

*The Kinetics of Chlorohydrin Formation. Part V.\* The Reaction between Hypochlorous Acid and Crotonic Acid in Buffered Solutions at 25° and 35°.*

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The study of the reaction in aqueous solution between hypochlorous acid and crotonic acid buffered by sodium crotonate to pH 4.73 was continued. The velocity equation for the reaction at  $35^\circ \pm 0.01^\circ$  conformed to the general equation derived by Craw and Israel (*J.*, 1952, 550) for the reaction at  $25^\circ \pm 0.01^\circ$ , viz.,

$$v = k_2^I[\text{HOCl}]\{[\text{R}\cdot\text{CO}_2\text{H}] + [\text{R}\cdot\text{CO}_2^-]\} + \{k_2^{\text{II}} + k_3^{\text{II}}[\text{R}\cdot\text{CO}_2\text{H}]\}[\text{HOCl}]^2$$

where  $\text{R} = \text{CH}_3\cdot\text{CH}\cdot\text{CH}\cdot$ . The activation energies of the individual reactions occurring between these compounds were calculated from the ratios of the specific rate constants at 25° and 35°. The effect of pH on the rate of addition of hypochlorous acid to crotonic acid was investigated at 25° and 35° and reasons have been advanced for the behaviour exhibited.

IN view of the satisfactory equation developed for the addition of hypochlorous acid to crotonic acid at 25° (Craw and Israel, *J.*, 1952, 550) this reaction was studied in an analogous manner at 35°. If it could be shown that the kinetics of the reaction at 35° could be expressed by an equation of the form

$$v = k_2^I[\text{HOCl}]\{[\text{R}\cdot\text{CO}_2\text{H}] + [\text{R}\cdot\text{CO}_2^-]\} + \{k_2^{\text{II}} + k_3^{\text{II}}[\text{R}\cdot\text{CO}_2\text{H}]\}[\text{HOCl}]^2 \quad (1)$$

\* Part IV, *J.*, 1952, 2327.

derived for the reaction at 25°, then the specific rate constants for the individual terms could be compared with a view to calculating the activation energies for these stages in this temperature interval.

The effect of pH on the rate of addition of hypochlorous acid to olefins has been noted previously. Israel, Martin, and Soper (*J.*, 1950, 1282) found that in the rate equation developed for the addition of hypochlorous acid to allyl alcohol,

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

$k_2^I$  increased and  $k_2^{II}$  decreased with increasing pH. More recently, Shilov, Kupinskaya, and Yasnikov (*Doklady Akad. Nauk S.S.S.R.*, 1951, 81, 435) found that the rate of addition of hypochlorous acid to trimethylallylammonium perchlorate decreased with increasing pH, becoming zero at pH 8.1.

In kinetic equations of the type so far established for crotonic acid, it is difficult to forecast the overall effect of a pH change. A pH change that increases the magnitude of one term in the equation may cause another to decrease while the overall result involves the sum of all the terms.

#### EXPERIMENTAL AND RESULTS

*Materials.*—Crotonic acid, from B.D.H., was recrystallised from light petroleum; it had m. p. 72°. Hypochlorous acid was prepared by a variation of the method used by Israel *et al.* (*loc. cit.*). The crude hypochlorous acid solution, distilled with yellow mercuric oxide in an all-glass apparatus in the dark, had b. p. 20—25°/15—20 mm. Solutions ranging in strength from 0.2—0.9M were obtained, but were diluted to 0.1M before storage in the dark at 4°. This stock solution kept well and was diluted as required.

The initial velocity,  $v_0$ , was plotted against the total olefin concentration for constant hypochlorous acid concentration for ten of the twelve series studied and these graphs indicated a linear relation of the form,

$$v_0 = k([\text{R}\cdot\text{CO}_2\text{H}]_0 + [\text{R}\cdot\text{CO}_2^-]_0) + v'_{\text{res}} \quad \dots \quad (3)$$

where both  $k$  and  $v'_{\text{res}}$  are functions of the hypochlorous acid concentration. From Pitzer's equation for the variation of the dissociation constant of weak acids with temperature (*J. Amer. Chem. Soc.*, 1937, 59, 2365) and the known value of the dissociation constant at 25°, *viz.*,  $2.03 \times 10^{-5}$ , the dissociation constant at 35° was calculated as  $2.05 \times 10^{-5}$ . The value of  $\text{p}K_a$  remained unchanged at 4.69 so that buffer solutions of the same composition were used in the experiments at both 25° and 35°. Therefore, as previously (*loc. cit.*), the ratio  $[\text{R}\cdot\text{CO}_2^-]_0/[\text{R}\cdot\text{CO}_2\text{H}]_0$  where  $\text{R} = \text{CH}_2\cdot\text{CH}:\text{CH}\cdot$  was kept constant and equal to 1.096, and equation (3) can be modified to equation (4),

$$v_0 = k'[\text{R}\cdot\text{CO}_2\text{H}]_0 + v'_{\text{res}} \quad \dots \quad (4)$$

