# Stability Constants and Rate Coefficients for Decarboxylation of Oxalacetic Acid and some Metal Oxalacetates

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Data collected at constant ionic strengths, from e.m.f. measurements of a glass electrode–calomel electrode cell, u.v. spectrophotometry, and a pressure-sensitive transducer, DVM, micro-computer system, have been used to calculate the stability constants of oxalacetic acid and some metal oxalacetates ML (L = oxalacetate, M = $Cu^{II}$, $Ni^{II}$, $Zn^{II}$, $Co^{II}$, or $Mn^{II}$) and the rate coefficients for decarboxylation of the species $H_2L$, HL, L, and ML. The stability constants of the ML species fit the Irving–Williams order ($Zn < Cu > Ni > Co > Mn$) but the order of the rate coefficients is $Zn < Cu > Ni \approx Co > Mn$, and while the stability constant order is $Ni > Zn$ the rate coefficient order is $Ni \approx Zn$.

Among the numerous studies[1–7] of metal-catalysed rates of decarboxylation of oxalacetate, that of Gelles and Salama[3,4] for the series $Cu^{II}$ to $Zn^{II}$ seems to be the most systematic search made so far to see if there is a relationship between the catalytic effects and the stability constants. They calculated the stability constants from pH measurements of a glass electrode|solution|calomel electrode cell and the rates of decarboxylation from timed manometric measurements of a sealed gas-evolution apparatus. Attempts were made to get a quantitative estimate of the relationship but several factors limited the precision to which this could be done. Rather long extrapolations of the pH measurements to zero time were needed to correct for drifts due to decarboxylation. The kinetic calculations were based on manually timed readings of a mercury manometer and the stability constants were calculated from data at low varying ionic strengths ($I$) (*ca.* 0.01 to *ca.* 0.03 mol $dm^{-3}$) and 25 °C whereas the kinetic work was done at $I = 0.1$ mol $dm^{-3}$ and 36.9 °C. A general form of activity coefficient expression was used to calculate the data at a common value of $I$ but such adjustments are considerable and approximate.

The present attempt to get more precise information relies on current experimental methods, namely digital voltmeter readings at short time intervals, u.v. kinetics spectrophotometry, and timed computer-controlled readings of a pressure-sensitive transducer. The media were set at constant and common ionic strengths by incorporation of $NaClO_4$.

The basic equations involved are (1)—(4) where $\beta_{MHL}$ re-

$$\beta_{011} = [HL]/[H][L] \quad (1)$$

$$\beta_{021} = [H_2L]/[H]^2[L] \quad (2)$$

$$\beta_{101} = [ML]/[M][L] \quad (3)$$

$$k_{obs.}c_1 = k_0[H_2L] + k_1[HL] + k_2[L] + k_{ML}[ML] \quad (4)$$

presents the stability constant, M the metal(II) ion, $c_1$ is the total oxalacetate concentration, $H_2L$, HL, L, and ML are oxalacetate species, H is the $H^+$ ion, $k_{obs.}$ the experimental rate coefficient while $k_0$, $k_1$, $k_2$, and $k_{ML}$ are those of the various species subject to decarboxylation. The evidence examined here and that of others[6,7] suggests that the rate contributions and concentrations of species such as MHL, $ML_2$, and $M_2L$ are small or negligible.

**Table 1.** Data for determinations of $\beta_{011}$ and $\beta_{021}$ values for oxalacetic acid at $I = 0.5$ mol $dm^{-3}$

