

CLI.—*Studies on the Walden Inversion. Part X.*
The Reaction between Water and the Phenylchloro-
acetate and Phenylbromoacetate Ions.

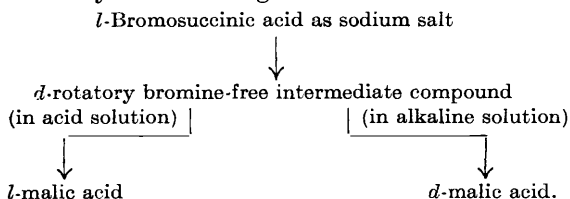
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RACEMISATION may be effected by two processes apparently distinct, namely (1) without displacement of groupings, and (2) during group-displacement. Catalytic racemisation falls under case (1). The generally accepted mechanism of (1) is that the racemisation is due either (*a*) to a tautomeric change, or (*b*) to an equilibrium existing between the original substance and the products formed by its dissociation, one of which is unsaturated at the asymmetric centre (compare Lowry, *Rep. Brit. Assoc.*, 1904; McKenzie and Widdows, *J.*, 1915, **107**, 702; McKenzie and Wren, *J.*, 1919, **115**, 602; Walden, "Optische Umkehrerscheinungen," 1919, V Kapitel). By such a mechanism the resulting mixture of optical isomerides, if not quite inactive, must contain an excess of the isomeride initially present, a Walden inversion thus being impossible. This statement, however, would not be applicable in the case of asymmetric catalytic racemisation (McKenzie and Smith, *Ber.*, 1925, **58**, 894). On the other hand, racemisation of type (2) may be effected by the occurrence of two simultaneous reactions, whereby both *d*- and *l*-isomerides of the product are formed as follows :

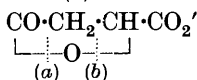


The two reactions, which may be identical from the ordinary kinetic standpoint, proceed with velocities, the coefficients of which, k_1 and k_2 , may be equal or different. The relative values of k_1 and k_2 might vary largely according to the experimental conditions, so that in some cases k_2 would be negligible in comparison with k_1 , when only one isomeride would result. When k_1 and k_2 become equal, the product would be entirely racemic; whilst, depending on the relative values of k_1 and k_2 , a complete range of intermediate activities of either sign is possible. By such a mechanism a Walden inversion may thus be effected. This view has been suggested in

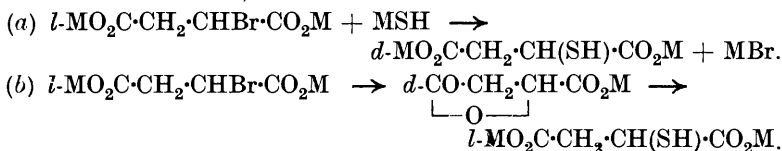
various forms many times previously (compare Fischer, *Annalen*, 1911, **381**, 126; Werner, *ibid.*, 1912, **386**, 68), and the experiments of Holmberg, whereby active products of either sign are produced from a given initial material, provide a proof for the case in which the mechanisms of the production of the two isomerides differ when deduced from the ordinary kinetic standpoint. Thus the kinetic results (Holmberg, *J. pr. Chem.*, 1913, **87**, 456) show that the conversion of sodium or silver *l*-bromosuccinate into malic acid proceeds through an intermediate stage, since definitely established as malolactone. If this reaction is carried out in acid solution, the product from *l*-bromosuccinic acid is *r*- and *l*-malic acids, whilst in alkaline solution *r*- and *d*-malic acids are formed. Holmberg represented this by the following scheme :



This scheme closely resembles the one used above, but the mechanism of the production of the malic acids from the lactone is not discussed, and appears to be more allied to Phillips's investigations (J., 1923, **123**, 22; Kenyon, Phillips, and Turley, J., 1925, **127**, 399; Phillips, *ibid.*, p. 2563) than to the present work, the reaction probably taking place by the fission of one or other of the bonds in malolactone as indicated in positions (a) and (b)

