the concentrations of triiodide and vanadic ions, and inversely proportional to the concentrations of the hydrogen and iodide ions. This result is in agreement with the postulation that the single rate determining step is one between hydrolyzed vanadic ions, VOH^{++}, and iodine molecules. Several possible rapid follow-up mechanisms have been suggested. The salt effect has been measured over the range of ionic strengths from 0.31 to 1.76, and a possible explanation for its large negative magnitude has been advanced.

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

The Mechanism of Substitution Reactions. Substitution of Bromine and Chlorine in Phenylbromo and Phenylchloroacetic Acids by Chloride and Bromide Ions in Aqueous Solution

BY M. J. YOUNG AND A. R. OLSON

When an optically active bromo compound is treated with chloride ion, a whole system of reactions is initiated. By making a kinetic study of the system of reactions which occurs when *l*-bromosuccinic acid is treated with chloride ion in aqueous solution, Olson and Long[1] were able to prove the correctness of the theory of the mechanism of substitution reactions advanced by Olson,[2] and by Bergmann, Polanyi and Szabo,[3] according to which configurational inversion accompanies every single-step substitution.

The present study deals with the kinetics of the corresponding system of reactions produced by treating *l*-phenylbromoacetic acid with chloride ion in aqueous solution. The results provide additional confirmation of the above-mentioned theory.

The relations between the heats of activation of the various reactions in the succinic system, studied by Olson and Long,[4] are again apparent in this system. The same is true of the temperature independent factors.

Preparation of Materials

Phenylbromoacetic acid and phenylchloroacetic acid were prepared from mandelic acid (phenylhydroxyacetic acid) by treatment with the corresponding phosphorus pentahalides, following the procedure given by Walden and Bischoff.[5] The acids were resolved by fractional crystallization of their morphine salts from methyl alcohol, following the procedure of McKenzie and Clough.[6] The products were shown to be chemically pure by the usual analyses. Complete resolution was not obtained in all cases but as is shown by the rate laws, optical purity is in no way essential. It is essential that the assumption that *l*-phenylchloroacetic acid and *l*-phenylbromoacetic acid have the same configuration be correct. This assumption is in accord with the opinion of those who have worked with such compounds.

Apparatus

For all measurements of optical activity a laboratory constructed polarimeter of the Lippich type was used, with monochromatic light (λ 5461) obtained from a mercury arc and suitable filters. The angle of rotation was determined from the deflection of the image of an illuminated scale, four meters distant, produced in a small plane mirror mounted nearly on the axis of the analyser, and reflected into a telescope parallel to the optic axis by means of a periscope arrangement. This device enabled rotations to be read directly to 0.007° (1 mm. of scale) and estimated to 0.001°. A given setting can be duplicated to 0.005°. A thermostat provided with glass windows was mounted directly on the polarimeter so that tubes did not have to be removed for observation.

Experimental Procedure

Due to the slowness with which the phenylhalogenoacetic acids dissolve in water, the following procedure was adopted. A weighed amount of the active acid was dissolved in 0.4 cc. of methyl alcohol. To this solution was added the required amount of 2.00 *N* perchloric acid (about 10 cc.) followed, after re-solution had occurred, by the required amount of 2.00 *N* halogen acid (about 10 cc.). The addition of so small an amount of methyl alcohol has no observable effect on the reaction rates. All solutions were prepared at the temperature of the experiment. After the solution process, the material was transferred rapidly to a 30-cm. polarimeter tube and placed in the thermostat. Zero time was taken as the moment of addition of halide ion. The time interval between this addition and the first reading was never more than four minutes. In all experiments the concentrations are: active acid 0.015 *M*, halide ion 1.00 *M*, hydrogen ion 2.00 *M*, unless otherwise specified.

The Formation of Mandelic Acid from Phenylhalogenoacetic Acids.—The detailed mechanism

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[1] A. R. Olson and F. A. Long, THIS JOURNAL, **56**, 1294 (1934).

[2] A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[3] Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

[4] A. R. Olson and F. A. Long, THIS JOURNAL, **58**, 393 (1936).