| Temp./°C | $10^2c_1$ | $10^3c_2$ | $10^4c_3$ | $10^4[H]$ | $\bar{n}_{H}$ |
|---|---|---|---|---|---|
| 25 | 1.468 | 0 | 5.107 | 73.27 | 1.536 |
| | 1.448 | 6.58 | 5.040 | 36.30 | 1.330 |
| | 1.402 | 22.29 | 4.879 | 1.369 | 0.435 |
| | 1.764 | 0 | 5.107 | 81.70 | 1.566 |
| | 1.730 | 9.80 | 5.007 | 30.68 | 1.285 |
| | 1.697 | 19.23 | 4.910 | 6.247 | 0.859 |
| | 1.665 | 28.30 | 4.818 | 0.829 | 0.324 |
| | 1.597 | 0 | 5.107 | 76.30 | 1.554 |
| | 1.566 | 9.80 | 5.007 | 25.79 | 1.241 |
| | 1.535 | 19.23 | 4.910 | 4.179 | 0.753 |
| | 1.516 | 25.32 | 0.952 | 4.848 | 0.356 |
| 30 | 0.759 | 9.80 | 7.300 | 34.77 | 1.287 |
| | 1.726 | 19.23 | 7.160 | 7.566 | 0.884 |
| | 2.037 | 16.13 | 7.210 | 20.65 | 1.142 |
| | 2.011 | 22.29 | 7.120 | 7.721 | 0.888 |
| | 1.986 | 16.13 | 7.210 | 19.41 | 1.126 |
| | 1.961 | 22.29 | 7.120 | 7.014 | 0.864 |
| | 2.067 | 0 | 14.90 | 102.30 | 1.577 |
| | 2.026 | 9.80 | 14.61 | 46.53 | 1.359 |
| | 1.987 | 19.23 | 14.33 | 13.85 | 1.035 |
| | 1.950 | 28.30 | 14.06 | 2.779 | 0.607 |
| | 1.914 | 37.04 | 13.80 | 0.255 | 0.136 |
| | 1.630 | 6.58 | 7.35 | 47.47 | 1.350 |
| | 1.609 | 12.99 | 7.26 | 19.56 | 1.116 |
| | 1.588 | 19.23 | 7.16 | 5.656 | 0.799 |
| | 1.568 | 25.32 | 7.02 | 1.411 | 0.421 |
| | 2.294 | 0 | 14.90 | 107.20 | 1.598 |
| | 2.263 | 6.58 | 14.70 | 68.92 | 1.470 |
| | 2.124 | 37.04 | 13.80 | 0.976 | 0.317 |
| 37 | 2.007 | 0 | 5.083 | 93.53 | 1.559 |
| | 1.882 | 31.11 | 4.766 | 1.183 | 0.367 |
| | 1.857 | 0 | 5.082 | 87.90 | 1.554 |
| | 1.742 | 31.11 | 4.766 | 0.617 | 0.238 |
| | 1.295 | 0 | 5.082 | 70.04 | 1.498 |
| | 1.253 | 16.05 | 4.919 | 4.178 | 0.725 |
| | 1.962 | 0 | 5.068 | 89.56 | 1.569 |
| | 1.840 | 31.03 | 4.754 | 0.943 | 0.334 |
| | 1.655 | 0 | 5.080 | 83.88 | 1.524 |
| | 1.666 | 0 | 5.080 | 84.54 | 1.523 |
| | 1.582 | 25.19 | 4.824 | 1.351 | 0.430 |
| | 1.494 | 0 | 5.080 | 79.59 | 1.500 |
| | 1.474 | 6.55 | 5.013 | 41.11 | 1.311 |
| | 1.428 | 22.18 | 4.854 | 1.632 | 0.469 |