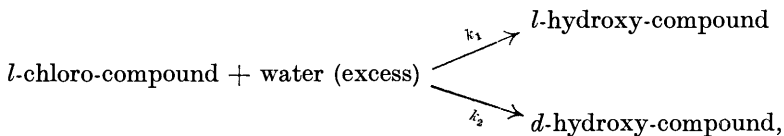


In the subsequent experiments on the xanthosuccinic acids and the thiolmalic acids (Holmberg, *J. pr. Chem.*, 1913, **88**, 553; *Arkiv Kemi, Min., Geol.*, 1916, **6**, No. 1; 1916, **6**, No. 8; Holmberg and Lenander, *ibid.*, 1917, **6**, No. 17) evidence from kinetic results shows the reaction to proceed both by direct substitution of the halogen and also *via* the lactone, and from experiments with the reactants in various concentrations, the following mechanism was put forward for the conversion into the thiolmalic acids (and similarly for the xanthosuccinic acids) :



The mechanisms for the production of the stereoisomeric thiolmalic acids (and xanthosuccinic acids) are here kinetically different, whereas in the present investigation the mechanisms are the same from the ordinary kinetic point of view.

Considered on a quantitative basis, the reaction (*e.g.*)



in order to fulfil the conditions of the above mechanism, must (from the results of kinetic measurements) be one of a simple order, and the value of k thus calculated will be equal to $k_1 + k_2$, whilst, from the results of measurements of the change of rotation of the solution of the active substance with time under the same conditions as employed for the inactive, the same value of k should result. To test these considerations the conversion of sodium *l*-phenylchloroacetate into sodium *r*- and *l*-mandelate has been carried out. The action of water on *l*-phenylchloroacetic acid, of water on sodium *l*-phenylchloroacetate, and of aqueous sodium hydroxide on sodium *l*-phenylchloroacetate was first studied by McKenzie and Clough (*J.*, 1908, **93**, 811; 1909, **95**, 777), who found that the mandelic acid produced was lævorotatory and that extensive racemisation occurred in these changes. The kinetics of the conversion of *r*-phenylchloroacetic acid and its sodium salt in aqueous solution, and also of the sodium salt in aqueous caustic soda solution, have been investigated (Senter, *J.*, 1915, **107**, 908), and it was shown that each of the above reactions is one and the same, namely, the reaction of water with the phenylchloroacetate ion. The best value for the velocity coefficient for the conversion of sodium *r*-phenylchloroacetate in aqueous sodium hydroxide solution at 25° was considered to be 0.00146, where time is measured in minutes, but the values of k actually found (*loc. cit.*, p. 914) at 25° for the sodium salt ($N/10$) were

- (a) in caustic soda ($N/10$), 0.00138, 0.00142, 0.00145,
 (b) ,, ,, ($N/5$), 0.00134, 0.00134, 0.00138.

Thus the reaction here dealt with is $\text{PhCHCl}\cdot\text{CO}_2' + \text{H}_2\text{O}(\text{excess}) \rightarrow \text{PhCH}(\text{OH})\cdot\text{CO}_2' + \text{NaCl}$ from the kinetic point of view. Table I gives the results of the corresponding polarimetric experiment, which was carried out as follows. To 150 c.c. of aqueous sodium hydroxide (0.1858*N*) at 24.85° were added 2.3037 g. of *l*-phenylchloroacetic acid with $[\alpha]_{D}^{18} = -191.5^\circ$ in benzene (resolved by the method of McKenzie and Clough, *loc. cit.*, except that the morphine salt was

decomposed by dilute aqueous ammonia). The acid rapidly dissolved to a clear, colourless solution, which was maintained at 24.85°. Samples were withdrawn at the times shown in Table I, and their rotations determined, using a 2-dcm. tube and the yellow mercury line.

TABLE I.

