260. *The Kinetics of Chlorohydrin Formation. Part I. The Reaction between Hypochlorous Acid and Allyl Alcohol in Aqueous Solution.*

By G. C. ISRAEL, J. K. MARTIN, and F. G. SOPER.

The addition of hypochlorous acid to allyl alcohol in aqueous solution has been found to conform to the kinetic equation $v = k_2^{\mathrm{I}}\,[\mathrm{HOCl}][\mathrm{C_3H_5{\cdot}OH}] + k_2^{\mathrm{II}}[\mathrm{HOCl}]^2$, where k_2^{I} and k_2^{II} are the specific reaction rates of two simultaneous reactions, k_2^{I} being that for the direct addition of hypochlorous acid to allyl alcohol, and k_2^{II} that for the formation of chlorine monoxide from hypochlorous acid in solution. The chlorine monoxide reacts with allyl alcohol as fast as it is formed to give the chlorohydrin.

KINETIC studies on the addition of hypochlorous acid to olefinic substances in aqueous solution have been carried out by Schilov and his co-workers, who studied the rates of addition to crotonic acid (Schilov and Kaniaev, *Trans. Inst. Chem. Tech. Ivanovo*, 1935, 19; *J. Phys. Chem. Russia*, 1934, **5**, 654), ethylene (Schilov, Kaniaev, and Otmennikova, *ibid.*, 1936, **8**, 909; Schilov, Soloduschenkov, and Kurakin, *ibid.*, 1939, **13**, 759; Schilov, Kaniaev, Domina, and Ionina, *ibid.*, p. 1242), and but-2-ene-1 : 4-diol (Schilov and Kaniaev, *ibid.*, 1937, **10**, 123). In no case did the results conform to any simple kinetic equation. In the case of ethylene, Schilov *et al.* observed that the reaction rate conformed approximately to the equation $v = k_2[\mathrm{HOCl}]^2$, where k_2 was almost but not entirely independent of the concentration of ethylene. The results of studies on crotonic acid and but-2-ene-1 : 4-diol were more complex and no satisfactory conclusion was reached. In each case, the results were rendered more complicated since these investigators studied the effects of addition of hydrochloric acid, which would react with the hypochlorous acid to give molecular chlorine. The rate of addition of chlorine to the double bond is some 100,000 times greater than that of hypochlorous acid (Schilov, Kaniaev, and Otmennikova, *loc. cit.*).

The major product with allyl alcohol is the chlorohydrin, 2-chloropropane-1 : 3-diol (Smith, *Z. physikal. Chem.*, 1918, **92**, 717). Earlier work by Henry (*J. pr. Chem.*, 1874, **10**, 185) reports the product as 3-chloropropane-1 : 2-diol. By analogy with bromine addition in aqueous media, where, following the addition of cationic bromine, the reaction is completed by any suitable anion (Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2344; Robinson, " Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry, 1932, p. 16), hypochlorous acid presumably donates its chlorine atom to the more negative unsaturated carbon atom, the reaction being completed by acceptance by the other carbon atom of a hydroxyl ion, present as such in the aqueous solution or relinquished by a water molecule. This should lead to the formation of the 2-chloro-derivative. Whether the orientation of the addition is affected by the presence of peroxides (cf. Kharasch and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 248) is uncertain, but redistillation of the allyl alcohol gave no appreciable alteration in its reactivity.

In a preliminary experiment, the velocity of reaction between hypochlorous acid and allyl alcohol in equal concentrations (0·002M.) was carried out, and the results were found to conform to the second-order velocity equation, 1/titre being a linear function of time; the values of k_2 are given in Table I, time being in minutes. When this same reaction was carried out in the presence of a borate buffer of pH 10, in which the hypochlorous acid is 99·8% ionised, very little reaction occurred in the same period of time (Table I) indicating that the reaction involves un-ionised hypochlorous acid and not the hypochlorite ion.

TABLE I.

$[HOCl]_0 = [C_3H_5{\cdot}OH]_0 = 0{\cdot}002$ mole l.$^{-1}$. Titres in ml. of N/500-$Na_2S_2O_3$. Temp. : 25·00° ± 0·01°.

Time		0	2	3	5	7	9	11	13	15	17
Titre	(*a*)	18·3	—	17·1	16·6	16·0	15·45	15·0	14·5	14·0	13·5
k_2		—	—	11·7	10·2	10·3	10·2	10·0	10·1	10·2	10·5
Titre	(*b*)	18·8	18·8	—	—	—	—	—	—	—	18·7

(*a*) Unbuffered. (*b*) Buffered to pH 10.