The effect of a large excess of one reactant was studied in the  $K'$  and  $L'$  series, but these results were not used in the determination of the velocity equation.  $k'$  and  $v'_{\text{res}}$  were calculated by the method of least squares for each of the ten series A'—J' (Table 1), and their variation with the concentration of hypochlorous acid was examined graphically. Results showed that  $k'$  and  $v'_{\text{res}}$  vary according to equations (5) and (6) respectively and the method of least squares was used to calculate the lines of best fit to be

$$k'/[\text{HOCl}]_0 = 2.096k_2^I + k_3^{II}[\text{HOCl}]_0 \quad \dots \quad (5)$$

$$\text{and} \quad v'_{\text{res}} = k_2^{II}[\text{HOCl}]_0^2 \quad \dots \quad (6)$$

where  $k_2^I = 7.1 \text{ l. mole}^{-1} \text{ min.}^{-1}$ ,  $k_3^{II} = 4.0 \times 10^3 \text{ l.}^2 \text{ mole}^{-2} \text{ min.}^{-1}$ , and  $k_2^{II} = 6.9 \text{ l. mole}^{-1} \text{ min.}^{-1}$ .

Substituting equations (5) and (6) in equation (4), we obtain the complete velocity equation,  $v_0 = 7.1[\text{HOCl}]_0([\text{R}\cdot\text{CO}_2\text{H}]_0 + [\text{R}\cdot\text{CO}_2^-]_0) + 4.0 \times 10^3[\text{HOCl}]_0^2[\text{R}\cdot\text{CO}_2\text{H}]_0 + 6.9[\text{HOCl}]_0^2$  (7)

This equation is represented in general form by equation (1). That equation (7) gives a reasonably accurate interpretation of the course of the reaction is confirmed since values of  $v_0$  calculated by using it are in good agreement with the observed values (see Table 1).

That this generalisation of initial velocity data is valid was shown by integrating equation (7) to give the variation of the concentration of hypochlorous acid with time. If the time for a

TABLE 1. Initial pH = 4.73. Temperature = 35° ± 0.01°.

Run no.	[HOCl] <sub>0</sub> × 10 <sup>3</sup>	$v_0$ (([R·CO <sub>2</sub> H] <sub>0</sub> + [R·CO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> ) × 10 <sup>5</sup> ) (moles l. <sup>-1</sup> min. <sup>-1</sup> ) × 10 <sup>5</sup>			Run no.	[HOCl] <sub>0</sub> × 10 <sup>3</sup>	$v_0$ (([R·CO <sub>2</sub> H] <sub>0</sub> + [R·CO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> ) × 10 <sup>5</sup> ) (moles l. <sup>-1</sup> min. <sup>-1</sup> ) × 10 <sup>5</sup>		
		obs.	calc.	obs.			calc.	obs.	calc.
A'1	1.54	2.0	4.3	4.7	G'1	3.48	2.0	17.7	17.9
A'2	1.54	4.0	7.5	7.8	G'2	3.45	4.0	27.5	27.1
A'3	1.53	6.0	10.5	10.8	G'3	3.45	6.0	37.6	36.6
A'4	1.53	8.0	13.8	13.9	G'4	3.45	8.0	47.6	46.1
A'5	1.53	10.0	16.8	16.5	G'5	3.45	10.0	56.4	55.4
B'1	1.96	2.0	6.7	6.9	H'1	3.98	2.0	22.3	22.6
B'2	1.96	4.0	10.9	11.2	H'2	3.96	4.0	34.4	34.1
B'3	1.95	6.0	14.7	15.3	H'3	3.94	6.0	45.6	45.3
B'4	1.95	8.0	18.9	19.6	H'4	3.94	8.0	57.0	56.9
B'5	1.95	12.0	26.9	28.0	H'5	3.94	10.0	67.7	68.4
C'1	2.44	2.0	9.8	9.9	I'1	4.44	2.0	28.9	27.5
C'2	2.44	4.0	16.2	15.6	I'2	4.45	4.0	43.6	41.5
C'3	2.44	6.0	22.1	21.3	I'3	4.42	6.0	55.7	54.8
C'4	2.43	8.0	27.5	26.9	I'4	4.42	8.0	70.7	68.6
C'5	2.42	10.0	32.7	32.6	I'5	4.39	10.0	79.2	81.3
D'1	2.84	2.0	12.7	12.7	J'1	4.64	2.0	26.7	29.7
D'2	2.81	4.0	19.5	19.5	J'2	4.64	4.0	43.7	44.5
D'3	2.81	6.0	26.5	26.6	J'3	4.64	6.0	59.3	59.3
D'4	2.81	8.0	33.9	33.6	J'4	4.63	8.0	74.6	74.0
D'5	2.81	10.0	40.7	40.5	J'5	4.63	10.0	88.4	88.8
E'1	3.04	2.0	13.8	14.2	K'1	10.00	2.0	84.1	121.3
E'2	3.03	4.0	21.7	22.0	K'2	10.07	4.0	169.5	176.1
E'3	3.03	6.0	30.3	29.9	K'3	10.08	6.0	252.7	229.6
E'4	3.03	8.0	38.2	37.6	L'1	2.42	12.0	38.8	38.2
E'5	3.03	10.0	47.7	45.6	L'2	2.42	16.0	52.6	49.6
F'1	3.46	2.0	17.5	17.8	L'3	2.40	20.0	66.0	60.2
F'2	3.45	4.0	27.6	27.1					
F'3	3.45	6.0	37.4	36.6					
F'4	3.44	8.0	45.9	45.8					
F'5	3.41	10.0	53.8	54.5					

