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

By (Mrs.) A. Chung and G. C. Israel.

[Reprint Order No. 6078.]

The addition of hypochlorous acid to allyl acetate in aqueous solutions buffered by equal quantities of sodium acetate and acetic acid to pH 4·70 has been studied. It is found that, above a certain minimum concentration of the ester, the velocity of reaction conforms to the kinetic equation

$$v = k_2^{I}[HOCl][C_3H_5OAc] + (k_2^{II} + k_3^{IV}[HOAc])[HOCl]^2 + k_2^{III}[HOCl][HOAc]$$

Below this minimum concentration, which varies with the concentration of hypochlorous acid, the kinetics of the reaction appear to be varying and consequently attempts to derive a kinetic equation were unwarranted.

The values found for the constants k_2^{II}, k_2^{III}, and k_3^{IV} agree with those found previously for the reaction between hypochlorous acid and allyl alcohol under similar conditions.

The kinetics of the addition of hypochlorous acid to various mono-olefinic compounds have been found by Israel and his co-workers to be complex. Consecutive reactions are believed to occur, the end-product in each case being the chlorohydrin (cf. Israel, Martin, and Soper, *J.*, 1950, 1282; Israel, *J.*, 1950, 1286; Craw and Israel, *J.*, 1952, 550; Reeve and Israel, *J.*, 1952, 2327; Craw, *J.*, 1954, 2510, 2515). In each reaction the term $k_2^{II}[HOCl]^2$ appeared in the kinetic equation, and it has been surmised that this represents the rate of formation of chlorine monoxide from hypochlorous acid: $2HOCl \longrightarrow Cl_2O + H_2O$. The potential ease of separation of positive chlorine from chlorine monoxide has been calculated to be 10^6 times greater than that from hypochlorous acid (Reeve and Israel, *loc. cit.*), and chlorine monoxide would therefore be expected to react as fast as it is formed. It follows that the value of k_2^{II}, the specific reaction rate for the formation of chlorine monoxide, should be independent of the nature of the ethylenic compound. Table 1 shows that this is not true for crotonic acid.

Table 1. *Values of* k_2^{II} *at* pH 4·7 *at* 25°.

Compound	k_2^{II} (l. mole^{-1} min.$^{-1}$)	Observers
Allyl alcohol	8·2	Israel
Crotonic acid	4·0	Craw and Israel
Tiglic acid	7·5	Craw
ββ-Dimethylacrylic acid	10·1	Craw (personal communication)

For allyl alcohol, the kinetic terms $(k_2^{III} + k_3^{II}[HOCl])[HOCl][HOAc]$ were found. The first term has been interpreted as the rate of formation of acetyl hypochlorite by the reaction, $HOCl + HOAc \longrightarrow AcOCl + H_2O$, the acetyl hypochlorite reacting with the allyl alcohol as fast as it is formed. Thus the value of k_2^{III} should also be independent of the nature of the ethylenic substance. This supposition has not been tested.

The term $k_3^{II}[HOCl]^2[HOAc]$ has been interpreted by Israel *et al.* (*locc. cit.*) as the rate of the acid-catalysed formation of chlorine monoxide. Doubt has been thrown on this mechanism by Craw (*J.*, 1954, 2515) who found that no such term appears in the kinetic equation for tiglic acid; he suggested an alternative mechanism to account for the appearance of the term when acetic or crotonic acid is present, and for its absence in the tiglic acid reaction. (For this reason, the corresponding specific reaction rate is denoted below by k_3^{IV}.)

In an effort to throw further light on these problems, it was decided to extend studies of the reaction to allyl acetate.

---

* Part VI, *J.*, 1954, 2515.

