# *The Kinetics of Chlorohydrin Formation. Part VI.* The Reaction between Hypochlorous Acid and Tiglic Acid at Constant* pH.

By D. A. Craw.

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The kinetics of the reaction between hypochlorous acid and tiglic acid in the presence of sodium tiglate have been investigated in aqueous solution of constant pH 4·73 at 25·00° ± 0·01° and 35·00° ± 0·01°. The reaction conforms to the velocity equation

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

where R = $CH_3{\cdot}CH{:}CMe{\cdot}$. The significance and the temperature dependence of the rate constants $k_2^{I}$ and $k_2^{II}$ are discussed. The values for the specific rate constants and the activation energies for the addition of hypochlorous acid to tiglic acid are given and compared with those for crotonic acid (Craw and Israel, *J.*, 1952, 550; Part V *).

The kinetics of the addition of hypochlorous acid to tiglic acid have not previously been investigated although the electrophilic addition of bromine and the nucleophilic addition of bromine catalysed by hydrogen bromide in acetic acid solution have been studied (Anantakrishnan and Venkataraman, *Proc. Indian Acad. Sci.*, 1940, **12**, *A*, 290; 1946, **23**, *A*, 312; Evans, Watson, and Robertson, *J.*, 1950, 1624). This work indicated that tiglic acid reacted 6—10 times faster than crotonic acid.

The products of the reaction between hypochlorous acid and tiglic acid have been studied by Melikov (*Annalen*, 1886, **234**, 224; 1890, **257**, 119) and by Bloomfield, Farmer, and Hose (*J.*, 1933, 800) who were interested in the relative amounts of the chloro-hydroxy-isomers formed. They observed that the addition to both the free acid and the sodium salt was rapid compared with that to crotonic acid and yielded water-soluble chlorohydrins, the β-chloro-α-hydroxy-isomer predominating.

In view of the satisfactory velocity equation developed for crotonic acid (*locc. cit.*), a similar kinetic investigation was applied to tiglic acid to study the effect of the α-methyl substituent.

## Experimental

*Materials.*—Tiglic acid, from B.D.H., was recrystallised from water; it had m. p. 64·5°. A stock tiglic acid–sodium tiglate buffer solution in which the ratio $[R{\cdot}CO_2^-]_0/[R{\cdot}CO_2H]_0 = 0{\cdot}513$ where R = $CH_3{\cdot}CH{:}CMe{\cdot}$ was prepared. This ratio was the theoretical value for a resultant pH of 4·73 (Ostwald, *Z. physikal. Chem.*, 1888, **3**, 242) and was kept constant throughout in order to minimise the effects of pH on the rate of addition. The application of Pitzer's equation (*J. Amer. Chem. Soc.*, 1937, **59**, 2365) for variation of the dissociation constant of weak acids with temperature gave a p$K_a$ value of 5·01 at 35° compared with 5·02 at 25°. This change was negligible and hence the same stock buffer solution was used at both these temperatures.

Hypochlorous acid was prepared by two different methods, one of which was described in the preceding paper. The other preparation was the non-aqueous method of Ourisson and Kastner (*Cong. Chim. ind., Compt. rend. XVIII Congr.*, Sept. 1938, p. 983) in which chlorine was passed into an agitated suspension of mercuric oxide in carbon tetrachloride at 0°. The reddish-brown solution of chlorine monoxide in carbon tetrachloride was shaken with yellow mercuric oxide, filtered, and stored at 4°. Fresh hypochlorous acid was prepared by extracting a small portion of this solution with water, but, as this aqueous extract usually smelt slightly of chlorine, it was always treated at least twice with freshly precipitated bismuth hydroxide and filtered.

*Kinetic Measurements.*—These were carried out by Israel, Martin, and Soper's method (*J.*, 1950, 1282). The greater reactivity of this olefin necessitated sampling at half-minute intervals.

## Results

The pH was measured 5 min. after the reaction was started and in all cases was slightly lower than the theoretical initial value of 4·73. The pH deviation increased with increasing

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* Part V, preceding paper.

hypochlorous acid concentration and may be explained by the rapid addition of hypochlorous acid to sodium tiglate, thereby altering the constitution of the buffer, and also by the presence of chloro-hydroxy-α-methylbutyric acids.

The symbol R below represents always $CH_3{\cdot}CH{:}CMe$; concentrations are expressed in moles $l.^{-1}$ and velocities in moles $l.^{-1}$ $min.^{-1}$.

