# **294.** *The Kinetics of the Decomposition of the Dichlorosuccinic Acids.*

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Holmberg (*J. pr. Chem.*, 1892, **46**, 394) studied the decomposition of the dichlorosuccinic acids (*a*) in alkaline and (*b*) in aqueous solution, at one temperature, 25°, and concluded that the reaction is bimolecular in the former case, and unimolecular in the latter, the changes being represented thus:

$$(a)\ \mathrm{CO_2H{\cdot}CHCl{\cdot}CHCl{\cdot}CO_2H + OH' \rightleftharpoons CO_2H{\cdot}CH{:}CCl{\cdot}CO_2H + H_2O + Cl'}$$

$$(b)\ \mathrm{CO_2H{\cdot}CHCl{\cdot}CHCl{\cdot}CO_2H \longrightarrow CO_2H{\cdot}CH{:}CCl{\cdot}CO_2H + HCl}$$

The unimolecular decomposition of the analogous dibromosuccinic acids has been exhaustively studied by van 't Hoff ("Studies in Chemical Dynamics," London, 1896), but no attempt has been made to determine the Arrhenius curve for the corresponding dichlorosuccinic acids.

(*a*) We therefore followed the bimolecular reaction between potassium hydroxide and the dichlorosuccinic acids at 25° by the method of Holmberg. Typical results are given in Table I, the velocity constants being calculated from the equation $kt = x/a(a - x)$, where $a$ is half the initial titre of the freshly made acid solution at room temperature, and $x$ the difference between the titre at time $t$ and the initial titre.

Table I.

*Decomposition in alkaline media at 25°.*

0·1527*N*-Dichlorosuccinic acid; $a$ = 17·40.

| $a - x$. | $t$ (hours). | $k \times 10^4$. |
|---|---|---|
| 12·51 | 2 | 112 |
| 9·70 | 4 | 115 |
| 8·60 | 5 | 117 |
| 7·85 | 6·25 | 112 |
| 7·18 | 7 | 117 |
| 2·84 | 26 | 114 |
| 2·56 | 30·5 | 112 |
|  | Mean | 114 |

0·08578*N*-*iso*Dichlorosuccinic acid; $a$ = 8·65.

| $a - x$. | $t$ (hours). | $k \times 10^4$. |
|---|---|---|
| 6·62 | 0·66 | 538 |
| 6·00 | 1 | 511 |
| 5·05 | 2·25 | 366 |
| 4·41 | 3 | 371 |
| 4·22 | 4·0 | 304 |
| 4·13 | 4·33 | 292 |

The velocity coefficients for the bimolecular decomposition of the dichloro-acid remain quite steady, but those for the *iso*-form show a considerable decrease. This anomalous behaviour could be accounted for by the fact that the *iso*-form changes slowly into the ordinary form during the course of the reaction.

The final product of the reaction between alkali and these acids was extracted with ether (after acidification) and found to be chlorofumaric acid, m. p. 191°, in each case.

(*b*) The temperature coefficients of the decomposition of the dichloro-acids in aqueous solution were studied by the original method of van 't Hoff. Velocity constants were calculated by means of the equation $kt = \log \frac{3}{2}T_0/(\frac{3}{2}T_0 - T_t) - \log \frac{3}{2}T_0/(\frac{3}{2}T_0 - T_x)$, where $T_0$ is the initial titre at room temperature, $T_x$ that in the unknown time $x$ which has elapsed since the commencement of the run, and $T_t$ the titre at any time $t$. The end products were again isolated and shown to be chlorofumaric acid in each case.

Prolonged boiling of chloromaleic acid with hydrochloric acid of the concentration *which might be produced during the reaction* failed to convert it into chlorofumaric acid. This definitely establishes the interesting point that chlorofumaric acid must be formed as such in the decomposition of these acids, and is not formed *via* the intermediate chloromaleic acid.

Some of the results of the unimolecular investigation are tabulated in Table II. The falling off of the velocity constants is again manifested in the case of the *iso*-acid, but it is of such small magnitude in aqueous solution (except at higher temperatures; contrast runs 3 and 4) that no serious error is made by assuming a mean of the calculated values of the velocity constants as a true value for $k$.

TABLE II.

*Decomposition in aqueous solution.*

1. 0·00923*N*-Dichlorosuccinic acid; $\tfrac{3}{2}T_0 = 22{\cdot}95$; temp. = 80°.

| $T_t$. | $F(T)$.* | $t$ (hours). | $k \times 10^4$. |
|---|---|---|---|
| 15·50 | 0·4876 | 0 | — |
| 16·15 | 0·5283 | 1 | 407 |
| 16·74 | 0·5677 | 2 | 400 |
| 17·28 | 0·6072 | 3 | 399 |
| 17·78 | 0·6473 | 4 | 399 |
| | | Mean | 400 |

2. 0·03492*N*-Dichlorosuccinic acid; $\tfrac{3}{2}T_0 = 20{\cdot}07$; temp. = 70°.

| $T_t$. | $F(T)$.* | $t$ (hours). | $k \times 10^4$. |
|---|---|---|---|
| 13·45 | 0·4816 | 0 | — |
| 13·72 | 0·4997 | 1 | 183 |
| 13·98 | 0·5179 | 2 | 181 |
| 14·25 | 0·5376 | 3 | 184 |
| | | Mean | 182 |

3. 0·0273*N*-*iso*Dichlorosuccinic acid; $\tfrac{3}{2}T_0 = 29{\cdot}32$; temp. = 70°.

| | | | |
|---|---|---|---|
| 20·02 | 0·4987 | 0 | — |
| 20·70 | 0·5316 | 1 | 329 |
| 21·32 | 0·5640 | 2 | 327 |
| 21·90 | 0·5965 | 3 | 326 |
| 22·45 | 0·6298 | 4 | 326 |
| | | Mean | 327 |

4. 0·0273*N*-*iso*Dichlorosuccinic acid; $\tfrac{3}{2}T_0 = 29{\cdot}06$; temp. = 90°.

| | | | |
|---|---|---|---|
| 20·38 | 0·5246 | 0 | — |
| 24·18 | 0·7747 | 1 | 2500 |
| 26·00 | 0·9774 | 2 | 2260 |
| 27·22 | 1·1983 | 3 | 2250 |
| 27·60 | 1·2987 | 4 | 1940 |

* $F(T) = \log \tfrac{3}{2}T_0 - \log (\tfrac{3}{2}T_0 - T_t)$.