Time.	θ_t (obs.).	θ_t (calc.).	k .	
			Differential.	Integral.
0 mins.	-[4.52]			
7	4.50			
39	4.24	-4.25	0.0019	0.00168
61	4.12	4.11	0.0013	0.00156
121	3.75	3.74	0.0016	0.00158
181	3.38	3.33	0.0018	0.00165
240	3.05	3.10	0.0018	0.00169
300	2.82	2.83	0.0014	0.00162
360	2.55	2.58	0.0018	0.00164
420	2.35	2.35	0.0014	0.00161
480	2.15	2.14	0.0016	0.00160
543	2.00	1.95	0.0012	0.00156
600	1.76	1.79	0.0024	0.00164
665	1.59	1.62	0.0017	0.00164
730	1.50	1.47	0.0010	0.00158
1510	0.54	0.50	0.0013	0.00154
1773	0.38	0.36	0.0017	0.00157
2037	0.26	0.28	0.0022	0.00166
2931	0.16	0.15	0.0011	0.00153
5 days	0.11			
8	0.10			
17	0.11		Mean 0.0016	Mean 0.00161

The values of k differential (column 4) are obtained from the formula

$$k = \frac{\delta\theta}{\delta t} \cdot \frac{2}{\theta_{t_2} + \theta_{t_1} - 2\theta_{\infty}}$$

where θ_{t_2} and θ_{t_1} are consecutive observations, $\delta\theta = \theta_{t_2} - \theta_{t_1}$ and $\delta t = t_2 - t_1$. The values of k thus calculated are irregular, as is only to be expected, since a small error in the determination of θ_t causes, by this method, a large variation in the coefficient. No drift in value, however, occurs, and the applicability to this case is thus shown of the integrated form (column 5) for a unimolecular reaction, namely, $k = \frac{2.3}{t} \log_{10} \frac{\theta_0 - \theta_{\infty}}{\theta_t - \theta_{\infty}}$.

This method of calculation does, however, suffer from the defect that great importance is placed on the value of θ_0 , but the mean value of k obtained by both methods is substantially the same. A duplicate determination using an acid with $[\alpha]_{D789} - 188^\circ$ gave $k = 0.00160$.

It would thus appear that the mechanism is in the main as postulated, but the divergence between the values of the coefficients

as thus calculated and those of Senter (*loc. cit.*) remains to be accounted for. The following experiment on sodium *l*-mandelate showed that under the conditions of the preceding experiments mandelic acid does not undergo catalytic racemisation, at least with any speed comparable with that of the displacement here studied. To 1.3865 g. of *l*-mandelic acid with $[\alpha]_{5780}^{15^{\circ}} = 159^{\circ}$ in water, was added a mixture of 50 c.c. of sodium chloride (0.2020*N*) and 50 c.c. of aqueous sodium hydroxide (0.1858*N*) at 24.85°. The solution was maintained at this temperature, and samples were withdrawn at intervals and their rotations determined, the yellow mercury line and a 2-dcm. tube being used. The results are shown below :

Time (hours)	0.10	2.05	12.05	30.5	50.0	3 days	9 days
Rotation ...	-3.25°	-3.43°	-3.35°	-3.43°	-3.44°	-3.44°	-3.44°

Thus no contributory factor here arises to produce the difference in the two values. There remains the slight possibility that the coefficient for sodium *l*-phenylchloroacetate is not the same as that for sodium *r*-phenylchloroacetate, but this was disposed of by carrying out experiments (*a*) and (*b*) below.

(*a*) To 1.4822 g. of *l*-phenylchloroacetic acid, with $[\alpha]_{5780}^{24^{\circ}} = 188^{\circ}$ at 24.85°, were added 100 c.c. of sodium hydroxide (0.2010*N*). Samples of 10 c.c. were withdrawn at times shown, and titrated against sulphuric acid (1.037 × *N*/20), phenolphthalein being used as indicator.

(*b*) This experiment was carried out simultaneously with (*a*), and the conditions were identical, except that 1.5816 g. of *r*-phenylchloroacetic acid were used.