**Table 2.** Stability constant determinations for metal oxalacetates from e.m.f. values

| | mol dm$^{-3}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| M$^{II}$ | $10^3c_1$ | $10^3c_2$ | $10^4c_3$ | $10^3c_4$ | $10^4$[H] | $\bar{n}$ | $\beta_{101}$ |
| Cu | 16.08[a] | 0 | 9.88 | 4.60 | 137.1 | 0.3493 | 6 660 |
| | 13.68[a] | 0 | 5.67 | 8.91 | 102.0 | 0.2441 | 6 660 |
| | 17.04[a] | 0 | 8.38 | 10.06 | 120.0 | 0.3119 | 6 200 |
| | 23.76[b] | 0 | 13.97 | 9.28 | 156.6 | 0.3512 | 5 570 |
| | 9.62[c] | 0 | 8.38 | 10.06 | 101.55 | 0.3451 | 16 900 |
| | 8.43[c] | 0 | 14.90 | 8.43 | 82.78 | 0.4194 | 16 000 |
| | 14.27[d] | 0 | 27.94 | 10.06 | 132.2 | 0.3253 | 9 550 |
| Zn | 16.33[a] | 20.00 | 6.23 | 3.07 | 5.43 | 0.2825 | 101 |
| | 18.54[a] | 12.82 | 4.91 | 2.91 | 24.78 | 0.0894 | 106 |
| | 16 73[a] | 18.63 | 5.55 | 3.23 | 7.37 | 0.2148 | 96 |
| | 19.49[b] | 21.60 | 6.99 | 3.08 | 8.63 | 0.2308 | 94 |
| | 12.44[c] | 15.82 | 2.83 | 1.98 | 7.20 | 0.3032 | 252 |
| | 22.26[c] | 24.54 | 2.74 | 3.06 | 10.18 | 0.3436 | 238 |
| | 16.05[d] | 18.63 | 5.55 | 3.23 | 6.99 | 0.3216 | 169 |
| | 18.09[d] | 21.88 | 5.69 | 1.95 | 5.49 | 0.3997 | 167 |
| Ni | 18.55[a] | 20.00 | 6.23 | 3.54 | 9.17 | 0.2991 | 157 |
| | 11.43[a] | 13.51 | 6.31 | 3.59 | 6.77 | 0.2485 | 156 |
| | 16.50[a] | 18.87 | 5.62 | 4.95 | 7.94 | 0.2894 | 156 |
| | 17.04[b] | 18.99 | 7.07 | 3.32 | 8.98 | 0.2852 | 149 |
| | 24.59[c] | 30.86 | 2.75 | 3.24 | 6.01 | 0.5788 | 352 |
| | 19.99[c] | 21.88 | 2.84 | 4.92 | 12.77 | 0.3533 | 367 |
| Co | 16.82[a] | 15.92 | 4.88 | 2.92 | 12.12 | 0.1134 | 67.2 |
| | 21.46[a] | 25.00 | 4.79 | 2.86 | 6.14 | 0.2341 | 65.0 |
| | 16.39[a] | 18.63 | 5.55 | 8.23 | 7.81 | 0.1472 | 65.3 |
| | 14.27[b] | 15.82 | 7.07 | 5.03 | 8.89 | 0.1388 | 70.7 |
| | 15.48[c] | 21.55 | 2.73 | 8.16 | 5.56 | 0.2893 | 168 |
| | 23.61[c] | 30.68 | 2.74 | 4.88 | 5.25 | 0.4142 | 169 |
| Mn | 16.55[a] | 19.74 | 6.15 | 8.78 | 5.70 | 0.0563 | 16.2 |
| | 17.67[a] | 21.43 | 5.34 | 12.14 | 5.44 | 0.0636 | 16.9 |
| | 15.89[a] | 15.15 | 4.64 | 13.99 | 11.90 | 0.0275 | 15.8 |
| | 18.44[b] | 20.96 | 6.69 | 6.16 | 7.32 | 0.0474 | 13.7 |
| | 21.44[c] | 23.81 | 2.66 | 6.13 | 9.13 | 0.0950 | 43.5 |
| | 23.70[c] | 29.41 | 2.63 | 6.05 | 5.52 | 0.1543 | 43.2 |

[a] $I$ = 0.5 mol dm$^{-3}$, 25 °C. [b] $I$ = 0.5 mol dm$^{-3}$, 30 °C. [c] $I$ = 0.1 mol dm$^{-3}$, 25 °C. [d] $I$ = 0.2 mol dm$^{-3}$, 25 °C.