TABLE 2. Temperature = 25° ± 0.01°.

Series no.	[HOCl] <sub>0</sub> × 10 <sup>3</sup>	(([R·CO <sub>2</sub> H] <sub>0</sub> + [R·CO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> ) × 10 <sup>5</sup> ) (moles l. <sup>-1</sup> min. <sup>-1</sup> ) × 10 <sup>5</sup>			pH <i>t</i> = 0	Series no.	[HOCl] <sub>0</sub> × 10 <sup>3</sup>	(([R·CO <sub>2</sub> H] <sub>0</sub> + [R·CO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> ) × 10 <sup>5</sup> ) (moles l. <sup>-1</sup> min. <sup>-1</sup> ) × 10 <sup>5</sup>			pH <i>t</i> = 0
		obs.	calc.	obs.				calc.	obs.	calc.	
A	3.14	2.0	1.50	7.5	4.21	E	3.10	8.0	6.00	22.3	4.21
	3.13	2.0	1.33	8.2	4.39		3.11	8.0	5.33	24.3	4.39
	3.14	2.0	1.00	9.6	4.69		3.09	8.0	4.00	24.0	4.69
	3.13	2.0	0.67	10.2	4.99		3.09	8.0	2.67	24.1	4.99
	3.13	2.0	0.50	10.7	5.17		3.09	8.0	2.00	23.8	5.17
B	3.11	4.0	3.00	12.5	4.21	F	3.24	8.0	6.00	21.4	4.21
	3.11	4.0	2.67	13.5	4.39		3.24	8.0	5.33	22.8	4.39
	3.10	4.0	2.00	14.4	4.69		3.24	8.0	4.00	24.5	4.69
	3.10	4.0	1.33	15.2	4.99		3.22	8.0	2.67	24.9	4.99
	3.11	4.0	1.00	15.7	5.17		3.22	8.0	2.00	25.0	5.17
C	3.05	6.0	4.50	17.0	4.21	G	3.07	10.0	7.50	27.0	4.21
	3.05	6.0	4.00	18.2	4.39		3.07	10.0	6.67	28.0	4.39
	3.04	6.0	3.00	18.7	4.69		3.06	10.0	5.00	28.2	4.69
	3.04	6.0	2.00	18.7	4.99		3.06	10.0	3.33	27.8	4.99
	3.05	6.0	1.50	19.4	5.17		3.07	10.0	2.50	27.6	5.17
D	3.08	8.0	6.00	21.5	4.21	H	2.98	10.0	7.50	21.7	4.21
	3.07	8.0	5.33	21.7	4.39		2.97	10.0	6.67	23.6	4.39
	3.07	8.0	4.00	23.2	4.69		2.97	10.0	5.00	25.5	4.69
	3.07	8.0	2.67	23.5	4.99		2.96	10.0	3.33	25.0	4.99
	3.07	8.0	2.00	23.7	5.17		2.96	10.0	2.50	25.0	5.17