EXPERIMENTAL

Materials.—Allyl acetate was left over crystalline ferrous ammonium sulphate for at least two days to remove any peroxides. It was then dried (Na_2SO_4) and fractionated in an all-glass apparatus. The product had b. p. 103°/760 mm., $n_D^{24.7}$ 1·4025 (Beilstein gives 103·5—104°/762·5 mm., n_D^{20} 1·40488). The 0·1M-aqueous solution of the ester was made up fresh before each series of experiments. This procedure was found to be necessary if after-blueing (unstable end-points during the titrations) was to be avoided during the rate measurements. Such after-blueing was clearly caused by the presence of peroxides in the allyl acetate, since on their removal sharp stable end-points were obtained. Solutions of the ester were found not to be appreciably hydrolysed for two days after being made up. For each series, the solutions of ester were used within 3½ hr.

Mercuric oxide was purified by dissolving it in perchloric acid and reprecipitating it with sodium hydroxide solution (de la Mare, Ketley, and Vernon, *J.*, 1954, 1290). Hypochlorous acid solution was prepared by saturating a suspension of the purified mercuric oxide in water with chlorine at about 0° and distilling the resultant mixture under reduced pressure in the dark below 35°. It kept reasonably well in dark bottles at about 0° and was diluted to the required concentration immediately before use. However, in no case was a solution used which had been kept for more than five days.

Sodium acetate–acetic acid buffer solutions were prepared from pure glacial acetic acid, pure sodium hydroxide (free from carbonate), and carbon dioxide-free water, so that the final concentration of the stock buffer solution was 0·1M with respect to acetic acid and to sodium acetate.

Kinetic Methods.—A new technique was developed in which the required volumes of the stock allyl acetate solution and of the buffer solution were treated with distilled water to make a total volume of 50 ml. To start the reaction, 50 ml. of the hypochlorous acid solution were added from a modified Stas pipette, which is fitted with a jacket through which water from the constant temperature bath was circulated. The side-arm, through which the pipette is filled, is slightly constricted at the point at which it is joined to the pipette so that drainage from the side-arm of variable quantities of solution is prevented. The flask was shaken gently during the addition of the hypochlorous acid and was removed immediately the pipette had emptied, no time being allowed for drainage. In a check series of experiments, the pipette was found to deliver 50·195, 50·205, 50·190, 50·225, 50·200 (mean 50·203 ± 0·022) g. of distilled water at 25°, the draining time being about 3·5 sec. Thus the volume of liquid delivered by the pipette was 50·25 ml. with an error less than 0·5%.

Aliquot parts (10 ml.) of the reaction mixture were removed at the appropriate times, run into acidified solutions of potassium iodide, and analysed.

All experiments were carried out at 25·00° ± 0·01°.

Rate Measurements.—Rate measurements and the determination of v_0 were carried out by the method described by Israel, Martin, and Soper (*loc. cit.*), the reaction mixture being sampled at quarter-minute or half-minute intervals. de la Mare, Ketley, and Vernon (*loc. cit.*) carried out kinetic measurements on the reaction between hypochlorous acid and phenol, mesitylene, or one of three aromatic ethers in the presence of perchloric acid and silver perchlorate, the perchlorate being present to ensure the absence of chloride and hence of free chlorine in the reaction mixture. Accordingly, experiments in which silver perchlorate was added and similar experiments without the addition of the perchlorate were carried out. The results of a typical pair of such experiments are given in Table 2.

TABLE 2.

$[HOCl]_0 = 4·775 \times 10^{-3}$; $[C_3H_5OAc]_0 = 5·0 \times 10^{-2}$; $[HOAc] = 5·0 \times 10^{-3}$; $[AgClO_4] = 0·127$.

Time (min.) ...	0·5	1·0	1·5	2·0	2·5	3·0
Titre (ml. $4·042 \times 10^{-3}$N-$Na_2S_2O_3$) ($AgClO_4$ present) ...	10·72	7·68	7·50	6·90	6·33	6·02
($AgClO_4$ absent) ...	20·95	19·36	18·00	16·77	—	14·63

