] where they are nearly coplanar with their carbon atoms and oriented *trans*. In this way the dipole-interaction energies *W* are minimized. For two electron-attracting *cis*-substituents, there seems little to choose between the 1,2-positions in either the chair-form or the boat-form of cyclohexane. The angles and distances for all possible positions appear to be very comparable. Also, at the angles and distances typical of *cis*-1,2-substituents, the interaction energy *W* is not very sensitive to small changes in geometry. Therefore, it seemed logical to compute *W* for *cis*-bromine and *cis*-chlorine neighboring groups using the same model as before,[2] *i.e.*, a model where the *trans*-bonds are coplanar.

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(7) R. C. Fuson and H. R. Snyder, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1942, p. 14.

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The Partial Molal Entropy of Cuprous Ion

BY Z. Z. HUGUS, JR.

The Bureau of Standards tables[1] give as the partial molal entropy of cuprous ion, −6.3 e.u. Such a value seems too negative in view of the known entropies of other plus one ions.[2]

Apparently the literature contains only two determinations of equilibrium in the reaction

$$Cu(c) + Cu^{++} = 2Cu^{+}$$

over a range of temperatures. Kawassiadis[3] studied this equilibrium in sulfate solutions in the temperature range 50–200°. His results when plotted as $-R \ln K$ against $1/T$ seem erratic, and have been discarded as unreliable. Heinerth[4] studied the same equilibrium in sulfate and perchlorate solutions in the temperature range 20–60°. He found that variation in cupric concentration caused no change within experimental error in the quotient $(Cu^{++})^{1/2}/(Cu^{+})$. Thus it appeared that the activity coefficients of cuprous and cupric ions tended to cancel. Heinerth regarded his results in perchlorate solutions as uncertain since there was evidence that perchlorate was reduced, and with this in mind only his results in sulfate solution have been taken into account.

From Heinerth's data one may calculate for the above reaction

$$\Delta F^\circ_{298} = +8.29 \text{ kcal.}$$

and

$$\Delta H_{298} = +18.78 \text{ kcal.}$$

the uncertainty in these values being ±0.1 kcal. Using the known entropies of Cu(c), 7.97 e.u.

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(1) Selected Values of Chemical Thermodynamic Properties, Series I, National Bureau of Standards, Washington, D. C. (1947, *et seq.*).

(2) See for example, K. K. Kelley, U. S. Bur. Mines Bull., No. 477 (1950).

(3) C. T. Kawassiadis, *Praktika Akad. Athenon*, **10**, 391 (1935).

(4) E. Heinerth, *Z. Elektrochem.*, **37**, 61 (1931).