435. *The Kinetics of Chlorohydrin Formation. Part IV.* The Reaction between Hypochlorous Acid and Ethyl Crotonate in the Presence of Sodium Acetate–Acetic Acid Buffers of Constant* pH.

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The kinetics of the addition of hypochlorous acid to ethyl crotonate in aqueous solutions in the presence of sodium acetate–acetic acid buffers of pH 4·74 have been studied and it is shown that the reaction conforms to the velocity equation :

$$v = k_2^{\mathrm{I}}[\mathrm{HOCl}][\mathrm{EtR}] + k_3^{\mathrm{II}}[\mathrm{HOCl}]^2[\mathrm{EtR}] + k_3^{\mathrm{III}}[\mathrm{HOCl}][\mathrm{HOAc}][\mathrm{EtR}]$$

where [EtR] is the concentration of ethyl crotonate. $k_2^{\mathrm{I}}[\mathrm{HOCl}][\mathrm{EtR}]$ is interpreted as the rate of direct interaction between hypochlorous acid and the ester, $k_3^{\mathrm{II}}[\mathrm{HOCl}]^2[\mathrm{EtR}]$ as the rate of reaction between chlorine monoxide and the ester, and $k_3^{\mathrm{III}}[\mathrm{HOCl}][\mathrm{HOAc}][\mathrm{EtR}]$ as the rate of interaction of acetyl hypochlorite and the ester. The velocity equation for this reaction has been compared with that for the reaction between hypochlorous acid and allyl alcohol under similar conditions, and the relative reactivities of hypochlorous acid and chlorine monoxide with ethyl crotonate have been determined and compared with the theoretical estimate of such relative reactivities.

STUDIES of the kinetics of addition of hypochlorous acid to allyl alcohol in aqueous solution (Parts I and II, *J.*, 1950, 1282, 1286) showed that in the presence of sodium acetate–acetic acid buffers acetic acid and hypochlorous acid form acetyl hypochlorite, which is a potential source of " positive chlorine " and, as fast as it is formed, reacts with the ethylenic linkage in allyl alcohol. Evidence was also obtained that chlorine monoxide, which is always present in aqueous solutions of hypochlorous acid, acts similarly.

Similar studies on the kinetics of addition of hypochlorous acid to crotonic acid (*J.*, 1952, 550) revealed a somewhat different type of kinetic equation although this was due to the different reaction conditions : the buffer was in this case a mixture of crotonic acid and sodium crotonate, so as to avoid the formation of different acyl hypochlorites. The kinetic equation found was :

$$v = k_2^{\mathrm{I}}[\mathrm{HOCl}]([\mathrm{HR}] + [\mathrm{R}^-]) + (k_2^{\mathrm{II}} + k_3^{\mathrm{II}}[\mathrm{HR}])[\mathrm{HOCl}]^2 \quad . \quad . \quad . \quad (1)$$

k_2^{II} has been interpreted as the specific reaction rate for the formation of chlorine monoxide, and k_3^{II} as the corresponding specific rate for the same reaction catalysed by un-ionised crotonic acid. Comparison of this equation with that found for the reaction involving allyl alcohol in the presence of sodium acetate–acetic acid buffers of pH 4·75, *viz.* :

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

shows that, on the basis of the interpretations advanced for the mechanism of the reactions, the values of k_2^{II} in equations (1) and (2) should be identical. However, it was found that k_2^{II} in equation (1) was $4·0 \pm 0·3$ and that in equation (2) $8·2 \pm 0·7$ l. mole^{-1} min.$^{-1}$. It should be noted that the pH was approximately the same in both cases and that the diffeıence exceeds the experimental error, considerable though this was. To investigate the effect of reaction conditions we have studied the kinetics of addition of hypochlorous acid to ethyl crotonate in the presence of sodium acetate–acetic acid buffers containing equal concentrations of acetate ion and un-ionised acetic acid. All experiments were carried out at $25·00° \pm 0·01°$.

EXPERIMENTAL

Materials.—Ethyl crotonate, prepared by esterification of pure crotonic acid, was washed thoroughly with water and sodium hydrogen carbonate solution, dried (MgSO$_4$), and redistilled. It had b. p. 137—139° and n_{D}^{20} 1·4238.

Hypochlorous acid was prepared as described in Part III (*loc. cit.*). The sodium acetate–acetic acid buffer was prepared by treating an acetic acid solution of suitable strength (from purified glacial acetic acid) with carbonate-free sodium hydroxide solution. The pH was checked with a Jones pH meter, standardised against potassium hydrogen phthalate solution (pH 4·01), and was found to be 4·74 (Calc., 4·75. Cf. Jeffery and Vogel, *J.*, 1932, 2829).