certain percentage decrease in the concentration of hypochlorous acid as obtained from this integration compares favourably with the time for the same percentage decrease evaluated from the experimental (log titre)-time curves, then it can be assumed that equation (7) for the initial velocity is representative of the velocity at any stage of the reaction. Calculations for 10 and 20% decreases in the concentration of hypochlorous acid showed satisfactory agreement between the observed and the calculated values, *e.g.*, for H'5,  $t_{1/10} = 0.6$  min. (obs.), 0.6 min. (calc.);  $t_{1/5} = 1.3$  min. (obs.), 1.4 min. (calc.).

To investigate the effect of a variation in pH on the rate of reaction, mixed crotonic acid-sodium crotonate buffers were prepared in which the ratio  $[\text{R}\cdot\text{CO}_2^-]_0/[\text{R}\cdot\text{CO}_2\text{H}]_0$  was equal to 1 : 3, 1 : 2, 1 : 1, 2 : 1, 3 : 1, corresponding to theoretical pH values of 4.21, 4.39, 4.69, 4.99, and 5.17 respectively.

The results obtained are listed in Tables 2 and 3 for data at 25° and 35° respectively.

TABLE 3. Temperature = 35° ± 0.01°.

(( $[\text{R}\cdot\text{CO}_2\text{H}]_0 +$ $[\text{HOCl}]_0$ ) $\times 10^3$ )		( $[\text{R}\cdot\text{CO}_2^-]_0 +$ $[\text{R}\cdot\text{CO}_2\text{H}]_0$ ) $\times 10^3$		pH	(( $[\text{R}\cdot\text{CO}_2\text{H}]_0 +$ $[\text{R}\cdot\text{CO}_2^-]_0$ ) $\times 10^3$ )		$v_0$	pH
$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^3$	$t = 0$	$\times 10^3$	$\times 10^3$	$\times 10^5$	$t = 0$
2.43	4.0	3.00	13.9	4.21	2.42	8.0	25.3	4.21
2.43	4.0	2.67	14.9	4.39	2.40	8.0	5.33	4.39
2.43	4.0	2.00	15.7	4.69	2.40	8.0	4.00	4.69
2.43	4.0	1.33	16.6	4.99	2.40	8.0	2.67	4.99
2.43	4.0	1.00	17.0	5.17	2.40	8.0	2.00	5.17

As seen in Table 2, the initial hypochlorous acid concentration was kept almost constant while the total olefin concentration was varied from 0.002 to 0.010M. The olefin concentration had a marked effect on the nature of the variation of velocity with pH. For low concentrations of crotonic acid plus sodium crotonate, the velocity increased steadily with pH throughout the range investigated, *e.g.*, series A, B, C. At higher concentrations of olefin, *e.g.*, series D, E, F, the increase in velocity with pH was not marked in the higher pH range 4.69—5.17, while in the G and H series the velocity reached its maximum value at a pH between 4.6 and 4.7.

## DISCUSSION

The significance of the rate constants of equation (1) has been discussed previously (*loc. cit.*), but in view of more recent work the following information may be added.

The complex first term of equation (1) possibly includes a term for the rate of formation of crotonyl hypochlorite from crotonic acid and hypochlorous acid. That the formation of these acyl hypochlorites is due to the undissociated carboxylic acid and not to the carboxylate ion has been demonstrated recently by Shilov and Kupinskaya (*Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 621) who found that the catalytic effect of carboxylic acid and hypochlorous acid mixtures disappeared at a pH about 7.5 where the amount of free hypochlorous acid was still high, but where the amount of free carboxylic acid became insignificant.

The term,  $k_3^{\text{II}}[\text{HOCl}]^2[\text{R}\cdot\text{CO}_2\text{H}]$ , has been interpreted as the formation of chlorine monoxide from hypochlorous acid under the catalytic influence of undissociated crotonic acid. This, however, cannot be the only reason for the occurrence of this term in the rate equation. As will be shown in later papers, this term does not appear in the corresponding rate equations for tiglic and  $\beta\beta$ -dimethylacrylic acid even though these acids are of approximately the same strength as crotonic acid.

The variation of the rate constants with temperature is summarised in Table 4.

