

CCLXI.—*The Walden Inversion. Part III.*

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IN Parts I and II (J., 1928, 2447 ; 1929, 1282) the author developed a new hypothesis of the reaction mechanism of the Walden inversion based upon the assumption that, when one of the radicals linked to the asymmetric carbon atom is split off, the optically active molecule oscillates between two configurations, each of which, by the addition of a new radical, can produce only one of the two possible optical antipodes.

Two types of Walden inversion are therefore postulated (see Part II) according as the scission is effected (1) spontaneously or by a molecule which is neither identical with nor contains the entering radical, or (2) by collision with a molecule containing the entering radical. In the first case both forms will be produced, for some of the incomplete molecules will react while in one phase, and others in the other phase, and the proportion of molecules retaining the original configuration can be calculated. In the second case, there is a definite distance between the entering radical and the vacant place at the moment of scission ; consequently only one form of the reaction product will be produced, and this may be of the inverted or of the original type according to the structure and size of the reacting molecules and to the time of oscillation.

Reactions between halogeno-acids (*e.g.*, bromosuccinic acid) and hydroxyl ions or other anions (*e.g.*, the xanthogenate ion) are examples of Type 1, and those between hydroxy-acids and phosphorus pentachloride are assumed to be examples of Type 2.

In the present paper the investigation of the stereochemical result of the reaction between a *l*-bromosuccinate and a xanthogenate is continued. In Part II (*loc. cit.*) a curve was obtained showing the relation between  $n$  (*i.e.*, the fraction of the reaction product which retains its original configuration) and  $c_x$  (*i.e.*, the mean of the concentrations of the xanthogenate ion at the beginning and end of the reaction) for values of the latter between 0.05 and 1.95*M*.

In all these experiments the concentration of the bromosuccinate ion was the same, and only  $c_x$  was varied, as this concentration was deemed the crucial one. Nevertheless, it was also thought necessary to ascertain the influence of variations in the concentration of the other component, and experiments were therefore made in which (1) both concentrations were varied simultaneously, and (2) one concentration was increased while the other was decreased in such a manner that their sum was kept constant. The ionic strength was kept constant throughout ( $\mu = 2.5$ ) by addition of indifferent salts except in one special experiment described later (No. 20). On the other hand, it has been necessary to avoid experiments in which the bromosuccinate was in excess, because the reaction product would then require fractionation, which would entail alteration in the stereochemical composition of the xanthogeno-succinic acid formed in the reaction.

The range of concentration has now been extended from  $c_x = 0.0005M$ , which is probably near the lower limit of concentrations in sufficiently accurate Walden inversion experiments, up to  $c_x = 8.95M$ , which corresponds to saturation of the solution with potassium xanthogenate during the whole course of the reaction. This last experiment, therefore, constitutes the exception in which the ionic strength was necessarily not 2.5.

As in preceding papers, it is assumed that  $n$  is proportional to the probability that the oscillating molecule reacts with the entering ion while in one of the oscillation phases whose configuration is identical with the original. But although this probability was provisionally regarded as proportional to  $c_x$  for a short range of concentrations, or for studies where the aim was only to procure a general survey of the relevant data in the literature, such a simple assumption is not valid for measurements over larger ranges of concentration. Consequently, it is necessary to replace the former equation,  $n = kc_x f$ , by one based upon a more exact treatment.

We assume now that this probability can be equated to that fraction of the reacting ions which, according to Maxwell's distribution law, possess speeds lying between such limits that they can produce collision during those periods wherein the oscillating molecule has its original configuration. A necessary condition for the whole theory is, of course, that the optically active molecule at the moment of splitting off a radical is not surrounded by the entering ions (referred to subsequently as X-ions) at all possible distances from the closest proximity to the maximum at the concentration concerned; for, if this were the case,  $n$  could only vary from unity at the highest concentrations (where all the oscillating molecules are closely surrounded by X-ions) down to 0.5 at the lowest concentrations (where both very small and very great distances could occur so that reaction could take place in all possible oscillation phases, producing practically equal amounts of *d*- and *l*-forms) and the reaction mechanism would not be capable of explaining a Walden inversion, of which the essential characteristic is that  $n < 0.5$ .