Eleven series each of approximately constant initial hypochlorous acid concentration were studied at 25·00° ± 0·01° and the results listed in Table 1.

TABLE 1.

| Run no. | $[HOCl]_0$ $\times 10^3$ | $([R{\cdot}CO_2H]_0 + [R{\cdot}CO_2^-]_0)$ $\times 10^3$ | $v_0 \times 10^5$ obs. | $v_0 \times 10^5$ calc. |
|---|---|---|---|---|
| A1 | 0·61 | 1·0 | 1·59 | 1·52 |
| A2 | 0·61 | 2·0 | 2·82 | 2·75 |
| A3 | 0·61 | 4·0 | 5·00 | 5·17 |
| A4 | 0·60 | 6·0 | 7·55 | 7·61 |
| A5 | 0·61 | 8·0 | 10·2 | 10·1 |
| B1 | 0·91 | 1·0 | 2·51 | 2·46 |
| B2 | 0·91 | 2·0 | 4·42 | 4·28 |
| B3 | 0·90 | 4·0 | 8·03 | 7·93 |
| B4 | 0·90 | 6·0 | 11·7 | 11·6 |
| B5 | 0·90 | 8·0 | 15·7 | 15·3 |
| C1 | 1·09 | 1·0 | 3·03 | 3·10 |
| C2 | 1·09 | 2·0 | 5·13 | 5·31 |
| C3 | 1·09 | 4·0 | 9·67 | 9·69 |
| C4 | 1·09 | 6·0 | 13·9 | 14·1 |
| C5 | 1·08 | 8·0 | 18·3 | 18·4 |
| D1 | 1·31 | 1·0 | 3·88 | 3·94 |
| D2 | 1·31 | 2·0 | 6·50 | 6·59 |
| D3 | 1·31 | 4·0 | 11·8 | 11·8 |
| D4 | 1·30 | 6·0 | 17·1 | 17·1 |
| D5 | 1·30 | 8·0 | 22·3 | 22·4 |
| E1 | 1·35 | 1·0 | 4·25 | 4·10 |
| E2 | 1·34 | 2·0 | 6·57 | 6·77 |
| E3 | 1·33 | 4·0 | 11·9 | 12·1 |
| E4 | 1·33 | 6·0 | 17·1 | 17·4 |
| E5 | 1·33 | 8·0 | 22·6 | 22·8 |
| F1 | 1·57 | 1·0 | 4·88 | 5·02 |
| F2 | 1·56 | 2·0 | 8·15 | 8·16 |
| F3 | 1·56 | 4·0 | 14·5 | 14·4 |
| F4 | 1·56 | 6·0 | 21·1 | 20·7 |
| F5 | 1·56 | 8·0 | 28·0 | 27·0 |
| G1 | 1·68 | 1·0 | 5·33 | 5·52 |
| G2 | 1·68 | 2·0 | 8·45 | 8·89 |
| G3 | 1·66 | 6·0 | 21·0 | 22·3 |
| G4 | 1·66 | 8·0 | 28·5 | 29·0 |
| H1 | 1·78 | 1·0 | 6·28 | 5·98 |
| H2 | 1·77 | 2·0 | 9·45 | 9·54 |
| H3 | 1·76 | 4·0 | 16·4 | 16·6 |
| H4 | 1·76 | 6·0 | 23·2 | 23·7 |
| H5 | 1·76 | 8·0 | 30·4 | 30·9 |
| I1 | 1·89 | 1·0 | 6·18 | 6·49 |
| I2 | 1·88 | 2·0 | 10·0 | 10·3 |
| I3 | 1·88 | 4·0 | 17·3 | 17·8 |
| I4 | 1·87 | 6·0 | 24·7 | 25·3 |
| I5 | 1·87 | 8·0 | 32·5 | 32·9 |
| J1 | 1·96 | 1·0 | 6·99 | 6·85 |
| J2 | 1·96 | 2·0 | 11·2 | 10·8 |
| J3 | 1·95 | 4·0 | 18·8 | 18·6 |
| J4 | 1·95 | 6·0 | 28·0 | 26·5 |
| J5 | 1·94 | 8·0 | 35·0 | 34·3 |
| K1 | 2·01 | 1·0 | 7·04 | 7·08 |
| K2 | 2·00 | 2·0 | 11·1 | 11·1 |
| K3 | 1·99 | 4·0 | 19·2 | 19·1 |
| K4 | 1·99 | 6·0 | 27·3 | 27·1 |
| K5 | 1·99 | 8·0 | 35·5 | 35·1 |