[5] Walden and Bischoff, *Ann.*, **279**, 122 (1894).

[6] McKenzie and Clough, *J. Chem. Soc.*, **93**, 818 (1908).

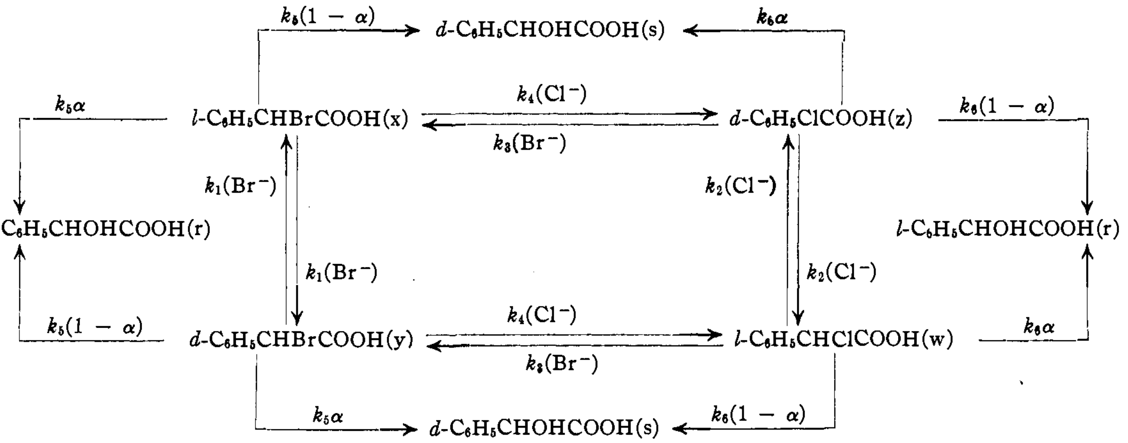
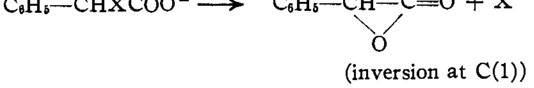


Fig. 1.—System of reactions occurring when l-phenylbromoacetic acid is treated with chloride ion in aqueous solution, assuming complete inversion accompanies each single-step substitution.

of the reactions between phenylbromoacetic acid or phenylchloroacetic acid and water, by which mandelic acid, hydrogen ion and halide ion are produced, is not completely understood in spite of the amount of investigation to which it has been subjected.[7,8,9] The specific rate, measured by the rate of formation of hydrogen ion, is in accord with the assumption that the undissociated acid reacts more slowly than its ion. Measurement of the decrease of optical activity with time makes it necessary to suppose that the ion can react with water in either of two different ways, one reaction producing a d-mandelic acid, and the other an l-mandelic acid. The following mechanism can account for this effect and is at the same time in accord with the theory that inversion in configuration accompanies each single-step substitution.

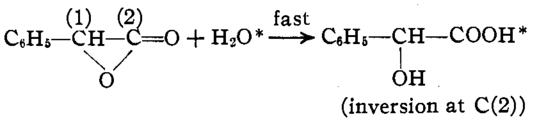
(1) $C_6H_5\text{—}\overset{(1)}{C}HX\text{—}\overset{(2)}{C}OOH + H_2O \xrightarrow{k_1} C_6H_5CHOHCOOH + H^+ + X^-$ (inversion at C(1))

(2) $C_6H_5\text{—}\overset{(1)}{C}HX\text{—}\overset{(2)}{C}OO^- + H_2O \xrightarrow{k_2} C_6H_5CHOHCOOH + X^-$ (inversion at C(1))

(3)


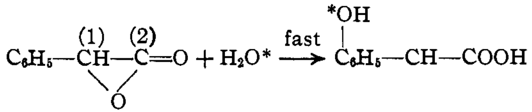
$C_6H_5\text{—}\overset{(1)}{C}HX\overset{(2)}{C}OO^- \xrightarrow{k_3} C_6H_5\text{—}CH\text{—}C{=}O + X^-$

(inversion at C(1))