TABLE 4.

	$k_2^{\text{I}}$	$k_2^{\text{II}}$	$k_3^{\text{II}}$
25° .....	4.5 <sub>1</sub>	4.0 <sub>1</sub>	2.0 <sub>4</sub> × 10 <sup>3</sup>
35° .....	7.1 <sub>4</sub>	6.8 <sub>9</sub>	4.0 <sub>0</sub> × 10 <sup>3</sup>
$k_{35^\circ}/k_{25^\circ}$ .....	1.58	1.72	1.94
$\Delta E$ (kcal./mole <sup>-1</sup> ) .....	8.38	9.87	12.10

$k_{35^\circ}/k_{25^\circ}$  represents the ratio of the rate constants for 35° and 25° respectively, and  $\Delta E$  is the activation energy calculated by using the Arrhenius equation and assuming that the probability factor of the non-exponential coefficient in this equation remains independent of the temperature in this interval.

We will now review the effects of pH on the reaction velocity and in order to explain these results it is important to examine the effect of a pH change in relation to equation (1). Since the variation of pH was studied for series of constant initial hypochlorous acid concentration, equation (1) may be modified, so that

$$v = k_a([\text{R}\cdot\text{CO}_2\text{H}] + [\text{R}\cdot\text{CO}_2^-]) + k_b + k_c[\text{R}\cdot\text{CO}_2\text{H}] \quad . \quad . \quad . \quad (8)$$

Again since in any one series in Table 2 the value of  $([\text{R}\cdot\text{CO}_2\text{H}]_0 + [\text{R}\cdot\text{CO}_2^-]_0)$  is constant, the variation of velocity with pH is given by :

$$\frac{\partial v}{\partial \text{pH}} = ([\text{R}\cdot\text{CO}_2\text{H}] + [\text{R}\cdot\text{CO}_2^-])\frac{\partial k_a}{\partial \text{pH}} + \frac{\partial k_b}{\partial \text{pH}} + [\text{R}\cdot\text{CO}_2\text{H}]\frac{\partial k_c}{\partial \text{pH}} + k_c \cdot \frac{\partial [\text{R}\cdot\text{CO}_2\text{H}]}{\partial \text{pH}} \quad . \quad . \quad . \quad (9)$$

The reasons advanced by Israel *et al.* (*loc. cit.*) for the variation of the rate constants in their velocity equation (2) should be applicable to equation (8) for crotonic acid. Thus  $\frac{\partial k_a}{\partial \text{pH}} > 0$  and  $\frac{\partial k_b}{\partial \text{pH}} < 0$ . Shilov and Kanyaev (*J. Phys. Chem. Russia*, 1934, 5, 654) found that the rate constant in the equation derived by them, *viz.*,  $v = k[\text{HOCl}]^2[\text{R}\cdot\text{CO}_2\text{H}]$ , decreased with increasing pH and, extending this finding to  $k_c$ , we see that  $\frac{\partial k_c}{\partial \text{pH}} < 0$ . Thus since the terms on the right-hand side of equation (9) differ in sign, it would be possible for  $\frac{\partial v}{\partial \text{pH}}$  to change from positive to negative with changes in the total olefin concentration. The partial derivatives of the first three terms in equation (9) with respect to total olefin concentration are constants (or zero). The last term, however, is the controlling factor and an examination of Table 2 shows that the variation of  $\frac{\partial [\text{R}\cdot\text{CO}_2\text{H}]}{\partial \text{pH}}$  with total olefin concentration is not constant, but increases markedly with total olefin concentration. Now  $\frac{\partial [\text{R}\cdot\text{CO}_2\text{H}]}{\partial \text{pH}}$  is negative and hence for large concentrations of olefin, this term becomes larger in magnitude (still retaining its negative sign) with the result that the other constant positive terms are exceeded to such an extent that  $\frac{\partial v}{\partial \text{pH}}$  decreases through zero, eventually to become negative.

It is possible to predict where this reversal of sign will take place; it will be near the  $\text{p}K_a$  value for crotonic acid (4.69) since it is here that the change  $\frac{\partial [\text{R}\cdot\text{CO}_2\text{H}]}{\partial \text{pH}}$  is a maximum. This is in agreement with the experimental findings given in Table 2.

It has been shown that the general velocity equations at 25° and 35° are similar, and thus the explanation of the variation of the velocity with pH at 25° should be applicable to a change in pH at 35°. Examination of Table 3 supports this view.

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