261. *The Kinetics of Chlorohydrin Formation. Part II. The Reaction between Hypochlorous Acid and Allyl Alcohol in the Presence of Sodium Acetate–Acetic Acid Buffers of Constant* pH.

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The reaction between hypochlorous acid and allyl alcohol in aqueous solutions buffered by equal quantities of sodium acetate and acetic acid to pH 4·75 has been found to conform to the kinetic equation $v = k_2^{\text{I}}[\text{HOCl}][\text{C}_3\text{H}_5\cdot\text{OH}] + (k_2^{\text{II}} + k_3^{\text{II}}[\text{HOAc}])[\text{HOCl}]^2 + k_2^{\text{III}}[\text{HOCl}][\text{HOAc}]$. The various terms in this equation are interpreted as : k_2^{I}, the specific rate for direct addition of hypochlorous acid to allyl alcohol; k_2^{II} and k_3^{II}, the specific rates of formation of chlorine monoxide from hypochlorous acid in solution, the latter representing the catalytic effect of the acetic acid present; and k_2^{III}, the specific rate of formation of acetyl hypochlorite by the reaction $\text{AcOH} + \text{HOCl} \longrightarrow \text{AcOCl} + \text{H}_2\text{O}$.

IN Part I (preceding paper) it was shown that the addition of hypochlorous acid to allyl alcohol in aqueous solution could be represented kinetically by the equation

$$v = k_2^{\text{I}}\,[\text{HOCl}][\text{C}_3\text{H}_5\cdot\text{OH}] + k_2^{\text{II}}\,[\text{HOCl}]^2$$

k_2^{I} being the specific rate for direct interaction between the two reactants, and k_2^{II} the specific rate of formation of chlorine monoxide from hypochlorous acid in solution. The chlorine monoxide so formed is probably a potentially better source of positive chlorine than is hypochlorous acid, and reacts readily with the ethenoid centre. The reaction is completed by addition of hydroxyl ions, possibly derived from water molecules, to the carbonium ion.

However, in Part I (*loc. cit.*) it was shown that the values of k_2^{I} and k_2^{II} may depend to some extent on the pH, and in order to avoid such variation, the reaction has now been investigated in the presence of equal quantities of sodium acetate and acetic acid. Since, for acetic acid, $K_a = 1{\cdot}776 \times 10^{-5}$ (Jeffery and Vogel, *J.*, 1932, 2829), the pH of all reaction mixtures was thus maintained at the value 4·75. All experiments were carried out at 25·00° ± 0·01°.

Preliminary experiments showed that the addition reaction is unaffected by the presence of a neutral salt such as potassium nitrate (cf. Schilov and Kaniaev, *Trans. Inst. Chem. Tech. Ivanovo*, 1935, 19) but that the reaction velocity is markedly increased by the addition of a sodium acetate–acetic acid buffer and that acetic acid is not consumed during the reaction. Further, the addition of sodium acetate to the buffer mixture caused only a small increase in the reaction velocity, whereas additions of acetic acid caused considerable increase. Similar effects, due to the free acid of the buffer, have been observed in other reactions involving hypohalous acids (Mauger and Soper, *J.*, 1946, 71; Painter and Soper, *J.*, 1947, 342; Wilson and Soper, *J.*, 1949, 3376), and are attributed to the formation of highly reactive acyl hypohalite : $\text{AcOH} + \text{HOX} \longrightarrow \text{AcOX} + \text{H}_2\text{O}$.

In the present investigation, the initial velocity, v_0, was determined by using the method described in Part I (*loc. cit.*) for varying concentrations of hypochlorous acid, allyl alcohol, and acetic acid. Table I shows the variation in the initial velocity, v_0, as the concentration of allyl alcohol is altered. By analogy with the kinetic equation which was found to represent the rate of addition of hypochlorous acid to allyl alcohol in unbuffered solutions, it was assumed that the initial velocity conformed to an equation of the type

$$v_0 = k_2^{\text{I}}\,[\text{HOCl}]_0[\text{C}_3\text{H}_5\cdot\text{OH}]_0 + v_{\text{res.}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $v_{\text{res.}}$ is the residual (initial) velocity which is independent of the concentration of allyl alcohol but dependent on the concentrations of both hypochlorous acid and acetic acid. This assumption is verified by the constancy of the values of k_2^{I} and of $v_{\text{res.}}$.