Actually it is improbable that xanthogenate ions will be found in very close proximity to the bromosuccinic ion, for the double negative charge of this ion will tend to keep them at as great a distance as possible. When the bromine atom is spontaneously split off, the excess of negative charge in the bromosuccinic ion is halved, and the repelling force exerted by this ion upon the surrounding xanthogenate ions being thus suddenly diminished, the bombardment of the amphoteric ion,  $-O\cdot CO\cdot CH_2\cdot \overset{+}{C}H\cdot CO\cdot O^-$ , begins from the mean molecular distance prevailing at that moment.

A corresponding conception can be used for all the Walden inversions classified in Type I (see above), since the author's assignment to this class of all inversions where the results are influenced by the concentration was based upon the common feature of a spontaneous expulsion of a negative radical and subsequent addition of a new radical present in the solution in the form of a negative ion.

The way in which the shape of the  $n$ -curve is affected by the duration of the several phases in the oscillating molecule must now be examined more closely. In our preliminary examination, we provisionally assumed that only one of the radicals remaining linked to the asymmetric carbon atom was oscillating, the other two being assumed to be at rest, but it was emphasised that this assumption was merely for the sake of simplicity. Only in molecules of very special structure (which it is proposed to investigate later) can the oscillation take place in this simple way, which would entail that the duration of the first phase is  $\theta/4$  and that of all the later

phases is  $\theta/2$ ,  $\theta$  being "the time of oscillation." In these circumstances all oscillating molecules reacting during the periods

$$0 - \frac{\theta}{4}; \frac{3\theta}{4} - \frac{5\theta}{4}; \frac{7\theta}{4} - \frac{9\theta}{4}; \dots$$

reckoned from the moment of their scission, would give a reaction product of the same configuration as the original asymmetric molecule, whereas molecules reacting during the alternate periods

$$\frac{\theta}{4} - \frac{3\theta}{4}; \frac{5\theta}{4} - \frac{7\theta}{4}; \frac{9\theta}{4} - \frac{11\theta}{4}; \dots$$

would give inversion. The corresponding  $n$ -curve for large values of  $c_x$  would be asymptotic to unity; as the values of  $c_x$  decreased, however, the curve would pass through a minimum below  $n = 0.5$ , and thereafter rise again and, through a sequence of ever decreasing maxima and minima, approach  $n = 0.5$  for  $c_x = 0$ .

For the general case the above picture of the state of an oscillating molecule would be far more complicated, for, not only one, but all three radicals will oscillate simultaneously, and though the corresponding  $n$ -curve will be of the type indicated, the shape and situations of the individual maxima and minima will become altered, except the maximum at the highest concentration.

In the case of the oscillating molecule,  $\text{H} > \text{C} < \begin{matrix} \text{CO}_2' \\ \text{CH}_2 \cdot \text{CO}_2' \end{matrix}$ , formed when the bromine atom is eliminated from the bromosuccinic ion, the oscillation of the hydrogen atom will probably begin first and dominate at the outset, but later the other two radicals will also make their oscillations felt, and consequently we can no longer expect the regular succession of the phases depicted above. It may happen that the return of one radical to its original position in the molecule (which would mean the return of the whole molecule to its original configuration, if the two other radicals had stayed at rest) will be compensated by the simultaneous oscillation of another radical, or perhaps even that the oscillation of one radical may be impeded by another, and such occurrences will give rise to phases of very different length.

The oscillations which are assumed to underlie the Walden inversions must not be expected to be identical with the atomic oscillations causing the infra-red spectra, but must rather be looked upon as oscillations of the *centres* for these infra-red oscillations, brought about by the splitting of the molecule and showing frequencies of quite a different order of magnitude. It is true that such oscillations may not have been observed elsewhere, but since the Walden inversion has not hitherto been explained in terms of already known molecular mechanics, it seems justifiable to resort

to *ad hoc* hypotheses, especially as there is nothing inherently improbable in that now advanced.