(4)


$C_6H_5\text{—}\overset{(1)}{C}H\text{—}\overset{(2)}{C}{=}O + H_2O^* \xrightarrow{\text{fast}} C_6H_5\text{—}\underset{OH}{CH}\text{—}COOH^*$

(inversion at C(2))

(5)


$C_6H_5\text{—}\overset{(1)}{C}H\text{—}\overset{(2)}{C}{=}O + H_2O^* \xrightarrow{\text{fast}} C_6H_5\text{—}\overset{*OH}{CH}\text{—}COOH$

(inversion at C(1))

Reactions (1), (2) and the sequence (3), (4) lead to a mandelic acid of configuration opposite to that of the $C_6H_5CHXCOOH$. The sequence (3), (5), involving a double inversion at C(1), leads to a mandelic acid of the same configuration as that of the $C_6H_5CHXCOOH$. The relative amounts of levo and dextro mandelic acids depend on the relation between the specific rates of the various reactions under the conditions of the experiment.

Although we failed to isolate the postulated lactone, a similar compound is known to be formed in the hydrolysis of bromosuccinic acid.

When the hydrogen-ion concentration is large, this mechanism predicts that l-$C_6H_5CHXCOOH$ will disappear at a specific rate $k_1 + \{(k_2 + k_3)k_a/(H^+)\}$, where k_a is the dissociation constant of $C_6H_5CHXCOOH$, and that d and l mandelic acids will appear at specific rates $k_1 + \{(k_2 + k_3\beta)k_a/(H^+)\}$ and $k_3(1-\beta)k_a/(H^+)$, respectively, where β is the fraction of the lactone hydrolyzing by reaction (4) and $(1-\beta)$ the fraction hydrolyzing by reaction (5). If the specific rate of disappearance of l-$C_6H_5CHXCOOH$ is represented by K, the specific rates of production of l and d mandelic acid can be represented by $K(\alpha)$, and $K(1-\alpha)$, respectively, where $\alpha = 1-\{k_3\beta k_a/[k_1(H^+) + k_2k_a + k_3k_a]\}$.

Rate Laws

Following the system of reactions and the notation shown in Fig. 1, we can write the differen-

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[7] (a) Senter and Tucker, *J. Chem. Soc.*, **109**, 690 (1916); (b) Senter, *ibid.*, **107**, 908 (1915); (c) Senter and Drew, *ibid.*, **107**, 638 (1915).

[8] A. McKenzie and N. Walker, *ibid.*, **107**, 1685 (1915).

[9] A. M. Ward, *ibid.*, 1184 (1926).

tial equations for the rate of change of the concentration of each substance.

(1) $dx/dt = -k_1(\mathrm{Br}^-)x + k_1(\mathrm{Br}^-)y + k_3(\mathrm{Br}^-)z - k_4(\mathrm{Cl}^-)x - k_5x$

(2) $dy/dt = -k_1(\mathrm{Br}^-)y + k_1(\mathrm{Br}^-)x + k_3(\mathrm{Br}^-)w - k_4(\mathrm{Cl}^-)y - k_5y$

(3) $dw/dt = -k_2(\mathrm{Cl}^-)w + k_2(\mathrm{Cl}^-)z - k_3(\mathrm{Br}^-)w + k_4(\mathrm{Cl}^-)y - k_6w$

(4) $dz/dt = -k_2(\mathrm{Cl}^-)z + k_2(\mathrm{Cl}^-)w - k_3(\mathrm{Br}^-)z + k_4(\mathrm{Cl}^-)x - k_6z$

(5) $dr/dt = k_5\alpha x + k_5(1 - \alpha)y + k_6\alpha w + k_6(1 - \alpha)z$

(6) $ds/dt = k_5\alpha y + k_5(1 - \alpha)x + k_6\alpha z + k_6(1 - \alpha)w$

(7) $d(\mathrm{Br}^-)/dt = k_4(\mathrm{Cl}^-)(x + y) - k_3(\mathrm{Br}^-)(w + z) + k_5(x + y)$

(8) $d(\mathrm{Cl}^-)/dt = -k_4(\mathrm{Cl}^-)(x + y) + k_3(\mathrm{Br}^-)(w + z) + k_6(w + z)$

For the determination of the angle of rotation only the quantities $(x - y)$, $(w - z)$ and $(r - s)$ need be calculated, for $\theta = C_1(x - y) + C_2(w - z) + C_3(r - s)$. For the evaluation of the six specific rates, a series of experiments was devised each involving only one unknown specific rate. This series, and the corresponding integrated rate laws, are shown in Table I.