Again, following the results obtained for the reaction in unbuffered solutions, it was assumed that the residual initial velocity, $v_{\text{res.}}$, conformed to the equation

$$v_{\text{res.}} = k_2^{\text{II}}\,[\text{HOCl}]_0^2 + k^{\text{HOAc}}\,[\text{HOAc}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_2^{II} is a constant and k^{HOAc} is independent of the concentrations of allyl alcohol and acetic acid, but dependent on the concentration of hypochlorous acid. That equation (2) is substantially correct is clear from Fig. 1, in which the values of $v_{\text{res.}}$ have been obtained from the experimentally determined values of the initial velocity, v_0, by using equation (1), the value of k_2^{I} being taken as 2·0 l. mole^{-1} min.$^{-1}$. From the graphs, the values of k^{HOAc} derived from the gradients, and of $v_{\text{res.}}$ extrapolated to [HOAc] = 0 are shown in Table II. Such extrapolated values of $v_{\text{res.}}$ are equal to $k_2^{\text{II}}\,[\text{HOCl}]_0^2$, and hence, the derived values of k_2^{II} are also given in that table.

TABLE I.

$10^3[HOCl]_0$.	$10^3[HOAc]_0 = 10^3[OAc^-]_0$.	$10^2[C_3H_5{\cdot}OH]_0$.	$10^5 v_0$.	k_2^I (mean).	$10^5 v_{res.}$.	$10^5 v_{res.}$ (mean).
2·07	1	0·5	9·29	2·03	7·20	7·35
		1·0	11·66		7·47	
		1·5	13·57		7·29	
		2·0	15·61		7·44	
4·03	1	0·8	27·5	2·11	21·7	20·7
		1·2	30·8		21·0	
		1·6	33·1		19·5	
		2·0	38·0		21·0	
3·83	3	0·8	41·0	1·93	35·1	35·1
		1·2	44·0		35·1	
		1·6	47·1		35·3	
		2·0	49·8		35·0	
3·84	4	0·8	49·3	1·85	43·6	43·6
		1·2	52·0		43·5	
		1·6	55·5		44·1	
		2·0	57·2		43·0	
4·02	5	0·8	60·2	1·74	54·6	54·7
		1·2	62·9		54·5	
		1·6	66·2		55·0	
		2·0	68·5		54·5	
4·69	2	0·4	39·9	2·23	35·7	36·2
		0·8	45·7		37·3	
		1·2	48·0		35·5	
		1·6	52·6		35·9	
		2·0	57·3		36·4	

Mean value of k_2^I over all experiments : 1·98 l. mole^{-1} min.$^{-1}$.

TABLE II.

$10^3[HOCl]_0$, mole l.$^{-1}$	1·95	2·07	2·92	3·93	4·91
$10^2 k^{HOAc}$, min.$^{-1}$	3·4	3·9	5·6	8·6	10·9
$10^5 v_{res.}$, mole l.$^{-1}$ min.$^{-1}$ (extrapolated)	3·0	3·5	6·6	11·6	21·4
k_2^{II}, l. mole^{-1} min.$^{-1}$	7·9	8·1	7·7	7·5	8·9

FIG. 1.