## Results and Discussion

The values of $\beta_{011}$ and $\beta_{021}$ were calculated from the e.m.f.s $E$ of the cell glass electrode | oxalacetic acid($c_1$), NaOH($c_2$), HCl($c_3$), NaClO$_4$ to constant $I$ | calomel electrode (*ca.* 0.5 mol dm$^{-3}$ NaCl) (A) by use of equations (5) and (6) and linear least-mean-squares analysis with equations (7) and (8). Values of $E$ at time

$$E = E^\circ(\text{cell}) - (RT\ln 10/F)\log[\text{H}] \quad (5)$$

$$\bar{n}_\text{H} = (2c_1 - c_2 + c_3 - [\text{H}])/c_1 \quad (6)$$

$$Y = \bar{n}_\text{H}/[\text{H}](1 - \bar{n}_\text{H}) \quad (7)$$

$$X = [\text{H}](2 - \bar{n}_\text{H})/(1 - \bar{n}_\text{H}) \quad (8)$$

$t$ = 0 were obtained by extrapolation of e.m.f.s taken at 0.5- or 1-min intervals for about 5 min; $E^\circ$(cell) was calculated from the value of $E$ when the cell contained only HCl and NaClO$_4$. The data are shown in Table 1 and the resultant β values in Table 5.

Values of $\beta_{101}$ for a series of metal oxalacetates were calculated from the e.m.f.s of cell (A) after the incorporation of M(ClO$_4$)$_2$ ($c_4$). An estimate of $E^\circ$(cell) was obtained as just described, and equation (5) then used to get an estimate of [H] after the additions $c_1$ and $c_2$. Then from the known values of $\beta_{011}$ and $\beta_{021}$ and equations (9)—(12) a precise value of $E^\circ$(cell)

$$[\text{L}] = (2c_1 + c_3 - c_2 - [\text{H}])/(2\beta_{021}[\text{H}]^2 + \beta_{011}[\text{H}]) \quad (9)$$

$$[\text{HL}] = \beta_{011}[\text{H}][\text{L}] \quad (10)$$

$$[\text{H}_2\text{L}] = (2c_1 + c_3 - c_2 - [\text{HL}] - [\text{H}])/2 \quad (11)$$

$$[\text{LB}] = c_1 - [\text{HL}] - [\text{H}_2\text{L}] \quad (12)$$

was obtained by adjusting it until | [L] − [LB] | was $< 10^{-7}$ mol dm$^{-3}$.

From the value of $E$ at $t$ = 0 after adding M(ClO$_4$)$_2$ solution, equations (5), (9), and (10) gave [H], [L], and [HL], whence values of $\beta_{101}$ were calculated from equations (13)—(15). The

$$[\text{H}_2\text{L}] = \beta_{021}[\text{H}]^2[\text{L}] \quad (13)$$

$$\bar{n} = (c_1 - [\text{HL}] - [\text{H}_2\text{L}] - [\text{L}])/c_4 \quad (14)$$

$$\beta_{101} = \bar{n}/[\text{L}](1 - \bar{n}) \quad (15)$$

answers are shown in Table 2 and summarised in Table 5.

**Table 3.** Rate coefficients of decarboxylation of oxalacetic acid by spectrophotometry at $I = 0.5$ mol dm$^{-3}$ and 37 °C[a]