TABLE I

(1) Initial conditions: $(x - y) = (x - y)_0$, $(w - z) = 0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 1\ M$, $(\mathrm{H}^+) = 2\ M$

Additional assumption: $k_1 >> k_5$ so that k_5 can be neglected. (Br^-) = constant

Rate law: $\Theta/\Theta_0 = e^{-2k_1(\mathrm{Br}^-)t}$

(2) Initial conditions: $(x - y) = 0$, $(w - z) = (w - z)_0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumption: Since (Cl^-) remains small, $k_2(\mathrm{Cl}^-)$ can be neglected compared to k_6

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-k_6t}$, $\Theta_\infty = C_3 (w - z)_0 (2\alpha - 1)$

(3) Initial conditions: $(x - y) = 0$, $(w - z) = (w - z)_0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 1\ M$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumption: (Cl^-) = constant

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-[2k_2(\mathrm{Cl}^-)+k_6]t}$, $\Theta_\infty = C_3(w - z)_0k_6(2\alpha - 1)/\{2k_2(\mathrm{Cl}^-) + k_6\}$

(4) Initial conditions: $A = (x - y) = (x - y)_0$, $(w - z) = 0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumptions: none

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-(2k_1A+k_5)t+\{2k_1A(1-e^{-k_5t})/k_5\}}$ $\Theta_\infty = C_3(x - y)_0 (2\alpha - 1)k_5/(2k_1A + k_5)$

(5) Initial conditions: $(x - y) = 0$, $(w - z) = (w - z)_0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 0$, $(\mathrm{Br}^-) = 1\ M$, $(\mathrm{H}^+) = 2\ M$

Additional assumptions: (1) $k_1 >> k_3$ so that ϕCHBr-COOH is racemized as fast as it is formed; *i. e.*, $(x - y) = 0$; k_5 makes no contribution to $(r - s)$.
(2) (Cl^-) is so small that $k_2(\mathrm{Cl}^-)$ and $k_4(\mathrm{Cl}^-)$ are negligible.
(3) (Br^-) = constant

Rate law: $(\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = e^{-[k_3(\mathrm{Br}^-)+k_6]t}$, $\Theta_\infty = k_6(w - z)_0C_3(2\alpha - 1)/(k_3(\mathrm{Br}^-) + k_6)$

(6) Initial conditions: $(x - y) = (x - y)_0 = A$, $(w - z) = 0$, $(r - s) = 0$, $(\mathrm{Cl}^-) = 1\ M$, $(\mathrm{Br}^-) = 0$, $(\mathrm{H}^+) = 2\ M$

Additional assumptions: (1) $k_3(\mathrm{Br}^-)$ can be neglected,
(2) $k_6 << k_5$,
(3) (Cl^-) = constant,
(4) $\Theta_\infty = 0$ (experimentally true)

Rate law: $\theta/\theta_0 = (1 + R)e^{-Q(t)} - Re^{-[2k_2(\mathrm{Cl}^-)+k_6]t}$

$R = [C_2/C_1]k_4(\mathrm{Cl}^-)/[2k_1A + k_4(\mathrm{Cl}^-) + k_5 - 2k_2(\mathrm{Cl}^-) - k_6]$

$Q(t) = [2k_1A + k_4(\mathrm{Cl}^-) + k_5]t - 2k_1A[(1 - e^{-[k_4(\mathrm{Cl}^-)+k_5]t})/(k_4(\mathrm{Cl}^-) + k_5)]$.