The variation of the initial velocity, $v_0$, with the total olefin concentration for constant initial hypochlorous acid concentration was investigated as described in the preceding paper and can be represented by the equation,

$$v_0 = k([R{\cdot}CO_2H]_0 + [R{\cdot}CO_2^-]_0) + v_{res} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

Values of $k$ and $v_{res}$ were evaluated for each series by the method of least squares, and their variation with the concentration of hypochlorous acid can be expressed by the equations

$$k = 20{\cdot}24[HOCl]_0 - 0{\cdot}007 \times 10^{-2} \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

and

$$v_{res} = 7{\cdot}49[HOCl]_0^2 - 0{\cdot}04 \times 10^{-5} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

The constant terms in these equations may be rejected without serious error, whence

$$k = k_2^{I}[HOCl]_0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

and

$$v_{res} = k_2^{II}[HOCl]_0^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Thus the complete velocity equation becomes

$$v_0 = k_2^{I}[HOCl]_0([R{\cdot}CO_2H]_0 + [R{\cdot}CO_2^-]_0) + k_2^{II}[HOCl]_0^2 \quad . \; . \; . \quad (6)$$

or by substitution of the values of the rate constants and expression of the equation generally,

$$v = 20{\cdot}2[HOCl]([R{\cdot}CO_2H] + [R{\cdot}CO_2^-]) + 7{\cdot}5[HOCl]^2 \quad . \; . \; . \quad (7)$$

The observed initial velocities compare reasonably with those calculated by equation (6) (see Table 1).

The satisfactory nature of this equation prompted an investigation at 35·00° ± 0·01°, and the nine series A′—I′ given in Table 2 resulted.

TABLE 2. Initial pH = 4·73. Temperature = 35·00° ± 0·01°.

| Run no. | $[HOCl]_0$ $\times 10^3$ | $([R{\cdot}CO_2H]_0 + [R{\cdot}CO_2^-]_0)$ $\times 10^3$ | $v_0 \times 10^5$ obs. | $v_0 \times 10^5$ calc. | Run no. | $[HOCl]_0$ $\times 10^3$ | $([R{\cdot}CO_2H]_0 + [R{\cdot}CO_2^-]_0)$ $\times 10^3$ | $v_0 \times 10^5$ obs. | $v_0 \times 10^5$ calc. |
|---|---|---|---|---|---|---|---|---|---|
| A′1 | 1·02 | 1·0 | 4·68 | 4·70 | F′1 | 2·00 | 1·0 | 10·9 | 11·5 |
| A′2 | 1·02 | 2·0 | 8·60 | 8·28 | F′2 | 2·00 | 2·0 | 18·4 | 18·4 |
| A′3 | 1·01 | 4·0 | 15·8 | 15·2 | F′3 | 1·98 | 4·0 | 31·5 | 31·9 |
| A′4 | 1·01 | 6·0 | 22·6 | 22·2 | F′4 | 1·97 | 6·0 | 44·6 | 45·6 |
| A′5 | 1·01 | 8·0 | 30·5 | 29·2 | F′5 | 1·97 | 8·0 | 59·0 | 59·3 |
| B′1 | 1·27 | 1·0 | 6·61 | 6·21 | G′1 | 2·21 | 1·0 | 13·0 | 13·2 |
| B′2 | 1·26 | 2·0 | 10·7 | 10·5 | G′2 | 2·21 | 2·0 | 21·1 | 20·9 |
| B′3 | 1·25 | 4·0 | 19·6 | 19·1 | G′3 | 2·17 | 4·0 | 33·9 | 35·5 |
| B′4 | 1·23 | 6·0 | 27·0 | 27·3 | G′4 | 2·18 | 6·0 | 51·8 | 50·9 |
| B′5 | 1·24 | 8·0 | 37·7 | 36·3 | G′5 | 2·15 | 8·0 | 65·9 | 65·3 |
| C′1 | 1·26 | 1·0 | 6·68 | 6·20 | H′1 | 2·50 | 1·0 | 15·7 | 15·8 |
| C′2 | 1·25 | 2·0 | 10·6 | 10·5 | H′2 | 2·50 | 2·0 | 24·7 | 24·4 |
| C′3 | 1·25 | 4·0 | 20·7 | 19·2 | H′3 | 2·46 | 4·0 | 39·5 | 41·1 |
| C′4 | 1·24 | 6·0 | 28·8 | 27·7 | H′4 | 2·45 | 6·0 | 56·8 | 58·0 |
| C′5 | 1·24 | 8·0 | 37·8 | 36·2 | H′5 | 2·45 | 8·0 | 75·7 | 75·0 |
| D′1 | 1·51 | 1·0 | 7·81 | 7·80 | I′1 | 2·81 | 1·0 | 18·6 | 18·6 |
| D′2 | 1·50 | 2·0 | 12·7 | 12·9 | I′2 | 2·79 | 2·0 | 26·1 | 28·1 |
| D′3 | 1·49 | 4·0 | 23·5 | 23·3 | I′3 | 2·77 | 4·0 | 45·4 | 47·2 |
| D′4 | 1·48 | 6·0 | 33·6 | 33·3 | I′4 | 2·73 | 6·0 | 62·1 | 65·5 |
| D′5 | 1·48 | 8·0 | 45·0 | 43·7 | I′5 | 2·73 | 8·0 | 82·3 | 84·4 |
| E′1 | 1·87 | 1·0 | 10·8 | 10·4 | | | | | |
| E′2 | 1·85 | 2·0 | 16·6 | 16·7 | | | | | |
| E′3 | 1·84 | 4·0 | 29·6 | 29·4 | | | | | |
| E′4 | 1·83 | 6·0 | 42·5 | 42·1 | | | | | |
| E′5 | 1·82 | 8·0 | 55·8 | 54·5 | | | | | |