The results of experiments showing the effect at 25·00° ± 0·01° of varying the concentration of allyl alcohol and hypochlorous acid are shown in Tables II—V, where : a = initial concn. of hypochlorous acid in moles l.$^{-1}$; b = initial concn. of allyl alcohol in moles l.$^{-1}$; x = amount in moles l.$^{-1}$ of either reactant which has been removed in time t; t = time in minutes; k_1 = specific reaction rate for the *first*-order reaction involving hypochlorous acid, *i.e.*, $k_1 = (2{\cdot}303/t)\log_{10} a(a - x)$; $k_2' =$ specific reaction rate for the *second*-order reaction involving both allyl alcohol and hypochlorous acid, *i.e.*,

$$k_2' = \frac{2{\cdot}303}{(b-a)t}\log_{10}\frac{a(b-x)}{b(a-x)};$$

k_2'' = specific reaction rate for the *second*-order reaction involving hypochlorous acid alone, *i.e.*, $k_2'' = x/[at(a - x)]$.

TABLE II.

$a = 0{\cdot}002$ mole l.$^{-1}$.

10^3b.	k_2'.	k_2''.
2	—	9·8
4	5·3	11·0
6	4·6	13·1
8	3·9	—

TABLE III.

Values of k_1 in min.$^{-1}$ ($\times 10^2$).

a	2	2	4	4
b	2	4	2	4
k_1	1·63	1·97	3·00	3·53

TABLE IV.

$a = 0{\cdot}002$ mole l.$^{-1}$.

10^3b.	10^2k_1.	k_1/b.	10^3b.	10^2k_1.	k_1/b.	10^3b.	10^2k_1.	k_1/b.
2	1·69	8·45	8	2·66	3·33	40	8·74	2·19
4	1·98	4·95	10	3·21	3·21	60	12·41	2·07
6	2·33	3·88	20	5·17	2·59	80	16·80	2·10

TABLE V.

$b = 0{\cdot}05$ mole l.$^{-1}$

10^3a (mole l.$^{-1}$).	10^2k_1 (min.$^{-1}$).
2	10·0
3	11·3
4	11·9

The results expressed in Tables II and III, which correspond to relatively low concentrations of allyl alcohol, show that the reaction is predominantly of the second order with respect to hypochlorous acid. In Table III, it is seen that the effect of doubling the concentration of the acid is nearly to double the value of k_1. Thus at low concentrations of the alcohol, $v \approx k_2''[HOCl]^2$. However, k_2'' is clearly not independent of the alcohol concentration.

The results expressed in Table IV show that k_1 becomes increasingly dependent on the alcohol concentration as the latter increases, and approaches proportionality with such concentration at $[C_3H_5{\cdot}OH] \approx 0{\cdot}06$ mole l.$^{-1}$. Thus at high concentrations of the alcohol, the reaction is predominantly of first order with respect to hypochlorous acid. The results given in Table V confirm this conclusion. At low concentrations (0·002M.) of the alcohol, doubling the concentration of hypochlorous acid quadruples the rate, whereas at high concentrations (0·05M.) the rate conforms to the expression $v = k_2'[HOCl][C_3H_5{\cdot}OH]$.

This change in the nature of the reaction is of the same type as that observed in similar addition reactions by Schilov *et al.* (*loc. cit.*) but for which no explanation was advanced. The present authors suggest that the results may be simply explained by assuming a kinetic equation of the form

$$v = k_2^{I}[HOCl][C_3H_5{\cdot}OH] + k_2^{II}[HOCl]^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where at high concentrations of the alcohol, the term $k_2^{I}[HOCl][C_3H_5{\cdot}OH]$ will largely determine the reaction velocity, and at low concentrations of the alcohol, the dominant term will be $k_2^{II}[HOCl]^2$. The first term of this equation represents the bimolecular attack of hypochlorous acid on the ethenoid centre, whilst the second is interpreted as the rate of formation of chlorine monoxide by the equation $2HOCl = Cl_2O + H_2O$, the chlorine monoxide reacting with the alcohol as rapidly as it is formed.

A similar type of kinetic expression would provide a satisfactory explanation of the observations of Schilov, Kaniaev, and Otmennikova (*loc. cit.*) that the velocity of addition of hypochlorous acid to ethylene in aqueous solution conforms approximately to the equation $v = k_2[HOCl]^2$, where k_2 is not quite independent of the concentration of ethylene.