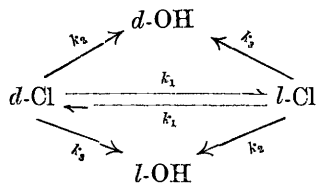
The results are in Table II, *k* being equal to $2.3/t. \log_{10} a/(a-x)$.

TABLE II.

<i>l</i> -Acid.			<i>r</i> -Acid.		
Time.	Titre.	<i>k</i> .	Time.	Titre.	<i>k</i> .
3 mins.	21.45		4 mins.	20.43	
60	20.38		60	19.13	
179	18.22	0.00128	180	16.84	0.00126
360	15.42	0.00131	360	13.89	0.00129
540	13.31	0.00129	540	11.57	0.00130
660	12.03	0.00131	660	10.20	0.00133
1500	7.41	0.00131	1500	5.10	0.00138
4 days	5.09		6 days	2.87	
	Mean	0.00130		Mean	0.00131

It thus appears certain there is a divergence between the values of *k* as determined from titres and from optical measurements, and this may be satisfactorily accounted for by assuming that, in addition to the displacement racemisation of the phenylchloro-

acetate ion, there is a simultaneous catalytic racemisation of this ion, so that the completed scheme would become :



If a is the initial concentration of d -chloro-compound, b the initial concentration of l -chloro-compound, x and y the amounts of d - and l -chloro-compounds respectively changed in time t ,

$$\text{then } dx/dt = k_1(a - x) - k_1(b - y) + (k_2 + k_3)(a - x) \quad (1)$$

$$\text{and } dy/dt = k_1(b - y) - k_1(a - x) + (k_2 + k_3)(b - y) \quad (2)$$

Integration of (1) and (2) gives

$$x = a - \frac{a + b}{2} e^{-(k_2 + k_3)t} - \frac{a - b}{2} e^{-(2k_1 + k_2 + k_3)t} \quad (3)$$

$$\text{and } y = b - \frac{a + b}{2} e^{-(k_2 + k_3)t} + \frac{a - b}{2} e^{-(2k_1 + k_2 + k_3)t} \quad (4)$$

For the hydroxy-compounds, if w_d and w_l are the concentrations of d - and l - forms, respectively, present at time t ,

$$\text{then } dw_d/dt = k_2(a - x) + k_3(b - y) \quad (5)$$

Substituting in (5) the values of x and y in (3) and (4) and integrating

$$\begin{aligned}
 w_d = & -\frac{a + b}{2} e^{-(k_2 + k_3)t} - \frac{k_2 - k_3}{2k_1 + k_2 + k_3} \cdot \frac{a - b}{2} \cdot e^{-(2k_1 + k_2 + k_3)t} \\
 & + \frac{(k_1 + k_2)a + (k_1 + k_3)b}{2k_1 + k_2 + k_3}
 \end{aligned}$$

Similarly

$$\begin{aligned}
 w_l = & -\frac{a + b}{2} e^{-(k_2 + k_3)t} - \frac{k_3 - k_2}{2k_1 + k_2 + k_3} \cdot \frac{a - b}{2} \cdot e^{-(2k_1 + k_2 + k_3)t} \\
 & + \frac{(k_1 + k_3)a + (k_1 + k_2)b}{2k_1 + k_2 + k_3}
 \end{aligned}$$

Thus at any time t , the observed rotation of the solution (θ_t) is equal to the rotation of the chloro-compounds + the rotation of the hydroxy-compounds, *i.e.*, $\theta_t = D_{Cl}\{(a - x) - (b - y)\} + D_{OH}(w_d - w_l)$, where D_{Cl} , D_{OH} are the rotations of unit concentrations

of *d*-chloro- and *d*-hydroxy-compounds, respectively, under the given conditions, *i.e.*,

$$\theta_t = D_{Cl}\{(a-b)e^{-(2k_1+k_2+k_3)t}\} + D_{OH} \cdot \frac{(k_2-k_3)(a-b)}{2k_1+k_2+k_3} \{1 - e^{-(2k_1+k_2+k_3)t}\}.$$