As previously, the variation of the initial velocity with the initial total olefin concentration for constant hypochlorous acid concentration was examined graphically and the line of best fit determined by the method of least squares. This variation may be represented for each of the series A′—I′ by

$$v_0 = k'([R{\cdot}CO_2H]_0 + [R{\cdot}CO_2^-]_0) + v'_{res} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The variation of $k'$ with hypochlorous acid concentration was nearly linear but a slight decrease in the value of $k'/[HOCl]_0$ is noticed in the values tabulated below:

| Series | $k'/[HOCl]_0$ | Series | $k'/[HOCl]_0$ | Series | $k'/[HOCl]_0$ | Series | $k'/[HOCl]_0$ |
|---|---|---|---|---|---|---|---|
| A′ | 35·98 | D′ | 35·56 | G′ | 34·71 | I′ | 32·94 |
| B′ | 35·00 | E′ | 34·98 | H′ | 34·20 | Mean : | 34·86 |
| C′ | 36·12 | F′ | 34·22 | | | | |

For this reason, the method of least squares was not used to determine the equation of this graph, but the arithmetic mean of the $k'/[HOCl]_0$ values enabled the variation of $k'$ with hypochlorous acid concentration to be represented by the equation

$$k' = 34{\cdot}86[HOCl]_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

*i.e.*,

$$k' = k_2^{I}[HOCl]_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The residual velocity, $v'_{res}$, varied with the hypochlorous acid concentration according to the equation

$$v'_{res} = 11{\cdot}20[HOCl]_0^2 + 0{\cdot}053 \times 10^{-5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and, rejecting this constant term as small compared with the observed velocities, we obtain the relation

$$v'_{res} = k_2^{II}[HOCl]_0^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Thus the complete velocity equation is

$$v = k_2^{\mathrm{I}}[\mathrm{HOCl}]_0([\mathrm{R{\cdot}CO_2H}]_0 + [\mathrm{R{\cdot}CO_2^-}]_0) + k_2^{\mathrm{II}}[\mathrm{HOCl}]_0^2 \quad . \quad . \quad . \quad (13)$$

Substituting of the values for the rate constants and expressing the equation generally gives

$$v = 34{\cdot}9[\mathrm{HOCl}]([\mathrm{R{\cdot}CO_2H}] + [\mathrm{R{\cdot}CO_2^-}]) + 11{\cdot}2[\mathrm{HOCl}]^2 \quad . \quad . \quad . \quad (14)$$

A comparison of the observed velocities with those calculated by equation (13) shows that this equation represents the initial course of the reaction with reasonable accuracy.

A comparison of the times for a certain percentage decrease in the hypochlorous acid concentration obtained from the observed data and from the integration of equations (7) and (14) showed satisfactory agreement. The generalisation of the initial velocity equations (6) and (13) to equations (7) and (14) was, therefore, justified.