| mol dm$^{-3}$ | | | | | |
|---|---|---|---|---|---|
| $10^3c_1$ | $10^3c_2$ | $10^4k_{obs.}$/ s$^{-1}$ | $10^2\alpha_0$ | $10^2\alpha_1$ | $10^2\alpha_2$ |
| 3.036 | 4.240 | 1.293 | 45.0 | 53.2 | 1.78 |
| 3.036 | 5.660 | 1.217 | 49.9 | 48.8 | 1.35 |
| 3.848 | 22.26 | 0.608 | 76.5 | 23.3 | 0.21 |
| 3.848 | 44.52 | 0.386 | 86.4 | 13.5 | 0.06 |
| 3.457 | 6.678 | 1.087 | 53.5 | 45.4 | 1.09 |
| 3.457 | 10.02 | 0.927 | 61.3 | 38.0 | 0.67 |
| 3.457 | 13.36 | 0.813 | 67.0 | 32.6 | 0.44 |
| 3.457 | 16.70 | 0.708 | 71.3 | 28.4 | 0.32 |
| 3.560 | 111.3 | 0.224 | 94.1 | 5.9 | 0.01 |
| 3.560 | 167.0 | 0.170 | 96.0 | 4.0 | — |
| 3.560 | 222.6 | 0.147 | 96.9 | 3.1 | — |
| 3.457[b] | 37.0 | 0.955 | 0.02 | 0.21 | 99.77[c] |
| 3.457[b] | 29.6 | 0.908 | 0.02 | 0.18 | 99.81[c] |
| 3.457[b] | 22.2 | 0.865 | — | 0.14 | 99.85[c] |

[a] Average standard deviation in $k_{obs.} = 0.3\%$. [b] Acetic acid +0.100 mol dm$^{-3}$ Na($O_2$CMe), $K_A = 3.067 \times 10^5$ mol dm$^{-3}$ (H. S. Harned and F. C. Hickey, *J. Am. Chem. Soc.*, 1937, **59**, 1284).

**Table 4.** Rate coefficients of decarboxylation of metal oxalacetates by spectrophotometry and by a transducer * at $I = 0.5$ mol dm$^{-3}$ and 37 °C

| | mol dm$^{-3}$ | | | | |
|---|---|---|---|---|---|
| $M^{II}$ | $10^3c_1$ | $10^3c_3$ | $10^3c_4$ | $10^5\ k_{obs.}$/ s$^{-1}$ | $10^4\ k_{ML}$/ s$^{-1}$ |
| Cu | 3.88 | 8.94 | 0.171 | 47.48 | 615 |
| | 3.88 | 8.94 | 0.256 | 69.16 | 647 |
| | 3.88 | 8.94 | 0.342 | 87.16 | 633 |
| | 3.85 | 11.31 | 0.356 | 70.38 | 632 |
| | 3.85 | 11.31 | 0.534 | 102.5 | 645 |
| | 3.85 | 11.31 | 0.712 | 131.6 | 638 |
| | 3.85 | 11.31 | 0.891 | 158.3 | 625 |
| Zn | 3.65 | 11.31 | 4.16 | 17.35 | 342 |
| | 3.65 | 11.31 | 8.32 | 25.73 | 352 |
| | 3.65 | 11.31 | 12.48 | 34.83 | 365 |
| | 3.65 | 11.31 | 16.64 | 42.98 | 363 |
| | 3.97 | 11.31 | 1.664 | 12.50 | 345 |
| | 3.97 | 11.31 | 2.494 | 14.20 | 352 |
| | 3.97 | 11.31 | 3.120 | 15.43 | 353 |
| | 18.28 * | 8.94 | 2.080 | 11.25 | 317 |
| Ni | 3.40 | 8.94 | 1.570 | 16.47 | 318 |
| | 3.40 | 8.94 | 3.150 | 22.92 | 333 |
| | 3.40 | 8.94 | 4.720 | 29.20 | 335 |
| | 3.40 | 8.94 | 5.250 | 31.37 | 337 |
| | 13.65 | 4.47 | 2.100 | 18.67 | 323 |
| | 13.65 | 4.47 | 3.150 | 23.15 | 337 |
| | 13.65 | 4.47 | 4.200 | 26.93 | 330 |
| | 23.35 * | 4.47 | 10.500 | 36.92 | 333 |
| Co | 3.96 | 11.31 | 22.90 | 11.83 | 363 |
| | 3.96 | 11.31 | 34.40 | 13.20 | 352 |
| | 3.96 | 11.31 | 45.80 | 14.63 | 350 |
| | 3.53 | 8.94 | 26.50 | 14.73 | 318 |
| | 3.53 | 8.94 | 53.00 | 19.20 | 327 |
| | 3.53 | 8.94 | 106.0 | 28.75 | 345 |
| | 23.73 * | 4.47 | 15.90 | 26.53 | 330 |
| Mn | 3.56 | 0 | 20.59 | 15.38 | 193 |
| | 3.56 | 0 | 30.88 | 17.62 | 188 |
| | 3.56 | 0 | 41.18 | 20.27 | 193 |
| | 19.88 * | 4.47 | 20.58 | 13.30 | 182 |