These and similar results show that the addition of silver perchlorate markedly affects the course of the reaction, approximately in proportion to the amount of silver perchlorate added even when the perchlorate is present in a concentration some twenty times greater than that of hypochlorous acid (as quoted in Table 2). On the other hand, the plot of the logarithms of the titres against time for the reaction carried out in the absence of the perchlorate was linear and gave, on extrapolation to zero time, a value of 1·355 corresponding to an initial titre of 22·65 ml. This value agrees with the titre (22·63 ml.) of the corresponding blank experiment in which 50 ml. of the same hypochlorous acid solution were added to 50 ml. of distilled water. The latter agreement suggests that there was little likelihood of the presence of free chlorine in the solution of hypochlorous acid used, since such free chlorine would react so much faster than hypochlorous acid, chlorine monoxide, or acetyl hypochlorite (cf. Shilov *et al.*, *Trans. Inst. Chem. Tech. Ivanovo*, **1935**, 19; *J. Phys. Chem. Russia*, 1934, **5**, 654; 1936, **8**, 909; 1937, **10**, 123; 1939, **13**, 759, 1242). It appears that addition of silver perchlorate catalyses the decomposition of hypochlorous acid under our conditions. Therefore, all our experiments were carried out without perchlorate.

To ensure that the stock hypochlorous acid solutions used had not decomposed appreciably and thus contained no free chlorine, a blank experiment was carried out in conjunction with each series of experiments. If the concentration in this blank run was appreciably greater than the initial concentration determined from the rate curves, the difference was assumed to be due to the presence of free chlorine and the results were rejected.

RESULTS

Variation of the Initial Concentration of the Ester.—The plot of the reaction velocity against the initial concentration of the ester, with constant initial concentration of the buffer, was linear only above a certain minimum ester concentration. The value of this minimum varied with the initial concentration of hypochlorous acid but in no case investigated was less than $[C_3H_5OAc]_0 = 2{\cdot}5 \times 10^{-2}$. The results obtained on using concentrations of the ester greater than this minimum are given in Table 3.

TABLE 3. 10^3[HOAc] = 5·0 *mole l.*$^{-1}$

10^3[HOCl] (mole l.$^{-1}$)	$10^2[C_3H_5OAc]$ (mole l.$^{-1}$)	$10^5 v_0$ (mole l.$^{-1}$ min.$^{-1}$) (obs.)	(calc.)	10^3[HOCl] (mole l.$^{-1}$)	$10^2[C_3H_5OAc]$ (mole l.$^{-1}$)	$10^5 v_0$ (mole l.$^{-1}$ min.$^{-1}$) (obs.)	(calc.)
1·078	3	9·61	9·53	3·229	3	39·51	39·85
	4	9·86	9·75		4	40·25	40·49
	5	10·01	9·96		5	41·01	41·14
	7	10·42	10·39		7	42·24	42·43
	9	10·85	10·82		9	43·74	43·72
1·846	4	19·13	19·00	4·303	3	60·45	60·60
	5	19·48	19·37		4	61·15	61·46
	6	19·85	19·74		5	62·15	62·32
	7	20·19	20·10		7	63·72	64·04
	8	20·68	20·41		9	65·40	65·77
2·755	3	31·74	31·87				
	4	32·26	32·42				
	6	33·32	33·53				
	7	33·95	34·08				
	8	34·47	34·63				

Analysis of the observed values of v_0 by the method of least squares shows that they conform to the equation

$$v_0 = v_{\text{res.}} + k[C_3H_5OAc] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The values of $v_{\text{res.}}$ and k so obtained are given in Table 4, from which it is clear that k is proportional to the concentration of hypochlorous acid, *i.e.*,

$$k = k_2^{\text{I}}[\text{HOCl}]_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

TABLE 4.