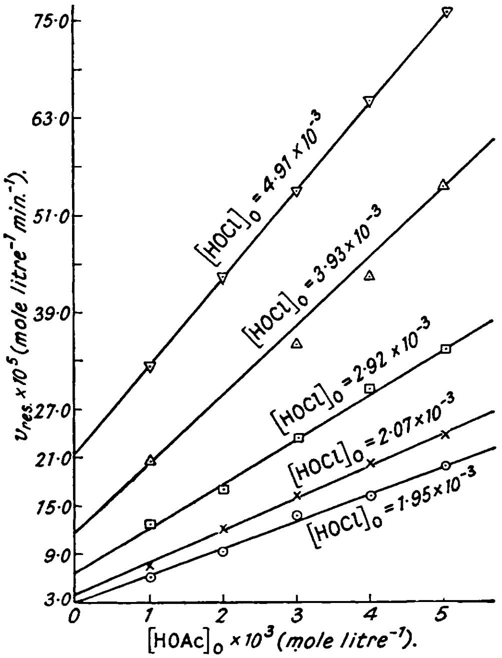
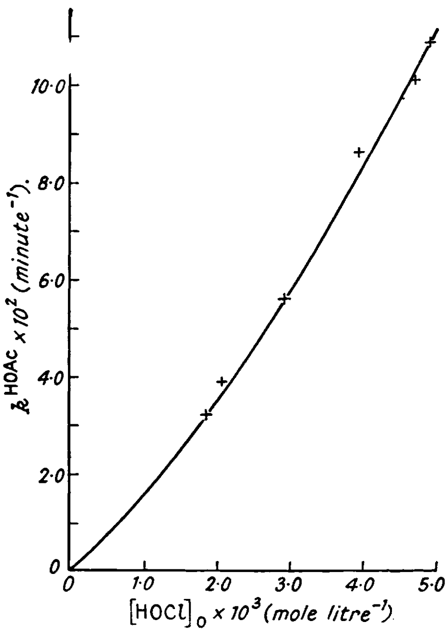


FIG. 2.



Whilst k_2^{II} is reasonably constant (mean value : 8·2 l. mole^{-1} min.$^{-1}$), k^{HOAc} may be expressed as a function of the concentration of hypochlorous acid by the equation

$$k^{HOAc} = k_3^{II} [HOCl]_0^2 + k_2^{III} [HOCl]_0 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

as may be seen from Fig. 2. This curve gives k_2^{III} as 14·5 l. mole⁻¹ min.⁻¹, and k_3^{II} as $1{\cdot}56 \times 10^3$ l.² mole⁻² min.⁻¹.

TABLE III.

			$10^5 v_0$.	
10^3[HOCl]$_0$.	10^3[HOAc]$_0$.	10^2[C_3H_5·OH]$_0$.	Calc.	Obs.
1·95	1	1·0	10·4	10·2
	2	1·0	13·9	13·3
	3	1·0	17·3	17·8
	4	1·0	20·7	20·2
	5	1·0	24·1	23·8
2·07	1	0·5	9·3	9·3
	1	1·0	11·4	11·7
	1	1·5	13·4	13·6
	1	2·0	15·5	15·6
	2	1·0	15·0	15·6
	3	1·0	18·7	19·4
	4	1·0	22·5	23·2
	5	1·0	26·2	27·1
2·92	1	1·0	18·3	18·5
	2	1·0	24·0	22·8
	3	1·0	29·5	29·2
	4	1·0	35·0	35·3
	5	1·0	40·6	40·3
4·03	1	0·8	28·0	27·5
	1	1·2	31·3	30·8
	1	1·6	34·5	33·1
	1	2·0	37·7	38·0
3·83	3	0·8	41·7	41·0
	3	1·2	44·8	44·0
	3	1·6	47·8	47·9
	3	2·0	50·9	49·8
3·84	4	0·8	50·1	49·3
	4	1·2	52·6*	52·0
	4	1·6	55·6	55·5
	4	2·0	58·7	57·2
4·02	5	0·8	61·5	60·2
	5	1·2	64·7	62·9
	5	1·6	68·0	66·2
	5	2·0	71·2	68·5
4·01	10	0·8	102·8	100·2
	10	1·2	106·0	105·7
	10	1·6	109·2	109·3
	10	2·0	112·4	113·9
4·69	2	0·4	42·3	39·9
	2	0·8	46·1	45·7
	2	1·2	49·3	48·0
	2	1·6	53·1	52·6
	2	2·0	57·4	57·3
4·91	1	1·0	40·5	42·1
	2	1·0	51·3	53·2
	3	1·0	62·3	63·7
	4	1·0	73·1	74·8
	5	1·0	84·0	85·9

