99. *The Kinetics of Chlorohydrin Formation. Part III.* The Reaction between Hypochlorous Acid and Crotonic Acid at Constant* pH.

By D. A. CRAW and G. C. ISRAEL.

The kinetics of the reaction between hypochlorous acid solutions and solutions containing such concentrations of crotonic acid and crotonate ion as to yield a constant pH 4·73 have been investigated at 25·00° ± 0·01°. The reaction velocity conforms to the expression

$$v = k_2^{\mathrm{I}}[\mathrm{HOCl}]([\mathrm{R{\cdot}CO_2H}] + [\mathrm{R{\cdot}CO_2^-}]) + (k_2^{\mathrm{II}} + k_3^{\mathrm{II}}[\mathrm{R{\cdot}CO_2H}])[\mathrm{HOCl}]^2$$

where R = $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}}$. k_2^{II} and k_3^{II} are interpreted as being the specific rates of formation of chlorine monoxide from hypochlorous acid, the latter being the specific rate of formation catalysed by crotonic acid. The value of k_2^{II} (4·0) for this reaction was found to be only half that (8·2) reported in Part II of this series for the reaction between hypochlorous acid and allyl alcohol at the same pH. No explanation of this discrepancy has as yet been found.

THE kinetics of addition of hypochlorous acid to crotonic acid were studied by Schilov and Kaniaev (*J. Phys. Chem. U.S.S.R.*, 1934, **5**, 654; *Trans. Inst. Chem. Tech. Ivanovo*, 1935, 19) who were unable to derive a definite kinetic equation to express the rate of the reaction. These workers observed that the reaction velocity was approximately proportional to the concentration of crotonic acid, increased as the pH increased, and was not affected by the presence of neutral salts. For relatively high concentrations of crotonic acid, the reaction velocity was found to be approximately proportional to the concentration of hypochlorous acid, but for relatively low concentrations of crotonic acid the reaction velocity varied approximately as the square of the hypochlorous acid concentration.

In view of the results obtained by Israel, Martin, and Soper (*J.*, 1950, 1282) and Israel (*ibid.*, p. 1286) for the kinetics of addition of hypochlorous acid to allyl alcohol, the reaction between hypochlorous acid and crotonic acid has been reinvestigated in solutions of pH 4·73. Since hypochlorous acid reacts with both un-ionised crotonic acid and crotonate ion, the ratio of the concentrations of these two species was kept throughout at $[\mathrm{R{\cdot}CO_2^-}]/[\mathrm{R{\cdot}CO_2H}] = 1{\cdot}096$ (R = $\mathrm{CH_3{\cdot}CH{:}CH{\cdot}}$). This served the purpose of maintaining the reacting solutions at a pH close to 4·73 (Vogel and Jeffery, *Chem. and Ind.*, 1937, 600; Ives, Linstead, and Riley, *J.*, 1933, 561) and thus avoiding catalytic effects caused by addition of a buffer such as acetate–acetic acid solutions (cf. Israel, *J.*, 1950, 1286).

In view of the probable complexity of the kinetic equation, the initial velocity, v_0, was determined in each experiment by the method described previously (Israel, Martin, and Soper, *loc. cit.*). In each case the pH of the reaction mixture was determined seven minutes after the commencement of the reaction. The results are summarised in Table 1.