$10^3[\text{HOCl}]_0$ (mole l.$^{-1}$)	$10^5 v_{\text{res.}}$ (mole l.$^{-1}$ min.$^{-1}$)	$10^3 k$ (min.$^{-1}$)	k_2^{I} (l. mole^{-1} min.$^{-1}$)	k_2^{II} (l. mole^{-1} min.$^{-1}$)
1·08	9·01	0·203	0·19	9·12
1·85	17·58	0·381	0·21	8·28
2·76	30·07	0·549	0·20	7·91
3·23	37·46	0·695	0·22	7·70
4·30	57·92	0·831	0·19	8·07
		Mean	0·20	8·22

The plot of $v_{\text{res.}}/[\text{HOCl}]_0$ varied linearly with $[\text{HOCl}]_0$ and could be represented by

$$v_{\text{res.}}/[\text{HOCl}]_0 = k_1 + k_2[\text{HOCl}]$$

or

$$v_{\text{res.}} = k_1[\text{HOCl}]_0 + k_2[\text{HOCl}]_0^2 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

where 10^2k_1 = 6·61 min.$^{-1}$ and k_2 = 15·74 l. mole^{-1} min.$^{-1}$.

Variation of the Concentration of the Acetate Buffer.—This variation was examined at constant concentrations of the ester, the results being given in Tables 5 *A*—*E*.

TABLE 5.

10^3[HOCl] (mole l.$^{-1}$)	10^3[HOAc] (mole l.$^{-1}$)	10^5v_0 (mole l.$^{-1}$ min.$^{-1}$)		10^3[HOCl] (mole l.$^{-1}$)	10^3[HOAc] (mole l.$^{-1}$)	10^5v_0 (mole l.$^{-1}$ min.$^{-1}$)	
		(obs.)	(calc.)			(obs.)	(calc.)
(*A*) 10^2[C$_3$H$_5$OAc] = 3·0 mole l.$^{-1}$.							
1·620	2	8·12	8·17	3·203	2	22·13	20·92
	4	13·18	13·23		4	34·31	33·57
	6	18·23	18·29		6	45·92	45·23
	8	23·28	23·35		8	56·80	54·88
	10	28·33	28·41		10	69·34	68·53
1·835	2	9·60	9·70	3·702	2	28·14	27·43
	4	15·52	15·56		4	41·13	41·49
	6	21·28	21·42		6	55·55	55·56
	8	27·21	27·29		8	70·78	69·62
	10	33·13	33·15		10	84·41	83·69
2·026	2	11·08	11·15	4·728	2	40·61	39·54
	4	17·66	17·74		4	59·33	60·07
	6	24·24	24·34		6	78·93	79·60
	8	30·82	30·93		8	98·22	99·13
	10	37·40	37·53		10	118·20	118·66
2·809	2	17·82	17·96				
	4	27·65	27·82				
	6	37·48	37·68				
	8	47·31	47·54				
	10	57·13	57·40				
(*B*) 10^2[C$_3$H$_5$OAc] = 4·0 mole l.$^{-1}$.							
0·919	2	4·07	4·08	3·068	2	20·98	21·13
	4	6·73	6·75		4	31·97	32·16
	6	9·38	9·41		6	42·96	43·19
	8	12·04	12·07		8	53·95	54·21
	10	14·70	14·71		10	64·94	65·24
1·537	2	7·87	7·91	3·808	2	29·19	29·43
	4	12·62	12·66		4	43·73	44·03
	6	17·37	17·42		6	58·27	58·63
	8	22·13	22·18		8	72·83	73·23
	10	26·88	26·94		10	87·35	87·83
2·311	2	13·80	13·92				
	4	21·49	21·66				
	6	29·17	29·39				
	8	36·86	37·13				
	10	44·55	44·87				
(*C*) 10^2[C$_3$H$_5$OAc] = 5·0 mole l.$^{-1}$.							
0·818	2	3·69	3·70	3·386	2	—	25·23
	4	6·03	6·04		4	37·51	37·75
	6	8·37	8·38		6	49·99	50·27
	8	10·71	10·73		8	62·46	62·79
	10	13·06	13·07		10	74·94	75·30
1·729	2	9·55	9·62	4·195	2	34·77	35·11
	4	14·99	15·08		4	51·29	51·72
	6	20·44	20·54		6	67·82	68·33
	8	25·87	26·00		8	84·35	84·93
	10	31·32	31·47		10	100·87	101·54
2·527	2	16·25	16·36	4·499	2	38·83	39·22
	4	24·87	25·00		4	57·12	57·49
	6	33·48	33·65		6	75·43	75·76
	8	42·09	42·29		8	93·37	94·03
	10	50·71	50·93		10	111·40	112·30
2·679	2	17·70	17·79				
	4	26·80	27·08				
	6	36·00	36·37				
	8	45·10	45·66				
	10	54·73	54·94				

TABLE 5. (*Continued.*)

(*D*) $10^2[C_3H_5OAc] = 6{\cdot}0$ mole l.$^{-1}$.