Since k_2' and k_2'' refer to the overall reaction and are unsatisfactory constants for indicating the specific rate, the initial velocity of the reaction was determined in subsequent work. Reasonable precision in this determination is possible if the time–titre values are plotted in such a way as to yield a linear or nearly linear graph. By substituting the known initial concentrations $[HOCl]_0$ and $[C_3H_5{\cdot}OH]_0$ and the measured initial velocity v_0 in equation (1), a series of simultaneous equations resulted, from which values of k_2^{I} and k_2^{II} were obtained. The results of this test of equation (1) are given in the four sections of Table VI, where concentrations are in mole l.$^{-1}$ and velocities in mole l.$^{-1}$ min.$^{-1}$.

TABLE VI.

$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.	$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.
1·95	1·0	6·3	6·4	2·00	3·0	13·3	13·3
1·98	2·0	10·0	9·8	2·00	4·0	16·6	16·6
1·92	2·5	11·0	11·0	1·95	5·0	19·3	19·3

k_2^{I} = 1·82, 1·52, 1·70, 1·61, 1·64; mean value, 1·66 l. mole^{-1} min.$^{-1}$.
k_2^{II} = 8·00, 8·78, 8.35, 8·43, 8·18, 8·13; mean value, 8·31 l. mole^{-1} min.$^{-1}$.

pH : 4·5.

$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.	$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.
2·54	0·8	8·8	9·1	2·54	1·6	13·4	13·1
2·54	1·2	11·5	11·1	2·54	2·0	14·8	15·2

k_2^{I} = 1·98 l. mole^{-1} min.$^{-1}$; k_2^{II} = 7·88 l. mole^{-1} min.$^{-1}$.

pH : 4·0.

$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.	$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.
3·99	0·8	19·3	19·7	3·90	1·6	23·9	23·4
3·99	1·2	22·3	22·0	3·88	2·0	25·0	25·4

k_2^{I} = 1·42 l. mole^{-1} min.$^{-1}$; k_2^{II} = 9·56 l. mole^{-1} min.$^{-1}$

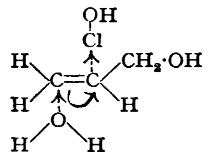
pH : 3·8.

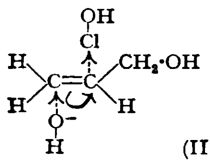
$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.	$10^3[HOCl]_0$.	$10^2[C_5H_3{\cdot}OH]_0$.	10^5v_0, obs.	10^5v_0, calc.
4·78	0·8	27·8	28·2	4·76	1·6	32·8	32·9
4·78	1·2	31·4	30·7	4·78	2·0	35·2	35·6

k_2^{I} = 1·29 l. mole^{-1} min.$^{-1}$; k_2^{II} = 10·21 l. mole^{-1} min.$^{-1}$.

In each of these sections, the initial velocities v_0, calc., have been obtained by using the corresponding values of the two rate constants, k_2^{I} and k_2^{II}. The results given in the tables demonstrate that equation (1) provides a satisfactory representation of the kinetics of the reaction.

The results of experiments in which the pH of the reaction mixture varied appear to indicate that both k_2^{I} and k_2^{II} alter to some extent with pH, the former increasing with increasing concentration of hydroxyl ion, and the latter with increasing hydrogen-ion concentration. For pH's 3·8, 4·0, and 4·5, k_2^{I} has the values 1·29, 1·42, and 1·98, whilst k_2^{II} has the values 10·21, 9·56, and 7·88, respectively. The exact nature of the dependence of the two rate constants on pH necessitates an examination of the kinetics of the reaction in buffered solutions. However, the catalysis by hydrogen ion of the formation of chlorine monoxide from hypochlorous acid would not be unexpected, since the hydrolysis of other acid anhydrides (the reverse reaction) is catalysed by hydrogen ions (cf. hydrolysis of acetic anhydride, Orton and Jones, *J.*, 1912, **101**, 1708). The tendency of the specific rate of the direct reaction, k_2^{I}, to increase with increasing hydroxyl-ion concentration is also to be expected as the formation of chlorohydrin may be completed by either a water molecule (I) or a hydroxyl ion (II). The latter would conceivably provide an easier reaction path.


(I.)


(II.)