From the results obtained by Schilov and Kaniaev (*locc. cit.*), it seemed likely that the kinetic equation would contain two terms, *viz.*, $k_2^{\mathrm{I}}[\mathrm{HOCl}]([\mathrm{R{\cdot}CO_2H}] + [\mathrm{R{\cdot}CO_2^-}])$ and $k_3^{\mathrm{II}}[\mathrm{HOCl}]^2[\mathrm{R{\cdot}CO_2H}]$, the latter being assumed to be dependent on the concentration of un-ionised crotonic acid and not on the concentration of crotonate ion, by analogy with the results obtained by Israel (*J.*, 1950, 1286) for the reaction between hypochlorous acid and allyl alcohol in the presence of acetate–acetic acid buffers. Thus, for constant concentrations of hypochlorous acid, the kinetic equation was assumed to be of the form, $v_0 = k_1[\mathrm{R{\cdot}CO_2H}]_0 + v_{\mathrm{res.}}$, since in all experiments the ratio $[\mathrm{R{\cdot}CO_2^-}]/[\mathrm{R{\cdot}CO_2H}]$ was constant and equal to 1·096. That the values of $v_0^{\mathrm{obs.}}$ vary linearly with $[\mathrm{R{\cdot}CO_2H}]_0$ is clear from Fig. 1 in which five of the seven series of experimental values have been plotted. In each case the best line was located by the method of least squares and the values of k_1 and $v_{\mathrm{res.}}$ so obtained are given in Table 2.

---

* Part II, *J.*, 1950, 1286.

That the residual velocity, $v_{\text{res.}}$, varies as the square of the concentration of hypochlorous acid, *i.e.*, is equal to $k_2^{\text{II}}[\text{HOCl}]^2$, is clear from Fig. 2, the best line being located by the method of least squares. The slope of this line gives $k_2^{\text{II}} = 4{\cdot}0$ l. mole^{-1} min.$^{-1}$.

TABLE 1. $[\text{R}{\cdot}\text{CO}_2^-] = 1{\cdot}096[\text{R}{\cdot}\text{CO}_2\text{H}]$. *Initial* pH = 4·73. *Temp.* = 25·00° ± 0·01°.

$10^3[\text{HOCl}]_0$ (mole l.$^{-1}$)	$10^3([\text{R}{\cdot}\text{CO}_2\text{H}] + [\text{R}{\cdot}\text{CO}_2^-])_0$ (mole l.$^{-1}$)	pH (after 7 min.)	10^5v_0 (mole l.$^{-1}$ min.$^{-1}$) (obs.)	10^5v_0 (mole l.$^{-1}$ min.$^{-1}$) (calc.)
1·00	2·0	4·60	1·6	1·5
0·99	4·0	4·65	2·6	2·6
0·99	6·0	4·69	3·6	3·7
0·99	8·0	4·69	4·8	4·7
0·99	10·0	4·65	5·8	5·8
0·99	12·0	4·65	7·1	6·9
1·90	2·0	4·68	3·8	3·9
1·89	4·0	4·71	6·0	6·3
1·90	8·0	4·70	11·3	11·1
1·89	10·0	4·69	13·6	13·5
1·89	12·0	4·69	15·8	15·8
2·96	2·0	4·50	7·9	7·9
2·96	4·0	4·55	12·8	12·3
2·96	8·0	4·57	21·4	21·0
2·95	10·0	4·59	25·8	25·3
2·95	12·0	4·57	30·4	29·7
3·01	2·0	—	8·4	8·1
3·00	4·0	—	12·5	12·6
2·97	8·0	—	20·8	21·2
3·00	10·0	—	25·6	25·9
2·97	12·0	—	30·0	30·2
3·10	2·0	4·52	8·0	8·6
3·11	4·0	4·63	13·4	13·3
3·09	8·0	4·67	22·1	22·5
3·08	10·0	4·70	27·0	27·0
3·08	12·0	4·70	30·4	31·6
3·90	2·0	4·44	13·0	12·6
3·90	4·0	4·54	19·5	19·1
3·91	8·0	4·54	34·1	32·2
3·90	10·0	4·58	40·6	38·6
3·90	12·0	4·60	47·2	45·0
4·33	2·0	4·06	14·6	15·1
4·30	4·0	4·18	22·2	22·4
4·31	8·0	4·30	36·9	37·6
4·30	10·0	4·33	44·3	45·0
4·29	12·0	4·40	50·8	52·3

TABLE 2.