1·523	2	8·38	8·42	3·039	2	22·17	22·03
	4	13·08	13·13		4	32·90	32·91
	6	17·79	17·84		6	43·62	43·79
	8	22·49	22·56		8	55·29	54·67
	10	27·19	27·29		10	65·79	65·61
2·280	2	14·53	14·63	3·799	2	30·34	30·83
	4	22·14	22·31		4	45·78	45·37
	6	29·74	29·96		6	59·50	59·91
	8	37·35	37·61		8	74·66	74·45
	10	44·95	45·26		10	88·37	89·06
2·675	2	18·01	18·30				
	4	27·33	27·57				
	6	36·59	36·84				
	8	45·92	46·11				
	10	56·36	55·39				

(*E*) $10^2[C_3H_5OAc] = 7{\cdot}0$ mole l.$^{-1}$.

1·021	2	5·20	5·27	3·063	2	22·67	22·91
	4	8·25	8·26		4	33·71	33·91
	6	11·24	11·25		6	44·77	44·91
	8	14·20	14·24		8	55·58	55·91
	10	17·19	17·24		10	66·64	66·91
1·781	2	10·67	10·73	3·558	2	28·73	28·60
	4	16·29	16·39		4	41·38	41·95
	6	22·03	22·05		6	55·07	55·30
	8	27·61	27·70		8	68·25	68·65
	10	33·44	33·36		10	81·53	82·00
2·082	2	13·23	13·26	4·134	2	35·68	35·97
	4	19·81	20·08		4	51·96	52·21
	6	26·90	26·90		6	68·14	68·53
	8	33·76	33·72		8	84·31	85·81
	10	40·42	40·54		10	—	101·09

For definite values of the concentrations of ester and of hypochlorous acid, it was found that the results could be represented by equations of the type :

$$v_0 = v'_{\text{res.}} + k'[\text{HOAc}] \qquad (4)$$

The values of $v'_{\text{res.}}$ and k' determined by the method of least squares are given in Table 6.

TABLE 6.

$10^2[C_3H_5OAc]_0$ (mole l.$^{-1}$)	$10^3[HOCl]_0$ (mole l.$^{-1}$)	$10^5v'_{\text{res.}}$ (mole l.$^{-1}$ min.$^{-1}$)	$10^2k'$ (min.$^{-1}$)	$10^2[C_3H_5OAc]_0$ (mole l.$^{-1}$)	$10^3[HOCl]_0$ (mole l.$^{-1}$)	$10^5v'_{\text{res.}}$ (mole l.$^{-1}$) min.$^{-1}$)	$10^2k'$ (min.$^{-1}$)
3·0	1·62	3·07	2·53	6·0	1·52	3·68	2·35
	1·84	3·73	2·94		2·28	6·92	3·80
	2·03	4·50	3·29		2·68	8·25	4·77
	2·81	7·99	4·91		3·04	11·03	5·43
	3·20	10·63	5·85		3·80	16·10	7·24
	3·70	13·34	7·11	7·0	1·02	2·24	1·50
	4·73	20·84	9·70		1·78	4·95	2·84
4·0	0·92	1·41	1·33		2·08	6·33	3·42
	1·54	3·12	2·38		3·06	11·74	5·49
	2·31	6·11	3·84		3·56	15·25	6·62
	3·07	9·99	5·50		4·13	19·51	8·10
	3·81	14·65	7·27				
5·0	0·82	1·35	1·17				
	1·73	4·11	2·72				
	2·53	7·64	4·31				
	2·68	8·36	4·62				
	3·39	12·55	6·24				
	4·20	18·24	8·26				
	4·50	20·82	9·07				