Solubility of Ethyl Crotonate in Water.—A saturated solution of the ester was hydrolysed with 0·0942N-sodium hydroxide at 25° for about 60 hours. The resultant solution was titrated with 0·0876N-hydrochloric acid. Duplicate experiments gave the concentration of the ester as 0·0825 and 0·0833M. For the kinetic experiments, a stock solution of strength 0·04M was found to be most suitable.

Kinetic Methods.—Preliminary experiments showed that the reaction between hypochlorous acid and ethyl crotonate occurred much more slowly than that between hypochlorous acid and allyl alcohol. Suitable quantities of ester and buffer solutions were made up with water to a total volume of 75 ml. The reaction was started by adding 25 ml. of hypochlorous acid solution of suitable concentration and shaking the resulting mixture. Samples, each of 10 ml., were withdrawn every 30 minutes and run into 10 ml. of 2% potassium iodide solution acidified with 10 ml. of 5N-acetic acid. The iodine liberated was titrated with sodium thiosulphate. The pH of each reaction mixture was also measured.

Determination of v_0.—The most satisfactory linear relation was obtained by plotting the reciprocal of the titre against time. Otherwise the method of determination was similar to that described in Part I (*loc. cit.*).

RESULTS

Experiments were carried out to determine separately the effect of varying the initial concentrations of the ester, buffer, and hypochlorous acid. Results are listed in Tables 1 and 2.

In each case the pH of the reaction mixture was slightly lower than that of the buffer used but remained almost constant during the course of the reaction.

TABLE 1. $[EtR]_0 = 1 \times 10^{-2}$M.

10^3[HOAc]	10^3[HOCl]$_0$	$10^6 v_0$ (mole l.$^{-1}$ min.$^{-1}$) Obs.	Calc.	10^3[HOAc]	10^3[HOCl]$_0$	$10^6 v_0$ (mole l.$^{-1}$ min.$^{-1}$) Obs.	Calc.
3	1·34	0·86	0·79	12	1·33	1·60	1·61
	2·04	1·47	1·45		2·05	2·57	2·71
	3·71	3·62	3·65		3·59	5·39	5·66
	3·86	4·08	3·89		4·63	8·02	8·10
	4·27	4·84	4·60		5·66	11·0	10·9
	6·15	9·04	8·51		6·09	11·8	12·1
	6·25	9·90	8·74		7·23	16·0	15·7
	7·95	14·2	13·4		8·63	19·2	20·7
	9·04	17·7	16·8	15	1·34	1·96	1·89
	9·07	17·4	16·9		2·04	2·82	3·11
	9·99	21·2	20·1		3·09	4·81	5·25
6	1·34	1·17	1·08		3·10	5·15	5·27
	2·05	1·78	1·87		4·17	7·99	7·85
	3·53	3·88	4·09		4·66	9·14	9·12
	4·97	7·21	6·94		6·12	13·3	13·5
	6·12	9·74	9·69		6·22	13·8	13·8
	6·59	11·5	11·0		6·23	13·9	13·8
	8·02	15·4	15·2		7·80	18·8	19·5
	9·08	19·2	18·8		8·26	20·5	21·0
	9·50	20·0	20·3		9·06	23·5	24·3
9	1·33	1·37	1·34		9·27	23·8	25·2
	2·04	2·20	2·28		9·37	24·1	25·6
	3·60	4·69	4·94				
	4·65	7·61	7·19				
	5·67	9·89	9·71				
	6·13	11·2	11·0				
	6·44	12·5	11·9				
	8·85	20·4	19·8				
	9·07	20·0	20·6				

TABLE 2. [HOAc] $= 5 \times 10^{-3}$M.

10^3[EtR]$_0$	4	8	12	16	20
10^3[HOCl]$_0$	10·32	10·25	10·25	10·14	10·12
$10^6 v_0$ (mole l.$^{-1}$ min.$^{-1}$) (obs.)	9·8	18·7	29·2	37·7	47·3
$10^6 v_0$ (mole l.$^{-1}$ min.$^{-1}$) (calc.)	9·1	18·2	27·0	35·3	43·9

A plot of the results given in Table 2 shows that the reaction velocity varies linearly with the concentration of the ester, even though the concentration of hypochlorous acid was not quite constant; thus,

$$v_0 \propto [\text{EtR}]_0 \qquad \qquad \qquad (3)$$

A plot of the variation of the initial velocity against the initial concentration of hypochlorous acid for constant concentrations of ester and of buffer was parabolic. Consequently it was assumed that this variation could be expressed by :

$$v_0 = k_A[\text{HOCl}]_0 + k_B[\text{HOCl}]_0^2 \qquad \qquad (4)$$

or

$$v_0/[\text{HOCl}]_0 = k_A + k_B[\text{HOCl}]_0 \qquad \qquad (5)$$

That this equation is of the correct type is clear from Fig. 1 (in which, for clarity, only three of

FIG. 1.