The rate laws for experiment series (1), (2), (3) and (5) follow in a perfectly straightforward manner from the differential equations; those for experiment series (4) and (6) involve an integral of the form

$$I = \int_0^t e^{-(a+b)t+[a(1-e^{-bt})/b]}dt$$

We have been unable to evaluate this integral exactly in terms of elementary functions. Olson and Long handled it by means of a series expansion and term by term integration. We have found the following procedure more convenient in this case. Integration by parts gives

$$I = \left\{(1 - e^{-(a+b)t+[a(1-e^{-bt})/b]}\right\} \Big/ (a + b) + \left\{a\int_0^t e^{-(a+2b)t+[a(1-e^{-bt})/b]}\,dt\right\} \Big/ (a + b)$$

The second integral can be neglected for two reasons. The integrand is smaller by a factor e^{bt}, and the coefficient a is small compared to 1, in the time units employed. The error introduced by this neglect is never more than 0.3%.

The constants appearing in expressions (1), (2), (3) and (5) can be evaluated by calculating one value from each observation and averaging the results in the usual manner, or by obtaining a value of the slope of the line

$$\ln (\Theta - \Theta_\infty)/(\Theta_0 - \Theta_\infty) = -kt$$

using the method of least squares. The expressions (4) and (6) cannot be solved explicitly for the unknown specific rates k_5 and k_4, respectively. In these cases a value of the specific rate was determined by a trial and error process to fit one observation; the remaining observations were plotted on a curve calculated using this constant, and agreement was found satisfactory in all cases. The results obtained are given in Tables II–VIII. The values of *k*(calcd.) are those obtained from the activation energies and temperature independent factors shown in Table VIII. All times are in minutes unless otherwise specified.

Results

TABLE II

$$l\text{-}C_6H_5CHBrCOOH + Br^- \overset{k_1}{=} d\text{-}C_6H_5CHBrCOOH + Br^-$$

T, °K.	No. of runs	(Br^-) moles/liter	k_1	Mean deviation, %	k_1 calcd.
288.1	2	0.984	0.004358	0.5	0.004363
298.1	2	.208	.01198	.1	....
298.1	3	.965	.01268	.3	.01251
303.23	2	.965	.01984	.3	.0209
307.02	2	.964	.02974	1	.03020
310.70	1	.960	.04294	..	.04294

TABLE III

$$l\text{-}C_6H_5CHClCOOH + H_2O \xrightarrow{k_6} C_6H_5CHOHCOOH + H^+ + Cl^-$$

T. °K.	No. of runs	k_6	Mean deviation. %
323.1	2	2.20×10^{-4}	2
308.1	2	3.65×10^{-5}	2
298.1	2	1.03×10^{-5}	2

TABLE IV

$$l\text{-}C_6H_5CHClCOOH + Cl^- \overset{k_2}{=} d\text{-}C_6H_5CHClCOOH + Cl^-$$

T, °K.	No. of runs	$k_{obsd.} = 2k_2(Cl^-)+k_6$	(Cl^-)	k_2	Mean deviation, %
308.1	2	5.067×10^{-4}	2.00	1.178×10^{-4}	1.6
323.1	2	2.660×10^{-3}	2.00	6.100×10^{-4}	1.5

TABLE V

$$l\text{-}C_6H_5CHClCOOH + Br^- \xrightarrow{k_{3'}} d\text{-}C_6H_5CHBrCOOH + Cl^-$$

T, °K.	No. of runs	$k_{obsd.} = k_3(Br^-)+k_6$	(Br^-)
322.54	6	3.260×10^{-3}	0.980
308.05	5	7.326×10^{-4}	.980
298.1	2	2.457×10^{-4}	.980

k_3	Mean deviation. %	k_3, calcd.
3.114×10^{-3}	1.5	3.104×10^{-3}
7.104×10^{-4}	1.9	7.141×10^{-4}
2.402×10^{-4}	2.0	2.397×10^{-4}

TABLE VI

$$l\text{-}C_6H_5CHBrCOOH + H_2O \xrightarrow{k_5} d\text{-}C_6H_5CHOHCOOH + H^+ + Br^-$$