$10^3[\text{HOCl}]_0$ (mean) (mole l.$^{-1}$)	0·99	1·89	2·95	2·99	3·09	3·90	4·30
10^2k_1 (min.$^{-1}$)	1·15	2·56	4·67	4·53	4·72	7·24	7·65
$10^5v_{\text{res.}}$ (mole l.$^{-1}$ min.$^{-1}$)	0·42	1·32	3·60	3·89	3·98	6·00	7·46

The variation of the values of k_1 with the concentration of hypochlorous acid is given by

$$k_1 = 2{\cdot}096k_2^{\text{I}}[\text{HOCl}]_0 + k_3^{\text{II}}[\text{HOCl}]_0{}^2$$

or

$$k_1/[\text{HOCl}]_0 = 2{\cdot}096k_2^{\text{I}} + k_3^{\text{II}}[\text{HOCl}]_0$$

as may be seen from Fig. 3 in which $k_1/[\text{HOCl}]_0$ has been plotted as ordinates against $[\text{HOCl}]_0$ as abscissæ. The best line through these points was determined by the method of least squares and in this way the values of the two constants were found to be $k_2^{\text{I}} = 4{\cdot}5$ l. mole^{-1} min.$^{-1}$ and $k_3^{\text{II}} = 2{\cdot}1 \times 10^3$ l.^{2} mole^{-2} min.$^{-2}$.

Thus the complete kinetic equation is shown to be :

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

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

$$v = 4{\cdot}5[\text{HOCl}]([\text{R}{\cdot}\text{CO}_2\text{H}] + [\text{R}{\cdot}\text{CO}_2^-]) + (4{\cdot}0 + 2{\cdot}1 \times 10^3[\text{R}{\cdot}\text{CO}_2\text{H}])[\text{HOCl}]^2 \quad \text{(ii)}$$

That equation (ii) 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).

The term $k_2^{\text{I}}[\text{HOCl}]([\text{R}{\cdot}\text{CO}_2\text{H}] + [\text{R}{\cdot}\text{CO}_2^-])$ in equation (i) is probably complex, and represents the rate of addition of hypochlorous acid to un-ionised crotonic acid, and to crotonate ion, and possibly also includes a term for the rate of formation of crotonyl hypochlorite (R·CO·OCl) from crotonic acid and hypochlorous acid (cf. Israel, *loc. cit.*).

However, the value of k_2^{I} is constant, since, in this investigation, the ratio of the concentrations of crotonate ion and crotonic acid was constant.

The second term $k_2^{II}[HOCl]^2$ probably represents the rate of formation of chlorine monoxide in solution by the reaction $2HOCl \longrightarrow Cl_2O + H_2O$. However, the value of k_2^{II} (4·0) for this reaction is distinctly lower than that obtained previously (8·2) for the reaction between allyl alcohol and hypochlorous acid (Israel, *loc. cit.*). A possible cause for the discrepancy may be found in the qualities of the hypochlorous acid used in the two investigations, since Ourisson and Kastner (Congr. Chim. ind., Compt. rend. XVIII Congr., Sept. 1938, p. 983) have reported that mercuric oxide is appreciably soluble in hypochlorous acid solutions. Since the solutions employed in the earlier work were stored over yellow mercuric oxide, appreciable quantities of mercuric hypochlorite would certainly be present therein. In the present investigation, mercury-free solutions of hypochlorous acid were used throughout.

FIG. 1.

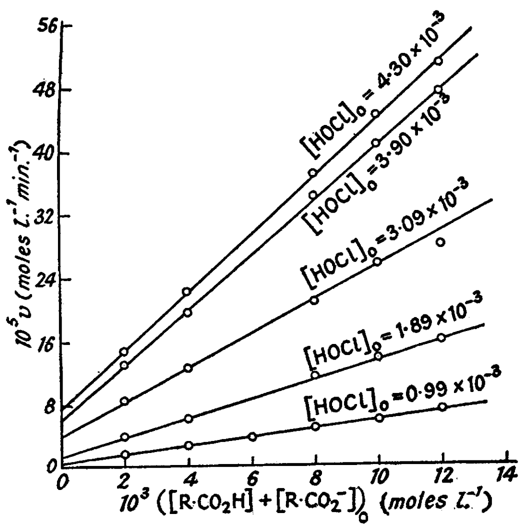


FIG. 2.