In the present case, $a = 0$, so that

$$\theta_t = -D_{Cl} \cdot b \cdot e^{-(2k_1+k_2+k_3)t} - D_{OH} \cdot b \cdot \frac{k_2-k_3}{2k_1+k_2+k_3} \{1 - e^{-(2k_1+k_2+k_3)t}\} \quad (6)$$

To evaluate k_1 , k_2 and k_3 , we have from (6) when $t = 0$,

$$\theta_0 = -D_{Cl} \cdot b = -4.52 \text{ (Table I)} \quad . \quad . \quad (7)$$

and when $t = \infty$,

$$\theta_\infty = -D_{OH} \cdot b \cdot \frac{k_2-k_3}{2k_1+k_2+k_3} = -0.11 \text{ (Table I)}.$$

Substituting in (6),

$$\begin{aligned} \theta_t &= -4.52e^{-(2k_1+k_2+k_3)t} - 0.11 + 0.11e^{-(2k_1+k_2+k_3)t} \\ &= -4.41e^{-(2k_1+k_2+k_3)t} - 0.11, \end{aligned}$$

$$i.e., \quad e^{(2k_1+k_2+k_3)t} = \frac{-4.41}{\theta_t + 0.11} = \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty},$$

$$\text{therefore } 2k_1 + k_2 + k_3 = \frac{2.3}{t} \log_{10} \frac{\theta_0 - \theta_\infty}{\theta_t - \theta_\infty} = 0.00161 \text{ (Table I)}$$

and $k_2 + k_3 = 0.00130$ (Table II), so that $k_1 = 0.000155$.

Further, from the data on p. 1188, 2.054 g. of mandelic acid (= 2.3037 g. of phenylchloroacetic acid) have rotation $-3.39^\circ = -D_{OH} \cdot b$.

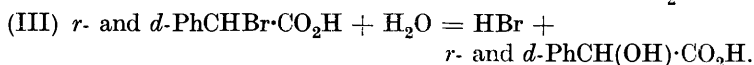
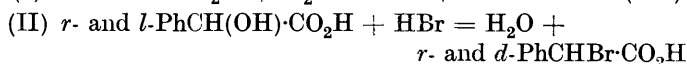
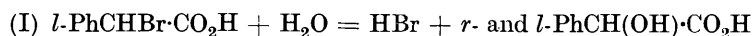
Therefore from (7), $-0.11 = -3.39 \frac{k_2-k_3}{0.00161}$, so that $k_2 - k_3 = 0.000052$, whence $k_2 = 0.000676$ and $k_3 = 0.000624$ and $\theta_t = -4.41e^{-0.00161t} - 0.11$.

For comparison with the observed values of θ_t , those values thus calculated are shown in column 3, Table I.

The divergence between the coefficients from the corresponding titration and optical experiments is thus satisfactorily accounted for by assuming that besides the displacement racemisation, there is also a catalytic racemisation.

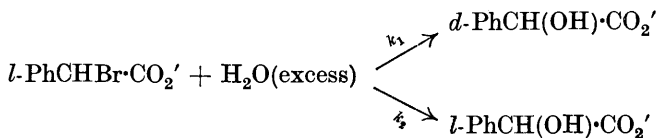
It becomes of interest to review in the same way the results of McKenzie and Walker (J., 1915, **105**, 1685) on the conversion of *l*-phenylbromoacetic acid and its sodium salt in aqueous and aqueous caustic soda solutions, in conjunction with the corresponding kinetic experiments of Senter and Tucker (J., 1916, **107**, 690). The experiments of Senter and Tucker on the reactions between water and *r*-phenylbromoacetic acid and its sodium salt, and also