T,°K.	No. of runs	k_5
324.0	2	0.00174
307.92	2	0.000318

TABLE VII

$$l\text{-}C_6H_5CHBrCOOH + Cl^- \xrightarrow{k_4} d\text{-}C_6H_5CHClCOOH + Br^-$$

T. °K.	No. of runs	k_4	k_4, calcd.
322.54	3	0.01582	0.01576
307.92	2	.003610	.003632
298.1	2	.001253	.001250

TABLE VIII

Reaction	$E_{\text{cal.}/\text{mole}}$	$A \times 10^{-9}$ (sec.$^{-1}$ moles^{-1} liters)
$l\text{-}C_6H_5CHBrCOOH + Br^-$	17,971 ± 150	3.13
$l\text{-}C_6H_5CHClCOOH + Cl^-$	21,683	4.74
$l\text{-}C_6H_5CHClCOOH + Br^-$	20,016 ± 87	1.90
$l\text{-}C_6H_5CHBrCOOH + Cl^-$	19,805 ± 100	6.93

No values of *E* and *A* for the hydrolysis reactions (Tables III and VI) were calculated for they would be of doubtful significance since the specific rates are complex averages over several reactions. The listed probable errors are mean deviations from the average of the values of *E* calculated for each temperature interval.

It can be shown that the introduction of the assumption of incomplete inversion in configuration, giving rise to the system of reactions appearing in Fig. 2, where the Greek letters represent in each case the fraction of the reaction occurring without inversion, results in an alteration of the rate laws which is not detectable except in the case of expression 6. In this case the new rate law is

$$\Theta/\Theta_0 = (1 + R)e^{-Q(t)} - Re^{-[2k_2(Cl^-)+k_6]t}$$

where $R = C_2k_4(Cl^-)(1 - 2\epsilon)/C_1[2k_1A + k_4(Cl^-)(1 - 2\epsilon) + k_5 - 2k_2(Cl^-) - k_6]$

$$Q(t) = [2k_1A + k_4(Cl^-)(1 - 2\epsilon) + k_5]t - \{2k_1A(1 - e^{-[k_4(Cl^-)+k_5]t})/[k_4(Cl^-) + k_5]\}$$

The effect which this modification has on the calculated value of θ for various times and for various values of ϵ is shown in Table IX for the

TABLE IX

Time min.	Θ cm. $\epsilon = 0$	$\Delta\Theta$ $\epsilon = 0.03$	$\Delta\Theta$ $\epsilon = 0.05$	$\Delta\Theta$ $\epsilon = 0.07$
0	−15.76	0	0	0
10	11.18	0	+0.01	+0.01
20	7.27	+0.01	+ .02	+ .03
30	3.98	− .02	− .03	.00
40	1.21	− .03	− .04	− .05
50	+1.09	− .03	− .06	− .07
60	2.45	− .03	− .06	− .08
70	4.52	− .03	− .05	− .09
80	5.75	− .03	− .05	− .08
90	6.75	− .03	− .04	− .08
100	7.54	− .02	− .03	− .07
150	9.48	− .01	− .02	− .03
200	9.72	− .01	− .01	− .01