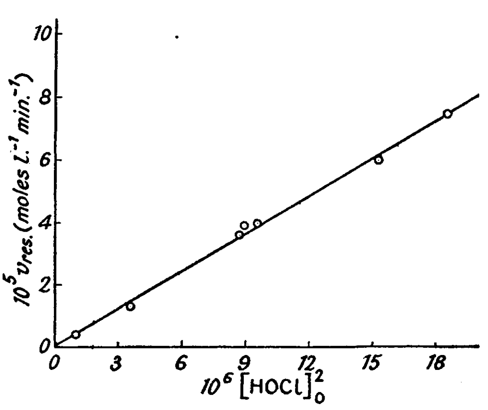
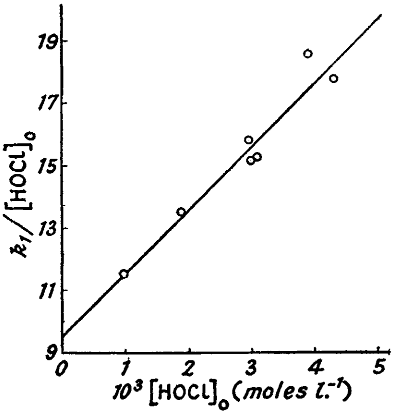


FIG. 3.



Again, as may be seen from Table 1, the pH of each reaction mixture was found to be rather less than the calculated value, an effect due partly to the hypochlorous acid added and partly to the presence of chlorohydroxybutyric acids and their salts. The lower pH of the various reaction mixtures would result in somewhat different values of the specific rate constants (cf. Schilov and Kaniaev, *loc. cit.*).

The final term $k_3^{II}[HOCl]^2[R\cdot CO_2H]$ in the kinetic equation may be interpreted as the rate of formation of chlorine monoxide from hypochlorous acid under the catalytic influence of un-ionised crotonic acid, it being assumed that crotonate ion is inactive in this respect (cf. Israel, *loc. cit.*). The value of k_3^{II} found is of the same order as that found by Israel for the catalytic effect of un-ionised acetic acid, a result which would be expected since crotonic acid and acetic acid are acids of approximately the same strength.

EXPERIMENTAL

Materials.—In this investigation, crotonic acid, from B.D.H., was recrystallised from light petroleum; it had m. p. 72°.

Hypochlorous acid was prepared by a method similar to that used by Israel, Martin, and Soper (*loc. cit.*) except that the distillate was not stored over mercuric oxide. Instead, it was treated with bismuth hydroxide, filtered, and stored in the dark at *ca.* 6°. Hypochlorous acid solutions were prepared from these stock solutions immediately before use by shaking them with a small amount of bismuth hydroxide, filtering them quickly, and diluting them to the required strength with distilled water. Such solutions gave negative tests for Bi^{+++} (cf. Vogel, " Qualitative Chemical Analysis," 3rd edn., Longmans, 1945, p. 152). In cases where hypochlorous acid had been stored over yellow mercuric oxide, appreciable amounts of mercuric ions were found in solution (cf. Ourisson and Kastner, *loc. cit.*).

Kinetic Measurements.—These were carried out by the method described previously (Israel, Martin, and Soper, *loc. cit.*).

pH *Measurements.*—A Leeds–Northrup pH meter was used for this purpose.

The authors acknowledge the helpful advice and criticisms offered by Professor F. G. Soper, University of Otago, Dunedin, N.Z. One of them (D. A. C.) acknowledges the award by the University of Tasmania of a Commonwealth Research Studentship.

UNIVERSITY OF TASMANIA, HOBART.

[*Received, July* 18*th*, 1951.]