The fraction of molecules having a speed exceeding a given value  $c_1$  is given by the expression (Jeans, "The Dynamical Theory of Gases")

$$\phi_1 = \frac{2}{\sqrt{\pi}} \int_{x_1}^{\infty} e^{-x^2} dx + \frac{2}{\sqrt{\pi}} x_1 e^{-x_1^2}$$

where  $x_1 = \sqrt{3/2} \cdot c_1/c$ ,  $c$  being the kinetic r.m.s. velocity,  $\sqrt{3RT/M}$ . If an oscillating molecule is to react during its first phase of oscillation, the relative velocity of the reacting ions must be such that they meet within the duration  $\theta_1$  of the first phase. The fraction of ions having this or a greater speed is denoted by  $\phi_1$ ;  $\theta_2$  denotes the duration of the first and the second phase together, and  $\phi_2$  the fraction of the ions which have a speed that enables them to traverse the said distance in the time  $\theta_2$ , and so on. Consequently we have

$$n = \phi_1 + (\phi_3 - \phi_2) + (\phi_5 - \phi_4) + \dots$$

In solution, however, the reacting ions will collide with extraneous molecules (*e.g.*, those of the solvent) before they meet, and the conditions for collisions between them are therefore obtainable from Einstein's theory (*Z. Elektrochem.*, 1908, 235) of the displacement of molecules and ions in solutions. His equation for the displacement  $\Delta$  of an ion during the time  $\tau$  is

$$\Delta = \sqrt{2RT/NK} \cdot \sqrt{\tau}$$

where  $R$ ,  $T$ , and  $N$  have their usual significance and  $K$  is given by the expression

$$K = 10^8 \times 9654 \times 96540/\lambda N \dots \dots (1)$$

Here  $\lambda$  denotes the mobility of the ion, expressed as the equivalent conductivity at infinite dilution. If the displacement  $\Delta$  is able to produce collision during the time  $\theta_1$ ,  $\Delta$  must be equal to the average distance between the reacting ions; this distance is often equated to  $1/\sqrt[3]{m}$ , where  $m$  denotes the molality, but owing to the difficulties in judging the state in a solution, we shall replace this expression by  $k_1/m^p$ , where the index  $p$  is determined experimentally (see p. 2022). For reasons explained later, we replace  $m$  by  $c_x$ , obtaining

$$k_1/c_x^n = \sqrt{2RT/NK} \sqrt{\theta_1}$$

Introducing the value of the r.m.s. velocity  $c$ , we obtain

$$c_1 \geq \frac{k_1}{c_x^n} \cdot \sqrt{\frac{3NK}{2M\theta_1}}$$

which gives the speed  $c_1$  necessary to produce collision in the first phase. The equation for  $x_1$  then becomes

$$x_1 = \frac{k_1}{c_x^v} \cdot \sqrt{\frac{3NK}{4RT\theta_1}}$$

Introducing the expression for  $K$  given by (1), expressing  $c_x$  as the number of ions present per c.c., and assigning the values  $T = 298$ ,  $R = 8.31 \times 10^7$ ,  $N = 6.05 \times 10^{23}$ , and  $\lambda = 55$ , we have

$$x_1 = \frac{k_1}{c_x^v} \cdot \frac{2.69 \times 10^{-5}}{\sqrt{\theta_1}} \dots \dots \dots (2)$$

As both of the reacting ions are in motion, a mean value 55 has been used for the mobility : that of the amphoteric ion is not known but it is assumed to be equal to that (62) of the univalent ion of malic acid, and similarly the mobility of the xanthogenate ion is estimated to be of the same order of magnitude as for the thiolacetic ion, *viz.*, 51. The factor  $k_1$  is dependent upon the activity coefficients and is constant at constant ionic strength ; it is equated to unity for the sake of simplicity.

The concentration  $c_x$  which enters into the equations for  $c_1$  and  $x_1$  is of decisive importance for the stereochemical result of the reaction. Although, for experimental purposes (see p. 2018), the concentration of the X-ions must always be greater than, or at least equal to, that of the bromosuccinic ion (referred to in the sequel as the B-ion), it might seem surprising that the sum of these two concentrations is not used instead of  $c_x$ . Two reasons justify the use of the latter, however. (1) The experimental results clearly indicate  $c_x$  as the required variable. (2) The validity of the procedure may be deduced from the following argument. A uniform distribution of the X-ions, if they were at rest, would place them at the corners of a cubic space lattice of side  $1/\sqrt[3]{c_x}$ , and in solutions where the B-ions have the same concentration, these might be placed in the centres of the cubes. In experiments where the concentration of the B-ions is less than that of the X-ions, the centres of some of the cubes cannot be occupied by B-ions, but by the  $\text{SO}_4''$  ions added to keep the ionic strength constant ; the distance from a B-ion to the nearest X-ion, however, remains the same.