* The relative contributions to the speed of the reaction may be of interest in a particular case. In this instance, for direct addition,

$$k_2^{I}[\mathrm{HOCl}]_0[\mathrm{C_3H_5{\cdot}OH}]_0 = 9{\cdot}2 \times 10^{-5},$$

for chlorine monoxide formation

$$k_2^{II}[\mathrm{HOCl}]_0^2 + k_3^{II}[\mathrm{HOCl}]_0^2[\mathrm{HOAc}]_0 = (12{\cdot}0 + 9{\cdot}2) \times 10^{-5},$$

and for acetyl hypochlorite formation,

$$k_2^{III}[\mathrm{HOCl}]_0[\mathrm{HOAc}]_0 = 22{\cdot}2 \times 10^{-5};$$

whence $v_0 = (9{\cdot}2 + 12{\cdot}0 + 9{\cdot}2 + 22{\cdot}2) \times 10^{-5} = 52{\cdot}6 \times 10^{-5}$ mole l.⁻¹ min.⁻¹.

Hence, it appears that the complete kinetic equation for the reaction between hypochlorous acid and allyl alcohol in the presence of acetic acid–acetate buffers is of the form

$$v = k_2^{I}\,[\mathrm{HOCl}][\mathrm{C_3H_5{\cdot}OH}] + (k_2^{II} + k_3^{II}\,[\mathrm{HOAc}])[\mathrm{HOCl}]^2 + k_2^{III}\,[\mathrm{HOCl}][\mathrm{HOAc}] \quad . \quad (4)$$

For equal concentrations of acetate ion and acetic acid (pH 4·75), equation (4) becomes

$$v = 2{\cdot}0[\mathrm{HOCl}][\mathrm{C_3H_5{\cdot}OH}] + (8{\cdot}2 + 1{\cdot}56 \times 10^3\,[\mathrm{HOAc}])[\mathrm{HOCl}]^2 + 14{\cdot}5\,[\mathrm{HOCl}][\mathrm{HOAc}] \quad . \quad (5)$$

That equation (5) gives a reasonably accurate representation of the kinetics of the reaction at pH 4·75 is shown in Table III, where the measured initial velocities are compared with those calculated from the equation.

As was shown in Part I (*loc. cit.*), the terms k_2^{I} [HOCl][C_3H_5·OH] and k_2^{II} [HOCl]² may be interpreted as the rate of direct addition of hypochlorous acid to the alcohol and the rate of formation of chlorine monoxide in solution, respectively. In a similar way, it is suggested that the term k_3^{II} [HOCl]²[HOAc] gives the rate of formation of chlorine monoxide catalysed by acetic acid. The fourth term, k_2^{III} [HOCl][HOAc], represents the rate of formation of acetyl hypochlorite by the reaction $\mathrm{HOCl} + \mathrm{HOAc} \longrightarrow \mathrm{AcOCl} + \mathrm{H_2O}$. The acetyl hypochlorite so formed is a potentially better source of positive chlorine than is hypochlorous acid.

It would appear that acetyl hypochlorite reacts much more rapidly than hypochlorous acid and is removed as rapidly as it is formed.

If this interpretation is correct, the specific rates of formation of chlorine monoxide, k_2^{II} and k_3^{II}, and of acetyl hypochlorite, k_2^{III}, should each be independent of the nature of the olefinic substance.

EXPERIMENTAL.

Materials.—The allyl alcohol was B.D.H. reagent, twice redistilled in an all-glass apparatus; b. p. 96·6—96·7° (uncorr.)/773 mm., n_D^{18} 1·4141. Hypochlorous acid solutions were obtained as described in Part I (*loc. cit.*). The sodium acetate–acetic acid buffer used was prepared by making an acetic acid solution of suitable strength from purified glacial acetic acid and partly neutralising it with carbonate-free sodium hydroxide solution.

Kinetic Measurements.—These have been described in Part I (*loc. cit.*). In most of the kinetic experiments, the required amount of the buffer was added to the solution of allyl alcohol, but no difference was observed when it was added instead to the hypochlorous acid solution.

The effect of neutral salt on the velocity of addition was examined by carrying out a series of reactions with constant concentrations of both allyl alcohol and hypochlorous acid and varying concentrations of potassium nitrate. No buffer was added in these experiments, the results of which are shown below.

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

$10^3[KNO_3]$, mole l.$^{-1}$	0	1	3	5
10^5v_0, mole l.$^{-1}$ min.$^{-1}$	4·40	4·46	4·47	4·47

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