between aqueous caustic soda and sodium *r*-phenylbromoacetate, showed that the main reaction in each case consists of the interaction of water and the phenylbromoacetate ion, exactly as for phenylchloroacetic acid. From the results on the bromo-acid, it was considered that in this case water also reacts with the undissociated acid, the reaction between water and the ion being some 120 times faster than between water and the undissociated acid. The main reaction here dealt with is, therefore, $\text{PhCHBr}\cdot\text{CO}_2' + \text{H}_2\text{O}(\text{excess}) \rightarrow \text{PhCH}(\text{OH})\cdot\text{CO}_2'$. As for the chloro-acid, the rate of reaction is thus dependent on the hydrogen-ion concentration, and development of hydrogen ions during the reaction causes a marked falling off in the value of the velocity coefficient. McKenzie and Walker found in some of their experiments that the reaction between water and *l*-phenylbromoacetic acid gave *d*- and *r*-mandelic acids, whilst in other cases *l*- and *r*-acids resulted, and to account for this the following scheme was put forward (*loc. cit.*, p. 1689) :



The changes of rotation involved in the cases on which this theory is based were very small. Thus from the data in Table I (*loc. cit.*, p. 1693) the change is from -0.02° to $+0.04^\circ$. Assuming that the *l*-rotation due to the mandelic acid when (I) is complete is -0.02° , if no racemisation at all took place in (II) and (III), then the rotation of the *d*-mandelic acid would be $+0.02^\circ$, and could not be $+0.04^\circ$ by this mechanism, although a difference of $\pm 0.02^\circ$ is within the limits of experimental error. If, however, it is assumed that (II) and (III) proceed at all, extensive racemisation would undoubtedly accompany both stages, so that for practical purposes the resultant mandelic acid would be optically inactive. Furthermore, these processes must be assumed to continue indefinitely, and by the above mechanism complete racemisation must ultimately result, but in the first experiment quoted (*loc. cit.*, p. 1692), the mandelic acid isolated after 3 weeks had $\alpha_D + 0.16^\circ$, $[\alpha]_D + 4.7^\circ$, whilst in the second experiment, the mandelic acid isolated after two months at 25° had $\alpha_D + 0.31^\circ$, $[\alpha]_D + 5.2^\circ$. It does not appear justifiable to base any accurate comparison on the third experiment (*loc. cit.*, p. 1692), in which an optically impure phenylbromoacetic acid ($[\alpha]_D - 70^\circ$) was used, when it was found that the rotation of the solution before isolation of the product was $\alpha_D - 0.16^\circ$, and of the mother-liquors after isolation was $\alpha_D - 0.45^\circ$; the rotation of

the mandelic acid isolated (= 18.2% of theory) is not recorded, and the rotations of the solutions in this case might well be due to some impurity present initially in the partly racemic phenylbromoacetic acid used. Thus it does not appear that McKenzie and Walker's scheme is correct. Also no explanation is apparent for the almost complete racemisation in stage (I). On the other hand, if the mechanism of the reaction is assumed in the main to be



where k_1 and k_2 are nearly equal, closer agreement between theory and experiment is obtained. In some cases, according to the conditions, k_1 may be greater than k_2 , corresponding with the production of a final dextrorotation, whilst if k_1 is less than k_2 , then the solution will remain levorotatory. This explanation is only tenable if the change of sign of rotation is in accord with the displacement effect as determined by titration, and whereas McKenzie and Walker's experiments showed the displacement to be complete before a final steady rotation value was obtained, the following experimental results did not confirm this.

Reaction between Water and r-Phenylbromoacetic Acid at 25°.

Water (250 c.c.) was added to *r*-bromo-acid (1.3438 g. = $N/40$ and 2.5088 g. = $1.867N/40$, respectively); in the case of the $N/40$ solution, 72 minutes elapsed before the solution was homogeneous, whilst for the $1.867N/40$ solution, 173 minutes were required. These times are reckoned as zero in each set of results. Samples (10 c.c.) were withdrawn and titrated against sodium hydroxide solution ($1.011N/40$), with phenolphthalein as indicator. The results are in Table III, k_1 and k_2 being calculated from the usual unimolecular formula.