For each concentration of the ester, plots of $k'/[\text{HOCl}]_0$ and $v'_{\text{res.}}/[\text{HOCl}]_0$ against $[\text{HOCl}]_0$ were linear. Thus k' and $v'_{\text{res.}}$ could be represented by

$$v'_{\text{res.}} = k_1{}^{\text{I}}[\text{HOCl}]_0 + k_2{}^{\text{II}}[\text{HOCl}]_0{}^2 \qquad (5)$$

and

$$k' = k_2{}^{\text{III}}[\text{HOCl}]_0 + k_3{}^{\text{IV}}[\text{HOCl}]_0{}^2 \qquad (6)$$

The values of the four constants k_1^{I}, k_2^{II}, k_2^{III}, and k_3^{IV} obtained by the method of least squares are given in Table 7 from which it is clear that k_2^{II}, k_2^{III}, and k_3^{IV} are reasonably constant and that k_1^{I} is directly proportional to the concentration of the ester, *i.e.*,

$$k_1^{\mathrm{I}} = k_2^{\mathrm{I}}[\mathrm{C_3H_5OAc}]_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

The value of k_2^{I} so obtained is in excellent agreement with the mean value quoted in Table 4.

TABLE 7.

$10^3[\mathrm{C_3H_5OAc}]_0$	k_1^{I} (min.$^{-1}$)	k_2^{I} (l. mole^{-1})	k_2^{II} (l. mole^{-1} min.$^{-1}$)	k_2^{III} (l. mole^{-1} min.$^{-1}$)	$10^{-3}k_3^{\mathrm{IV}}$ (l.^{2} mole^{-2} min.$^{-1}$)
3·0	0·564	0·19	8·22	13·0	1·63
4·0	0·803	0·20	7·99	13·0	1·61
5·0	0·975	0·20	8·08	13·0	1·60
6·0	1·240	0·21	7·69	12·8	1·73
7·0	1·337	0·19	8·20	13·2	1·54
Mean	——	0·20	8·04	13·0	1·62

Combination of equations (4), (5), (6), and (7), gives the complete velocity equation

$$v_0 = k_2^{\mathrm{I}}[\mathrm{HOCl}]_0[\mathrm{C_3H_5OAc}]_0 + k_2^{\mathrm{II}}[\mathrm{HOCl}]_0^2 + k_2^{\mathrm{III}}[\mathrm{HOCl}]_0[\mathrm{HOAc}] + k_3^{\mathrm{IV}}[\mathrm{HOCl}]_0^2[\mathrm{HOAc}] \quad . \quad (8)$$

That this provides a satisfactory representation of the course of the reaction has been confirmed in three ways.

(*a*) Combination of equations (1), (2), and (3) and substitution of the values of the relevant constants gives

$$v_0 = 0{\cdot}20[\mathrm{HOCl}]_0[\mathrm{C_3H_5OAc}]_0 + 6{\cdot}61 \times 10^{-2}[\mathrm{HOCl}]_0 + 15{\cdot}74[\mathrm{HOCl}]_0^2 \quad . \; . \quad (9)$$

as the velocity equation for constant [HOAc] $= 5 \times 10^{-3}$.

Comparison with equation (8) shows that

$$k_2^{\mathrm{III}}[\mathrm{HOAc}] = 6{\cdot}61 \times 10^{-2} \text{ when } [\mathrm{HOAc}] = 5 \times 10^{-3}$$

i.e.,

$$k_2^{\mathrm{III}} = 13{\cdot}2 \text{ l. mole}^{-1} \text{ min.}^{-1}$$

Also,

$$k_2^{\mathrm{II}} + k_3^{\mathrm{IV}}[\mathrm{HOAc}] = 15{\cdot}74 \text{ when } [\mathrm{HOAc}] = 5 \times 10^{-3}$$

Substitution of the mean value of k_3^{IV} from Table 7 thus gives $k_2^{\mathrm{II}} = 7{\cdot}64$ l. mole^{-1} min.$^{-1}$.