The movements of the ions, and other disturbing factors, require that the cube root should be replaced by a different power of  $c_x$ , and the experimental results show that, instead of  $p = 0.333$ , the index  $p = 0.2$  gives good agreement between the theoretical curve and the experimentally found values of  $n$ . The main shape of the curve is only slightly influenced by small variations in  $p$ . The factors which determine the value of  $p$  cannot be discussed here, but we may

mention that probably not all collisions produce reaction, and that, on the other hand, ions from more remote layers may occasionally be able to collide and produce reaction.

The experimental results and the theoretically calculated values of  $n$  are collected in Table I, where B and X represent the bromosuccinate and xanthogenate radicals respectively. As the calculation is a little troublesome, and since it is of interest to see how the collisions are distributed over the several phases, the values of  $x$  and  $\phi$  are given in Table II. The values of  $\phi$  were read from a curve drawn for this purpose through points calculated by the aid of a table of the "error" function (see Jeans, *op. cit.*).

In the calculation of  $n$ , the value of  $\theta_1$  was provisionally left open and equation (2) used in the form  $x_1 = K'/c_X^{0.2}\sqrt{\theta_1}$ ; by the method of trial, it was then found that the value

$$K'/\sqrt{\theta_1} = 0.886 \dots \dots \dots (3)$$

TABLE I.

( $\mu = 2.5$  except in No. 20).

No.	Composition of mixture.					$\sqrt[3]{c_X}^*$	$n$ .	
	Na <sub>2</sub> B.	KX.	Na <sub>2</sub> SO <sub>4</sub> .	KNO <sub>3</sub> .	$c_X$ .		Found.	Calc.
1	0.001	0.001	0.499	0.999	0.0005	0.079	0.19	0.180
2	0.002	0.002	0.498	0.998	0.001	0.100	0.08	0.125
3	0.004	0.004	0.496	0.996	0.002	0.126	0.07	0.087
4	0.006	0.006	0.494	0.994	0.003	0.144	0.06	0.071
5	0.008	0.008	0.492	0.992	0.004	0.159	0.06	0.063
6	0.010	0.010	0.490	0.990	0.005	0.171	0.07	0.058
7	0.020	0.020	0.480	0.980	0.010	0.215	0.07	0.055
8	0.040	0.040	0.460	0.960	0.020	0.271	0.10	0.079
9	0.060	0.060	0.440	0.940	0.030	0.311	0.14	0.111
10	0.080	0.080	0.420	0.920	0.040	0.342	0.18	0.142
11	0.100	0.100	0.400	0.900	0.050	0.368	0.16	0.171
12	0.200	0.200	0.300	0.800	0.100	0.464	0.25	0.274
13	0.300	0.300	0.200	0.700	0.150	0.531	0.31	0.345
14	0.400	0.400	0.100	0.600	0.200	0.585	0.36	0.396
15	0.500	0.500	0.000	0.500	0.250	0.630	0.37	0.439
16	0.400	0.600	0.100	0.400	0.400	0.737	0.47	0.521
17	0.300	0.700	0.200	0.300	0.550	0.819	0.55	0.576
18	0.200	0.800	0.300	0.200	0.700	0.888	0.60	0.614
19	0.100	0.900	0.400	0.100	0.850	0.947	0.64	0.645
20	0.200	8.95	—	—	8.95	2.076	0.86	0.884

(const.)

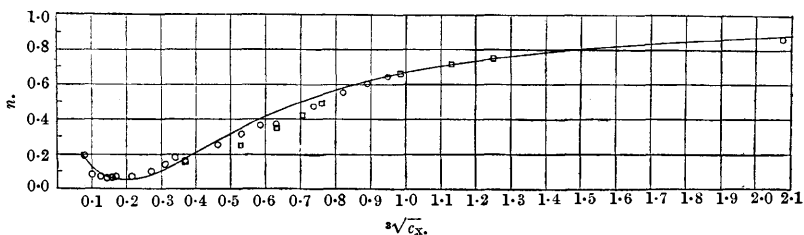
\* This col. is added because this function of  $c_X$  is used for plotting the curve of Fig. 1 (see p. 2025).

should be used. In determining this it must be remembered that the part of the experimental curve which goes from the highest concentrations to the minimum for  $n$ , represents collisions mainly in the first and the second phase, namely,  $\phi_1$  in the first and  $\phi_2 - \phi_1$  in the second; the fraction  $\phi_3 - \phi_2$  occurring in the third phase is

TABLE II.