The theoretical final titres are 19.78 c.c. and 36.93 c.c., respectively. The above data confirm the results of Senter and Tucker (*loc. cit.*, p. 694) and McKenzie and Walker (*loc. cit.*, p. 1693) that the value of the velocity coefficient in $N/40$ solution is appreciably higher than in $1.867 \times N/40$ solution (McKenzie and Walker state their results as $k \times 10^{-3}$, whereas they should be $k \times 10^{-2} \times 2.3$). This difference is in accord with the different relative concentrations of phenylbromoacetate ions in the two solutions, for, in the reactions

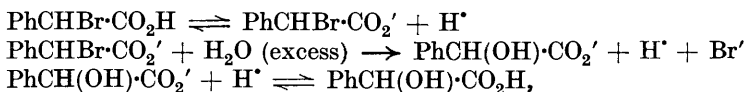


TABLE III.

N/40.			1.867 × N/40.		
Time.	Titre.	k_1 .	Time.	Titre.	k_2 .
0 mins.	12.7		0 mins.	25.5	
15	13.3	0.00596	15	26.3	0.00480
30	13.9	0.00626	30	27.0	0.00465
60	14.2	0.00401	60	27.5	0.00318
90	15.0	0.00442	90	28.1	0.00284
120	15.5	0.00425	120	28.6	0.00261
150	15.9	0.00407	150	29.2	0.00258
180	16.2	0.00385	180	29.9	0.00268
210	16.6	0.00388	210	30.4	0.00264
240	16.9	0.00381	240	30.7	0.00251
270	17.1	0.00366	270	31.3	0.00260
330	17.5	0.00350	330	31.8	0.00240
390	17.8	0.00334	390	32.0	0.00213
450	18.1	0.00328	450	32.5	0.00208
510	18.4	0.00330	510	32.9	0.00202
570	18.6	0.00324			
25 hrs.	19.3		24 hrs.	36.0	
47	19.7		45½	37.0	
72	19.7		70½	37.0	

if a_1 is the initial concentration of bromo-acid and α_1 the degree of dissociation, the initial concentration of phenylbromoacetate ion is $a_1\alpha_1$ and therefore the initial rate of reaction is $k\alpha_1a_1$, whereas the rate in Table III is actually measured by k_1a_1 , so that $k = k_1/\alpha_1 = k_2/\alpha_2$ similarly. Now $\alpha_1 = 0.3106$ for N/40-solution, since the dissociation constant for phenylbromoacetic acid is 0.0035 (Senter and Tucker, *loc. cit.*, p. 692) and $k_1 = 0.00406$, taking the mean value in Table III (since the initial values are irregular), so that $k = 0.013$. Similarly for 1.867N/40-solution, $\alpha_2 = 0.2390$ and $k_2 = 0.00284$, giving $k = 0.012$.

The important point of difference, however, is that whereas McKenzie and Walker's titration experiment showed the displacement of halogen to be complete after 25½ hours, in the present experiments all the halogen was not displaced in this time, but was complete only after some 50 hours, for the initial rate of reaction falls off rapidly as the reaction proceeds, owing to the accumulation of hydrogen ions in the system.

Reaction between Water and 1-Phenylbromoacetic Acid at 25°.

The optical kinetic experiment of McKenzie and Walker (*loc. cit.*, p. 1693) was also repeated, but in this case a 4-dcm. tube was used and measurements were made both for the yellow and the green mercury lines. Accordingly 0.3011 g. of *l*-bromo-acid with $[\alpha]_{D_{5461}}^{177} - 177^\circ$ in benzene was dissolved in 30 c.c. of water (= 1.867N/40) at 25°. Solution occupied 62 minutes, and this is shown as zero-time in Table IV. The values of k are calculated for a unimolecular reaction.

TABLE IV.