The fact that the term $k_2^{II}[HOCl]^2$ is independent of the concentration of the alcohol, necessitates, on the interpretation offered, that chloride monoxide is removed as rapidly as it is formed and it must, therefore, be much more highly reactive than hypochlorous acid. This would be expected from the potential ease of separation of positive chlorine from chlorine monoxide and from hypochlorous acid. The ratio of the ionisation constants of these two substances into positive chlorine is given by

$$\frac{[Cl^+][OCl^-]}{[Cl_2O]} \Big/ \frac{[Cl^+][OH^-]}{[HOCl]} = \frac{[HOCl]^2}{[Cl_2O]} \cdot \frac{[H^+][OCl^-]}{[HOCl]} \cdot \frac{1}{[H^+][OH^-]} = \frac{K_a}{K_{Cl_2O}K_w}$$

where K_{Cl_2O}, the equilibrium constant for the reaction $2HOCl \rightleftharpoons Cl_2O + H_2O$, has the approximate value 10^{-3} (Goldschmidt, *Ber.*, 1919, **52**, 753). Since K_a for hypochlorous acid is 4×10^{-8}, the calculated relative potential ease of ionisation of chlorine monoxide and hypochlorous acid to give positive chlorine is approximately 4×10^9, in harmony with the postulated high reactivity of chlorine monoxide.

EXPERIMENTAL.

Materials.—The allyl alcohol was B.D.H. reagent and was fractionated immediately before use in an all-glass apparatus; b. p. 96·5° (uncorr.)/753 mm.

Hypochlorous acid solutions were prepared by bubbling chlorine through a suspension of yellow mercuric oxide in distilled water. The acid solution was obtained by distillation of the resulting mixture under vacuum at as low a temperature as possible (not greater than 30°). The distillate was collected in a receiver cooled in ice and was stored over yellow mercuric oxide until required.

Kinetic Measurements.—All experiments were carried out at 25·00° ± 0·01°. The hypochlorous acid solution was prepared daily by centrifuging the stored solution and diluting the resulting liquid to a suitable strength with distilled water.

In all preliminary experiments, the reaction was carried out by placing the required amount of the stock allyl alcohol solution together with distilled water in the reaction flask. The reaction was started by adding the requisite volume of the hypochlorous acid solution. 10-Ml. samples of the reaction mixture were withdrawn at suitable intervals and run into 10 ml. of 2% potassium iodide solution acidified with 5 ml. of 5M-acetic acid, and the liberated iodine titrated with thiosulphate.

In later experiments, results of which are recorded in Table VI, the reaction was carried out by pouring simultaneously equal volumes of solutions of the two reactants into a suitable reaction flask, temperature equilibrium being maintained throughout.

The results of a typical experiment carried out using the latter method, are given in the following table; 10 ml. of approximately 0·05M-hypochlorous acid were diluted to 50 ml. in a standard flask. Similarly, 8 ml. of 0·2M-allyl alcohol were diluted to 50 ml., and the reaction started by mixing the two solutions so obtained.

$[HOCl]_0 = 4{\cdot}76 \times 10^{-3}$ mole l.$^{-1}$, $[C_3H_5{\cdot}OH]_0 = 1{\cdot}6 \times 10^{-2}$ mole l.$^{-1}$.

pH = 3·8. Temp. = 25·00° ± 0·01°.

Time (mins.)	0	1	2	3	4	5	6
Titre (ml. of N/250-$Na_2S_2O_3$)	23·82	22·22	20·76	19·38	18·16	17·07	16·08
$\log_{10}$ titre	1·377	1·347	1·317	1·287	1·259	1·232	1·206

For experiments in which the pH was measured, a sample of the reaction mixture was examined in a Macbeth direct-reading pH meter. The pH showed little or no variation during the reaction. The different pH values recorded in the last three sections of Table VI are undoubtedly due to the accumulation of small quantities of chloric acid in the stored hypochlorous acid solution through decomposition. Such traces of chloric acid are sufficient to depress the pH markedly but are scarcely detectable analytically. Further, the chloric acid does not appear to interfere with the course of the reaction except in so far as the pH is affected.

Determination of v_0.—To determine the initial velocity in each reaction mixture, it was necessary to find a suitable linear relationship between titre and time. It was found that the plot of $\log_{10}$ titre against time was satisfactory in this respect in the early stages of the reaction (up to 5 minutes). Extrapolation of the linear portion to zero time gave the value of the initial titre and hence the initial concentration of hypochlorous acid in the reaction mixture. The initial value quoted in the foregoing table was obtained in this way.

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UNIVERSITY OF OTAGO, DUNEDIN, NEW ZEALAND. [*Received, December 28th,* **1949**.]