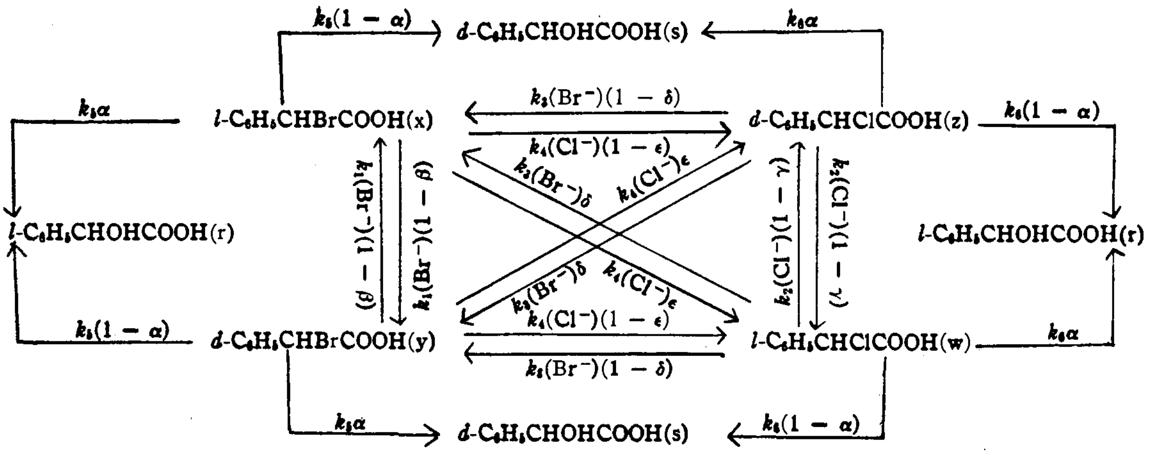

Fig. 2.—System of reactions occurring when *l*-phenylbromoacetic acid is treated with chloride ion in aqueous solution, assuming some substitution without inversion can occur.

experiments at 322.54°K. The curve calculated for $\epsilon = 0$ on which the experimental points have been superimposed is shown in Fig. 3. ($\Delta\theta$ is taken positive when the value for $\epsilon = 0$ is larger in absolute magnitude than that for $\epsilon \neq 0$.)

Since the average deviation of the experimental points from the calculated curve is 0.06 cm. with no trend, one can conclude that inversion is complete within the limits of detectability (5%). The rather large limits on ϵ are a result of the small value of A, the initial concentration of bromo acid, made necessary by its slow solubility. $\Delta\theta$ is directly proportional to A.

Discussion of Results

The results obtained are compared with those of Olson and Long[4] in Table X.

TABLE X

Reaction	Activation energy cal./mole Phenyl-acetic system	Succinic system	Δ	Collision number × 10^{-9} sec.$^{-1}$ moles^{-1} liters Phenyl-acetic system	Succinic system	Ratio
1 BrA + Br$^-$	17,971	21,800	3829	3.13	14.9	4.76
2 ClA + Cl$^-$	21,683	24,770	3087	4.74	8.42	1.78
3 ClA + Br$^-$	20,016	23,540	3524	1.90	6.24	3.28
4 BrA + Cl$^-$	19,805	23,650	3845	6.93	39.5	5.71

(1) The difference between the activation energies of the two series is nearly the same for all reactions, although it is somewhat larger for the bromo acids than for the chloro acids. This 3600 calories is a composite of the alterations in bond strength and resistance to inversion brought about by substituting $-CH_2COOH$ for C_6H_5 in the reacting molecule. Nothing quantitative can be said about the relative contributions of the two factors.

(2) The fact that the activation energy of the exchange reactions (the same for both within experimental error) is closer to that of ClA + Cl$^-$ than to that of BrA + Br$^-$ may mean that the unstable intermediate (BrACl)$^-$, where A is the rest of the molecule resembles (ClACl)$^-$ more closely than (BrABr)$^-$.

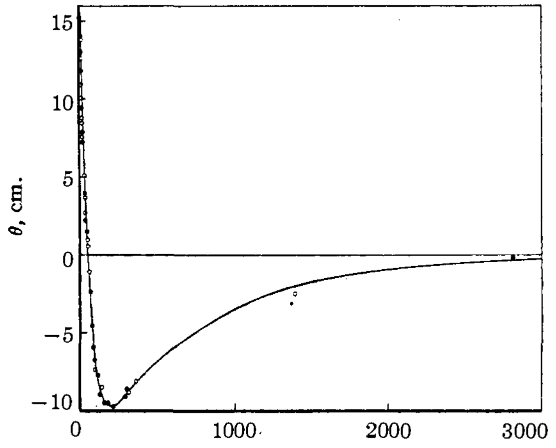

Fig. 3.—Angle of rotation plotted against time for the reaction between *l*-phenylbromoacetic acid and chloride ion in aqueous solution at 322.54°K.