Time.	$\alpha_{5750}^{25^\circ}$	k .	$\alpha_{5461}^{25^\circ}$	k .
0 mins.	-4.25°		-4.67°	
15	-3.98	0.00427	-4.37	0.00428
30	-3.76	0.00397	-4.09	0.00428
45	-3.56	0.00382	-3.87	0.00404
60	-3.29	0.00414	-3.65	0.00397
90	-2.92	0.00409	-3.21	0.00401
120	-2.64	0.00384	-2.85	0.00396
150	-2.34	0.00384	-2.57	0.00382
180	-2.08	0.00382	-2.27	0.00383
210	-1.83	0.00385	-2.03	0.00378
240	-1.67	0.00373	-1.83	0.00371
270	-1.48	0.00373	-1.63	0.00370
330	-1.20	0.00364	-1.32	0.00361
390	-1.00	0.00350	-1.05	0.00358
450	-0.77	0.00355	-0.85	0.00351
570	-0.53	0.00336	-0.55	0.00340
690	-0.33	0.00332	-0.36	0.00328
25 hrs.	+0.04	0.00275	+0.05	0.00265
30 $\frac{1}{2}$	+0.07		+0.09	
34 $\frac{1}{2}$	+0.08		+0.10	
49 $\frac{1}{2}$	+0.12		+0.14	
120	+0.11		+0.14	

The final change in the rotation of the solution is thus to be attributed to the completion of the displacement reaction, and stages (II) and (III) of McKenzie and Walker's scheme become unnecessary. For comparison, the various results in the two papers previously referred to, calculated on the basis of a unimolecular reaction, are summarised in the following table, together with the present results.

Experiment.	k (Titration).	k (Optical).
(1) <i>l</i> -Acid, 25°	—	0.00373
<i>r</i> -Acid, 25°	0.00284	—
(2) <i>l</i> -Acid, 36.8°	0.0142	0.0161
(3) Sodium salt of <i>l</i> -acid, 24.8°	—	0.0166
" " of <i>r</i> -acid, 25°	0.0147	—
(4) Sodium salt of <i>l</i> -acid, sodium hydroxide, 24.1°	—	0.0179
" " of <i>r</i> -acid, sodium hydroxide, 25°	0.0181	—
	0.0175	

In cases (1), (2), and (3), the individual values of k fall off with time, so that the mean values above are calculated over corresponding time intervals. There is a general agreement throughout between the two series of coefficients, but those from the optical measurements are higher than those based on titrations; this difference would agree, as also in the case of the chloro-acid, with a catalytic racemisation of the phenylbromoacetate ion occurring simultaneously with the displacement racemisation. The catalytic racemisation of phenylbromoacetic acid in aqueous acetone solution was clearly demonstrated by McKenzie and Walker (*loc. cit.*, p. 1694). The mechanisms of the conversions of phenylbromoacetic acid and

its sodium salt to mandelic acid and sodium mandelate thus agree with the mechanism above suggested much better than with that advanced previously.

Discussion of Results.

The above results show that the reaction of water with *l*-phenylchloroacetate and *l*-phenylbromoacetate ions yields simultaneously both *l*-mandelate and *d*-mandelate ions by the same simple reaction from the kinetic point of view, the one reagent thus behaving both "normally" and "abnormally" at the same time in this reaction. The production of phenylaminoacetic acids of either sign from a given phenylchloroacetic acid (Senter and Drew, J., 1915, **105**, 638; 1916, **107**, 1091) or phenylbromoacetic acid (Senter and Tucker, J., 1918, **113**, 140) by reaction with ammonia in various solvents is explicable on the above basis, for the relative values of the velocity coefficients will certainly depend on the solvent medium (compare Senter, Drew, and Martin, J., 1918, **113**, 155). In the case of the other conversions similarly studied (Senter, Drew, and Martin, *loc. cit.*; Senter and Ward, J., 1924, **125**, 2137; 1925, **127**, 1847), it would appear probable that the relative values of the two velocity coefficients differ more widely, agreeing with the production of the same isomeride in excess for all solvents studied.

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