The values of k_2^{II} and k_2^{III} so obtained are in good agreement with those quoted in Table 7.

(*b*) From a statistical point of view, analysis of the results quoted in Table 6 would be expected to give a more reliable value for the constant k_2^{III} than that obtained from equation (9). Therefore, it is probably more satisfactory to substitute the mean values of k_2^{III} and k_3^{IV} from Table 7 into the equation

$$v_{\mathrm{res.}} = k_2^{\mathrm{II}}[\mathrm{HOCl}]_0^2 + k_2^{\mathrm{III}}[\mathrm{HOCl}]_0[\mathrm{HOAc}] + k_3^{\mathrm{IV}}[\mathrm{HOCl}]_0^2[\mathrm{HOAc}] \quad . \; . \quad (10)$$

[which follows by combining equations (1), (2), and (8)] to obtain the value of k_2^{II}. The resultant values for this constant are shown in column 5 in Table 4. When it is remembered that this procedure tends to cause the accumulation of experimental errors in the corresponding values of k_2^{II}, the results show a reasonable constancy and the mean value of this constant is in good agreement with that quoted in Table 7. The overall mean value of k_2^{II} is thus found to be 8·13 l. mole^{-1} min.$^{-1}$.

(*c*) Substitution of the values of the four constants in equation (8) gives the velocity equation

$$v_0 = 0{\cdot}20[\mathrm{HOCl}]_0[\mathrm{C_3H_5OAc}]_0 + 8{\cdot}13[\mathrm{HOCl}]_0^2 + 13{\cdot}0[\mathrm{HOCl}]_0[\mathrm{HOAc}] + 1{\cdot}62 \times 10^3[\mathrm{HOCl}]_0^2[\mathrm{HOAc}] \quad . \; . \; . \; . \; . \; . \; . \quad (11)$$

Equation (11) was used to calculate the values of v_0 given in column 4 in each of Tables 3 and 5 *A*—*E* from which it is clear that there is a satisfactory agreement between the observed and the calculated values of v_0.

DISCUSSION

The form of the derived kinetic equation is identical with that reported earlier, the values of the constants k_2^{II}, k_3^{II}, and k_3^{IV} being in reasonable agreement (Table 8).

TABLE 8.

Ethylenic compound	k_2^{II} (l. mole^{-1} min.$^{-1}$)	k_2^{III} (l. mole^{-1} min.$^{-1}$)	k_3^{IV} (l.^{2} mole^{-2} min.$^{-1}$)
Allyl alcohol	8·2	14·5	1·56
Allyl acetate	8·13	13·0	1·62

However, it was observed during this investigation that presence of traces of chlorine affected the values of the derived constants seriously. For this reason, great care was taken to ensure that the hypochlorous acid solutions used contained no free chlorine. The differences in the values of the constants quoted in Tables 1 and 8 may well be due to the interference of traces of chlorine. We propose to investigate this further.

Nevertheless, the agreement obtained provides strong evidence that the interpretations of the terms $k_2^{\mathrm{II}}[\mathrm{HOCl}]^2$ and $k_2^{\mathrm{III}}[\mathrm{HOCl}][\mathrm{HOAc}]$ given by Israel (*loc. cit.*) are correct. The interpretation of $k_3^{\mathrm{IV}}[\mathrm{HOCl}]^2[\mathrm{HOAc}]$ given by Craw (*loc. cit.*) appears to be the more plausible, although we have obtained no evidence for this view in this investigation.

The value of k_2^{I} (0·20) is approximately one-tenth of the corresponding value found for allyl alcohol (1·98, Israel, *loc. cit.*). This is to be expected since allyl acetate would be much less reactive than the corresponding alcohol in view of the deactivating effect of the acetyl group due to its tendency to withdraw electrons from the ethylenic bond.

We acknowledge the continued encouragement and interest of Professor J. E. Driver and record our appreciation to Mr. A. J. Berry who supplied us with the details of the Stas pipette.

UNIVERSITY OF HONG KONG, HONG KONG. [*Received, January 27th,* 1955.]