## DISCUSSION

In the general velocity equation, the term $k_2^{\mathrm{I}}[\mathrm{HOCl}]([\mathrm{R{\cdot}CO_2H}] + [\mathrm{R{\cdot}CO_2^-}])$ represents, as in the case of crotonic acid, contributions from a number of simultaneous reactions concerned with the direct attack of hypochlorous acid on either undissociated tiglic acid or tiglate ion and with the possible rate-determining formation of α-methylcrotonyl hypochlorite.

The only other term found in this equation, $k_2^{\mathrm{II}}[\mathrm{HOCl}]^2$, probably represents the rate of formation of chlorine monoxide from hypochlorous acid.

No term involving the product $[\mathrm{HOCl}]^2[\mathrm{R{\cdot}CO_2H}]$ was found for the tiglic acid reaction. In the case of crotonic acid (*locc. cit.*) this term had been explained as the acid-catalysed formation of chlorine monoxide from hypochlorous acid. It is strange that such a term does not occur for tiglic acid whose strength is approximately the same as that of crotonic acid. Other reactions could take place to account for this term, but they must be capable of explaining its occurrence with allyl alcohol (Israel, *J.*, 1950, 1286) and crotonic acid and its non-inclusion in the velocity equations for the more reactive tiglic and ββ-dimethylacrylic acid. That is, the rate-determining step of any set of composite reactions evolved to explain this finding must be influenced by the reactivity of the olefin.

Consider the following reactions :

$$2\mathrm{HOCl} \rightleftharpoons \mathrm{Cl_2O + H_2O} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

$$\mathrm{R{\cdot}CO_2H + Cl_2O} \longrightarrow \mathrm{R{\cdot}CO{\cdot}OCl + HOCl} \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

$$\mathrm{R{\cdot}CO{\cdot}OCl + R{\cdot}CO_2H} \longrightarrow \mathrm{(R'{\cdot}CO_2H)^+ + R{\cdot}CO_2^-} \quad . \quad . \quad . \quad \text{(iii)}$$

where $\mathrm{R'} = \mathrm{CH_3{\cdot}CHCl{\cdot}CMe{\cdot}}$ or $\mathrm{CH_3{\cdot}CH{\cdot}CMeCl{\cdot}}$. These equations provide a probable solution to the problem provided the formation of acyl hypochlorites by step (ii) is slower in the case of acetic and crotonic acids than the formation of chlorine monoxide by step (i), and faster than this forward reaction in the case of tiglic and ββ-dimethylacrylic acids. In this latter case, the chlorine monoxide is used up as fast as it is formed and step (i) becomes rate-determining. However, our knowledge of the relative rates of the reactions above is limited by the small amount of information available about these acyl hypochlorites.

If we assume absence of change in the non-exponential coefficient of the Arrhenius equation in the temperature interval from 25° to 35°, the activation energies for the separate processes involving $k_2^{\mathrm{I}}$ and $k_2^{\mathrm{II}}$ calculated from the ratios of the rate constants at the two temperatures are 9·89 and 7·33 kcal. mole$^{-1}$ respectively. The corresponding values for crotonic acid were 8·38 and 9·87 respectively. The probability factor, *P*, was calculated for both tiglic and crotonic acid to see whether the increased value for the rate constant $k_2^{\mathrm{I}}$ was due to an increase in the activation energy, to a change in the probability factor, or to both. The value of *P* for tiglic acid was about 68 times that for crotonic acid and thus the higher value of $k_2^{\mathrm{I}}$ for tiglic acid can be attributed to changes in both the activation energy and *P*. This is not surprising as the presence of a methyl group near the point of attack would cause disturbances of both an electrical and a geometrical character. The presence of the α-methyl substituent in tiglic acid increased the rate of attack by hypochlorous acid almost five-fold.

Where the variation in $P$ is of prime importance, a change in the mechanism of a reaction is suspected. The variable nature of $k_2^{II}$, which should be independent of the olefin, with the olefin persisted, and this may be due to a change in mechanism where the absence of the term $k_3^{II}[HOCl]^2[R\cdot CO_2H]$ for the tiglic acid equation results in an increased contribution from the term $k_2^{II}[HOCl]^2$ with a subsequent effect on $k_2^{II}$.

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UNIVERSITY OF TASMANIA, HOBART, TASMANIA.
[Present address: DIVISION OF APPLIED CHEMISTRY,
N.R.C., OTTAWA, CANADA.]

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