FIG. 2.
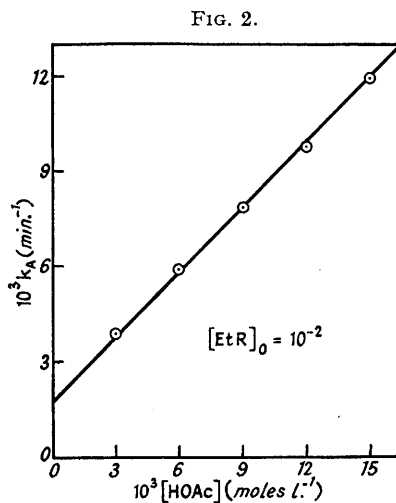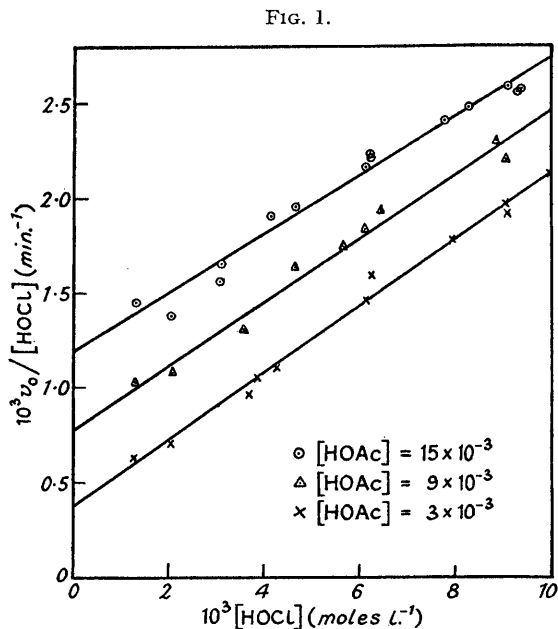
the five sets of values in Table 1 are plotted), the best lines being located by the method of least squares. The values of k_A and k_B obtained for each plot are :

$10^3[\text{HOAc}]$	3	6	9	12	15
10^3k_A	0·385	0·591	0·784	0·979	1·195
k_B	0·175	0·165	0·168	0·158	0·154

k_B is thus reasonably constant, the mean being 0·164 l. mole^{-1} min.$^{-1}$. On the other hand the variation of k_A with the concentration of acetic acid is clear from Fig. 2, from which it was deduced that k_A was given by

$$k_A = 1·70 \times 10^{-4} + 6·83 \times 10^{-2}[\text{HOAc}] \qquad \qquad (6)$$

Combination of equations (3), (4), and (6) gives the complete velocity equation as :

$$v_0 = k_2^{\text{I}}[\text{HOCl}]_0[\text{EtR}]_0 + k_3^{\text{II}}[\text{HOCl}]_0^2[\text{EtR}]_0 + k_3^{\text{III}}[\text{HOCl}]_0[\text{EtR}]_0[\text{HOAc}] \qquad (7)$$

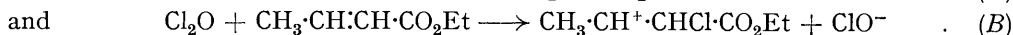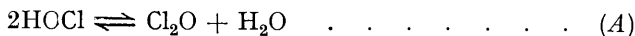or, by substitution of the values for the three rate constants :

$$v_0 = 1·70 \times 10^{-2}[\text{HOCl}]_0[\text{EtR}]_0 + 16·4[\text{HOCl}]_0^2[\text{EtR}]_0 + 6·83[\text{HOCl}]_0[\text{EtR}]_0[\text{HOAc}] \qquad (8)$$

That equation (8) provides a satisfactory interpretation of the course of the reaction may be seen from Tables 1 and 2, in which values of v_0 calculated from this equation are seen to be in satisfactory agreement with the experimental values.

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<div style="text-align:center">DISCUSSION</div>

In equation (7), k_2^{I} is obviously the specific reaction rate for the direct interaction of hypochlorous acid and ethyl crotonate. The value ($1\cdot70 \times 10^{-2}$) found shows that, in ethyl crotonate, the ethylenic bond is much less reactive than that in allyl alcohol (cf. Part II, *loc. cit.*) or crotonic acid (Part III, *loc. cit.*), no doubt owing to the deactivating effect of the carbethoxyl group on the ethylenic linkage.