No.	$c_{x_2}$	$x_1$	$\phi_1$	$x_2$	$\phi_2$	$n$ , calc.
1	0.0005	4.053	0.000	0.676	0.820	0.180
2	0.001	3.528	0.000	0.588	0.875	0.125
3	0.002	3.071	0.000	0.512	0.913	0.087
4	0.003	2.832	0.001	0.472	0.930	0.071
5	0.004	2.674	0.003	0.446	0.940	0.063
6	0.005	2.557	0.005	0.426	0.947	0.058
7	0.010	2.226	0.020	0.371	0.965	0.055
8	0.020	1.937	0.057	0.326	0.978	0.079
9	0.030	1.787	0.094	0.298	0.983	0.111
10	0.040	1.687	0.127	0.281	0.985	0.142
11	0.050	1.614	0.158	0.269	0.987	0.171
12	0.100	1.405	0.264	0.234	0.990	0.274
13	0.150	1.295	0.337	0.216	0.992	0.345
14	0.200	1.223	0.390	0.204	0.994	0.396
15	0.250	1.170	0.434	0.195	0.995	0.439
16	0.400	1.064	0.517	0.177	0.996	0.521
17	0.550	0.999	0.572	0.166	0.996	0.576
18	0.700	0.952	0.610	0.159	0.996	0.614
19	0.850	0.915	0.642	0.152	0.997	0.645
20	8.95	0.572	0.884	—	—	0.884

FIG. 1.



The curve is drawn through the theoretically calculated points.  
 ○ represents the experimentally found values of  $n$  given in this paper ( $\mu = 2.5$ ).  
 □ " " " " " " " " Part II.

nearly zero since  $\phi_2$  in these experiments is very nearly 1.0. The minimum in the curve occurs when almost all the collisions take place in the second phase and only very few in the two neighbouring phases, and the very low experimental value of  $n$  at the minimum (*i.e.*, the high value of  $1-n$ ) shows that the second phase is much longer than the first: actually, calculation from the experiments showed that  $\theta_2$  (*i.e.*, the sum of the two first phases) is equal to  $36\theta_1$ , consequently  $x_2 = x_1/6$ . Since it may be calculated that even at the lowest concentrations 82% of the collisions take place in the first and the second phase, it may be assumed that practically no collisions occur later than the third phase, and although the experiments afford no data from which to calculate the duration of this phase, it appears to be legitimate to equate  $\phi_3$  to 1.0 throughout.

Fig. 1 shows the theoretically calculated curve and also the values of  $n$  found experimentally in the present work and in Part



II (*loc. cit.*). The lower value of the ionic strength employed in Part II, and the use of a *l*-bromosuccinic acid of slightly lower rotatory power than the acid now employed, account for these points being somewhat below the curve. For convenience in plotting,  $\sqrt[3]{c_x}$  is used for abscissæ instead of  $c_x$ .

Although the duration of even the first phase does not depend upon the oscillation of one single radical, from it we can obtain an approximate estimate of the frequency of the oscillations which, according to our theory, are the cause of the Walden inversions of both types. By putting  $K' = 2.69 \times 10^{-5}$  in (3) we get  $\theta_1 = \theta/4 = 9.2 \times 10^{-10}$  and the corresponding frequency  $\nu = 1/\theta = 2.7 \times 10^8$ .