In accordance with the equation of Arrhenius, the plot of log $k$ against the reciprocal of the absolute temperature gave a linear relationship for both these acids. The experimental results are tabulated below.

*Dichlorosuccinic acid.*

| Temp. | 25° | 70° | 80° | 83° | 87° | 89° |
|---|---|---|---|---|---|---|
| $10^4k$(hr.$^{-1}$) | 0·9* | 182 | 400 | 530 | 800 | 900 |

iso*Dichlorosuccinic acid.*

| Temp. | 25° | 60° | 70° | 80° | 90° |
|---|---|---|---|---|---|
| $10^4k$ (hr.$^{-1}$) | 2·18* | 120 | 327 | 802 | 2230 |

* Holmberg (*loc. cit.*).

It will be observed that, at any given temperature, the velocity of the decomposition of the *iso*-form proceeds at almost twice the rate of the ordinary form. The values for the critical increments ($E$) and the $\log_e B$ terms of the Arrhenius equation are given in the following table, data for the corresponding dibromo-acids being included for comparison.

| Acid. | $E$. | $\log_e B$. | $E/\log_e B$. |
|---|---|---|---|
| Dibromo- | 22,800 | 22·74 | 1002 |
| *iso*Dibromo- | 22,700 | 24·73 | 918 |
| Dichloro- | 23,200 | 22·60 | 1027 |
| *iso*Dichloro- | 23,000 | 23·42 | 982 |

Data for the dibromosuccinic acids were obtained from the work of van 't Hoff, but he gives only one value for the velocity constant of the *iso*dibromosuccinic acid decomposition, *viz.*, $10^7k$ (50°) = 311. Holmberg (*loc. cit.*) furnishes another value, $10^7k$ (25°) = 15·8, and from these two values the above results for this acid have been computed.

The extraordinarily high value for $E/\log_e B$ bears out the conclusions previously reached by Lewis and Hudleston (J., 1932, 1399) regarding the fortuity of Syrkin's (*Z. anorg. Chem.*, 1931, **199**, 28) and Holzschmidt's (*ibid.*, **200**, 82) equations. The faster rate of decomposition of the *iso*-forms is obviously dependent on the higher values of $\log_e B$, but no precise definition has yet been given to this term, Eyring and Daniels (*J. Amer. Chem. Soc.*, 1930, **52**, 1472) regarding it as representing the frequency of oscillation of a valency bond in the disrupting molecule.

According to Brönsted's equation as applied to unimolecular changes, the velocity of reaction is given by the equation $-dx/dt = kf_AC_A/f_{A^*}$, where $f_{A^*}$ is the activity coefficient of the activated form, and $f_A$ that of the normal form. Since $f_A = f_{A^*}$, the addition of neutral salts should not influence the rate of such decompositions. That this is true for the dichlorosuccinic acids is shown by the following results.

| Temp. | Acid. | $k$. | $Na_2SO_4$ (mols./litre). | Temp. | Acid. | $k$. | $Na_2SO_4$ (mols./litre). |
|---|---|---|---|---|---|---|---|
| 90° | *iso*Dichloro- | 0·223 | 0·000 | 80° | Dichloro- | 0·0400 | 0·000 |
| 90 | *iso*Dichloro- | 0·220 | 0·200 | 80 | Dichloro- | 0·0395 | 0·100 |

## EXPERIMENTAL.

Fumaric acid (m. p. 283—285°) was readily obtained from pure maleic acid by boiling it with hydrochloric acid and recrystallising from hot water. Dichloro- and *iso*dichloro-succinic acids were prepared by the method of Terry and Eichelberger (*J. Amer. Chem. Soc.*, 1925, **47**, 1067), *viz.*, by the weight chlorination of sodium maleate and sodium fumarate respectively, in the dark at 5°. After chlorination, the flask was sealed and kept for a few days, the excess chlorine being then removed by a current of air. The solution was repeatedly extracted with ether, the extract dried (sodium sulphate), and the ether evaporated in a vacuum desiccator. Dichlorosuccinic acid (Found : Cl, 36·9; equiv., 92·7. Calc. : Cl, 37·9%; equiv., 93·5) had m. p. 213°; yield 74·5%. The *iso*-acid (Found : Cl, 37·3%; equiv., 93·5) had m. p. 173°; yield 75%. Terry and Eichelberger found a maximum yield of about 65% in both cases.

In the kinetic measurements, the amount of the dichlorosuccinic acid decomposed at any instant was determined by direct titration with standard alkali, phenolphthalein being used as indicator. The cold solution of the *iso*-acid was titrated immediately after being made up, in order to determine $T_0$, because this acid shows measurable decomposition even at room temperature; $T_0 \neq T_t$ at time 0·0 hour.

## SUMMARY.

The energies of activation for the decomposition of the dichlorosuccinic acids have been determined, and compared with those for the corresponding dibromo-acids. Syrkin's and Holzschmidt's equations are criticised.

Added electrolyte exerted a negligible influence on the reaction velocity.

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