The constant k_3^{II} may be interpreted in terms of the attack of chlorine monoxide on the ethylenic linkage. This is a three-stage process, the first being the equilibrium formation of chlorine monoxide. As indicated in Part I (*loc. cit.*), chlorine monoxide may be expected to be a better source of positive chlorine than is hypochlorous acid. However, the lower reactivity of ethyl crotonate, compared with that of allyl alcohol, causes the attack of chlorine monoxide on the ester to be the slower and hence the rate-determining step. The first two stages are thus :

$$2HOCl \rightleftharpoons Cl_2O + H_2O \qquad \qquad (A)$$

and $\qquad Cl_2O + CH_3 \cdot CH{:}CH \cdot CO_2Et \longrightarrow CH_3 \cdot CH^{+} \cdot CHCl \cdot CO_2Et + ClO^{-} \qquad (B)$

The final stage is the reaction between the carbonium ion and any convenient anion (in this case, hydroxyl ion since dilute aqueous solutions have been used).

For the equilibrium (A) we have :

$$K_{Cl_2O} = [Cl_2O]/[HOCl]^2 \approx 10^{-3} \text{ (Goldschmidt, *Ber.*, 1919, 52, 753)} \qquad (9)$$

and for the reaction (B) :

$$v_{Cl_2O} = k_{Cl_2O}[Cl_2O][EtR] = k_{Cl_2O} K_{Cl_2O}[HOCl]^2[EtR] \qquad (10)$$

Comparison of equation (10) with equation (7) shows that

$$k_3^{II} = k_{Cl_2O} K_{Cl_2O}$$

and by substitution of the values for k_3^{II} and K_{Cl_2O} :

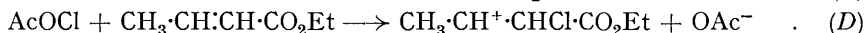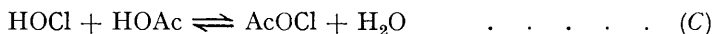$$k_{Cl_2O} = 1\cdot64 \times 10^4$$

The relative reactivities of chlorine monoxide and hypochlorous acid as shown by their relative rates of reaction with ethyl crotonate are thus :

$$k_{Cl_2O}/k^{I} = (1\cdot64 \times 10^4)/(1\cdot70 \times 10^{-2}) \approx 10^6$$

i.e., chlorine monoxide is 10^6 times as effective as hypochlorous acid in attack on the ethylenic bond and hence as a potential source of chlorine cations (cf. the value 4×10^9 estimated for this ratio in Part I).

In the reaction between hypochlorous acid and allyl alcohol in the presence of sodium acetate–acetic acid buffers (cf. Part II), it was assumed that the term $(k_2^{II} + k_3^{II}[HOAc])[HOCl]^2$ of equation (2) represented the rate of formation of chlorine monoxide, the latter reacting with the alcohol as fast as it was formed. In this term, k_3^{II} was interpreted as the specific rate for the formation of chlorine monoxide catalysed by un-ionised acetic acid. The fact that the corresponding term $k_4^{II}[HOAc][HOCl]^2[EtR]$ was not found in the rate equation for the reaction involving ethyl crotonate is to be expected since, in the latter reaction, the chlorine monoxide present is presumably in equilibrium with hypochlorous acid. This confirms the interpretation given (Part II) for the term k_3^{II} in equation (2).

In a similar way, the constant k_3^{III} in equation (7) may be interpreted in terms of the interaction of acetyl hypochlorite and ethyl crotonate. This interaction is also a three-stage process, the first two stages being :

$$HOCl + HOAc \rightleftharpoons AcOCl + H_2O \qquad \qquad (C)$$

$$AcOCl + CH_3 \cdot CH{:}CH \cdot CO_2Et \longrightarrow CH_3 \cdot CH^{+} \cdot CHCl \cdot CO_2Et + OAc^{-} \qquad (D)$$

For the equilibrium (C),

$$K_{AcOCl} = [AcOCl]/[HOCl][HOAc]$$

whence for the rate-determining stage (D),

$$v_{\text{AcOCl}} = k_{\text{AcOCl}}[\text{AcOCl}][\text{EtR}]$$
$$= k_{\text{AcOCl}} K_{\text{AcOCl}}[\text{HOCl}][\text{HOAc}][\text{EtR}]$$

It follows that

$$k_3{}^{\text{III}} = k_{\text{AcOCl}} K_{\text{AcOCl}}$$

The value of the equilibrium constant K_{AcOCl} is still unknown and thus it is not possible to obtain a value for the relative reactivities of acetyl hypochlorite and hypochlorous acid from this reaction.

Finally, it is clear that the studies described here do not explain the discrepancy observed in the values already reported for the specific rate for the formation of chlorine monoxide from hypochlorous acid. To investigate this, it will be necessary to use unsaturated compounds of reactivity similar to that of crotonic acid and of allyl alcohol.