#### EXPERIMENTAL.

The experimental method was exactly the same as that used in Part II (*loc. cit.*). The *l*-bromosuccinic acid had  $[\alpha]_{578}^{25} = -76.6^\circ$ . The solutions containing potassium xanthogenate, the necessary amounts of neutral salts required to give a constant ionic strength, and the appropriate volume of approximately 2*M*-sodium hydroxide solution were prepared as before, and, having been brought to 25°, were rapidly poured over the weighed quantity of *l*-bromosuccinic acid which was dissolved by several minutes' violent shaking. The reaction mixture was then placed in a thermostat at 25° for about 72 hours. The xanthogenosuccinic acid formed by the reaction was liberated by addition of a slight excess of dilute sulphuric acid, extracted with ether, and, after the extract had been dried by anhydrous calcium chloride and the ether removed by evaporation at room temperature, obtained as yellowish-white crystals.

For determinations of the rotatory power, solutions of approximately 0.6 g. of the acid in 10.0 c.c. of ethyl acetate were measured at 25.0° with the yellow mercury line ( $\lambda = 578 \mu\mu$ ). For the calculation of  $n$ , the rotation of pure *l*-xanthogenosuccinic acid was taken as  $[\alpha]_{578}^{25} = -107^\circ$ , as previously.

The experimental details are collected in Table III. Only Expt. No. 20, in which the solution was kept constantly saturated with potassium xanthogenate, needs special explanation. In a preliminary experiment the solubility of this salt at 25° was estimated by stirring a portion of the solid salt with water in a flask placed in the thermostat for several hours, adding 27.35 c.c. of 1*M*-hydrochloric acid to the saturated solution, filtering off the precipitated xanthogenic acid, and titrating the filtrate with 2*M*-sodium hydroxide (required, 9.20 c.c.); hence, the solubility is calculated to be 8.95*M*. In Expt. No. 20, 80 g. of potassium xanthogenate were added with constant stirring to 40.1 c.c. of water and 9.91 c.c. of 2*M*-sodium

TABLE III.

No.	Weight (g.) of				Vol. (c.c.) of		$[\alpha]_{578}^{25^{\circ}}$
	<i>l</i> -B.	KX.	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O.	KNO <sub>3</sub> .	2 <i>M</i> -NaOH.	Total mixture.	
1	0.394	0.3206	321.6	202.0	1.99	2000	-69.78°
1a	0.394	0.3206	321.6	202.0	1.99	2000	-61.08
2	0.788	0.6412	320.9	201.8	3.97	2000	-89.80
3	0.788	0.6413	159.9	100.7	3.97	1000	-93.03
3a	0.788	0.6413	159.9	100.7	3.97	1000	-93.93
4	1.182	0.9618	159.2	100.5	5.96	1000	-95.04
5	1.576	1.2824	158.6	100.3	7.92	1000	-94.48
6	0.985	0.8015	78.98	50.03	4.96	500	-92.77
7	1.970	1.603	77.38	49.53	9.92	500	-92.60
8	1.970	1.603	37.07	24.26	9.92	250	-86.74
9	2.364	1.923	28.36	19.00	11.91	200	-77.05
10	2.364	1.923	20.32	13.95	11.91	150	-68.12
11	2.955	2.405	19.33	13.65	14.89	150	-72.18
12	3.940	3.206	9.666	8.088	19.85	100	-52.81
13	2.955	2.405	3.222	3.539	14.89	50	-41.63
14	3.940	3.206	1.611	3.033	19.85	50	-30.52
15	4.925	4.008	0	2.528	24.81	50	-27.17
16	3.940	4.809	1.611	2.022	19.85	50	- 7.33
17	2.955	5.611	3.222	1.517	14.89	50	+ 9.87
18	3.940	12.82	9.666	2.022	19.85	100	+21.72
19	2.955	21.64	19.33	1.517	14.89	150	+30.24
20	1.967	80.0	—	—	9.91	50	+77.32

hydroxide solution; when saturation was complete, 1.9672 g. of *l*-bromosuccinic acid were added, and rapid stirring was continued for 21 hours. The solution was then acidified and treated as in the other experiments.

In order to test the reproducibility of the values of  $n$  at the lowest concentrations used, Expts. Nos. 1 and 3 were repeated with the utmost care. The results (Nos. 1a and 3a, Table III) indicate that, even at these very low concentrations, the reproducibility is such as to leave no doubt as to the shape and direction of the curve.

Finally, since the shape of the curves for the activity coefficients at the higher concentrations is not known with accuracy, it was deemed advisable to weigh the quantities of the indifferent salts more accurately than would otherwise be required to obtain a sufficiently well-defined value of the ionic strength.