(3) The collision numbers of reactions involving Cl$^-$ are larger than those involving Br$^-$, while those involving bromo acids are larger than those involving chloro acids, and the collision number of the exchange reaction BrA + Cl$^-$ is larger than that of ClA + Br$^-$ in the ratio one would expect from the two tendencies in combination.

A calculation of the total number of collisions for comparison with the observed collision number is somewhat arbitrary because of the uncertainty in collision diameter. The arbitrary selection of a value 1.75 times the length of the bond to be formed, leads to a steric factor of from $^1/_{40}$ to $^1/_{10}$. The face centered addition of X^- at C_6H_5CHY-$COOH$ leads to an orientation factor of less than $^1/_2$ for $C_6H_5CHYCOOH$; solvation of X^- may introduce an additional orientation factor. Furthermore, one must take into account the efficiency of transfer between translational and vibrational energy which Rice[10] has found to vary widely from case to case. The most that one can say is, that there is nothing in the collision numbers to invalidate the given picture of the reaction.

The correlation between the kinetic and thermodynamic interpretations of a chemical equilibrium leads to a relation between the ratio of the collision numbers of the forward and reverse reaction and the standard entropy change. For reactions (3) and (4) this relation is

$$R \ln (A_4/A_3) = S^0(\text{Br}^-) + S^0(\text{Cl}A) - S^0(\text{Cl}^-) - S^0(\text{Br}A)$$

where S^0 is the molal entropy of the given substance when its concentration is 1 M in an ideal aqueous solution, based on $S^0(\text{H}^+) = 0$ for comparison. Latimer, Schutz and Hicks[11] give 5.9 e. u. as the difference between $S^0(\text{Br}^-)$ and $S^0(\text{Cl}^-)$. Using this value, and the experimental values of A_4 and A_3 we calculate that the difference in entropy between solutions of l-BrA and l-ClA is 2.7 ± 1 e. u., a not unreasonable result.

Rice and Gershinowitz[12] have made use of the relation between entropy and collision number to develop a method for calculating the collision numbers of bimolecular associations. The reactions studied can be looked upon as being of this type followed by the almost instantaneous decomposition of the associated pentavalent carbon "complex." We have applied this method in calculating the collision numbers of the four reactions, omitting consideration of vibrational entropy, and calculating moments of inertia from rough geometrical models of the reactants. The results are shown in Table XI.

TABLE XI

Reaction	$A \times 10^{-9}$ calcd.	$A \times 10^{-9}$ obsd.
(1) l-$C_6H_5CHBrCOOH + Br^-$	3.22	3.13
(2) l-$C_6H_5CHClCOOH + Cl^-$	6.43	4.74
(3) l-$C_6H_5CHClCOOH + Br^-$	3.54	1.90
(4) l-$C_6H_5CHBrCOOH + Cl^-$	6.33	6.93

Considering the nature of the calculation the agreement is striking. All of the features of the general reaction picture (inversion, face centered addition) have been included in the calculation and no additional ones.

Summary

The specific rates in aqueous solution of the following four reactions, at several temperatures in the interval 15–50°, have been determined.

(1) $l\text{-}C_6H_5CHBrCOOH + Br^- = d\text{-}C_6H_5CHBrCOOH + Br^-$

(2) $l\text{-}C_6H_5CHClCOOH + Cl^- = d\text{-}C_6H_5CHClCOOH + Cl^-$

(3) $l\text{-}C_6H_5CHClCOOH + Br^- \longrightarrow d\text{-}C_6H_5CHBrCOOH + Cl^-$

(4) $l\text{-}C_6H_5CHBrCOOH + Cl^- \longrightarrow d\text{-}C_6H_5CHClCOOH + Br^-$

It was shown that reaction 4, which alone provides information on this point, is accompanied by complete inversion in configuration, in accord with the theory.

The activation energies of the four reactions bear relations to each other similar to those in the corresponding reactions of the halogenosuccinic acids.

The collision numbers of the four reactions, considered from a kinetic viewpoint, are not in disagreement with what might have been predicted from the theory. They are in close agreement with values calculated by a statistical mechanical method embodying the essential features of the theory.

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