Rates of decarboxylation of oxalacetic acid were obtained from timed u.v. absorptions at *ca.* 280 nm of the solutions oxalacetic acid($c_1$), NaOH($c_2$), HCl($c_3$), $NaClO_4$ to $I = 0.5$ mol dm$^{-3}$ (**B**) and oxalacetic acid($c_1$), acetic acid($c_5$), Na($O_2$CMe)($c_6$), $NaClO_4$ to $I = 0.5$ mol dm$^{-3}$ (**C**). Calculation of the rates was based on the matrix inversion method of Moore.[8] This involves starting with estimated absorptions $A$ at $t = 0$ and $t = \infty$. The program adjusted these and the value of $k_{obs.}$ until $A$ at $t = 0$ was constant (to 0.001). The results are shown in Table 3 and summarised in Table 5.

One obtains equation (16) where $\alpha_0 = [H_2L]/c_1$, $\alpha_1 =$

$$k_{obs.} = k_0\alpha_0 + k_1\alpha_1 + k_2\alpha_2 \qquad (16)$$

$[HL]/c_1$, and $\alpha_2 = 1 - \alpha_0 - \alpha_1$. For solutions (**B**), a first estimate of $[H] \approx c_3 + c_1/4$ was used with equation (9) to get [L], with equation (11) to get $[H_2L]$, and equation (10) to get [HL]. The latter was compared with equation (17) whence with

$$[HL] = c_1 - [L] - [H_2L] \qquad (17)$$

equation (18) the cycle starting at equation (9) was continued

$$[H] = 2c_1 + c_3 - c_2 - [HL] - 2[H_2L] \qquad (18)$$

until the two calculations of [HL] agreed to $<10^{-7}$ mol dm$^{-3}$ so that the α values could be calculated.

Solutions (**C**) were used to get an assessment of $k_2$. Starting estimates were $\alpha_0 = 0$, $[MeCO_2H] = c_5$, $[NaX] = 0$, and $[O_2CMe] = c_6$, then from equation (12) of ref. 2 and equation (19) one obtains equation (19).

$$\alpha_1 = 1 - \alpha_0 - \alpha_2 \qquad (19)$$

From ref. 2, equation (20) can be written, so one gets [HL] =

$$\alpha_2 = ([O_2CMe]/[MeCO_2H])(1 - \alpha_0)/ (\beta_{011}/K_A + [O_2CMe]/[MeCO_2H]) \qquad (20)$$

$\alpha_1 c_1$,$[H] = \alpha_1/(\beta_{011}\alpha_2)$, $\alpha_0 = [H]\alpha_1\beta_{021}/\beta_{011}$, $[L] = c_1 - [HL] - [H_2L]$, $[MeCO_2H] = c_5 + 2c_1 - [HL] - [H] - 2[H_2L]$, $[O_2CMe] = c_5 + c_6 - [MeCO_2H]$ and $[NaX] = [O_2CMe]$, where $K_A$ is the concentration association constant of acetic acid. The cycle starting at equation (20) was continued until $|[O_2CMe] - [NaX]|$ was $<10^{-7}$ mol dm$^{-3}$. The resulting values of $\alpha_2$ (Table 3) were $>0.997$ and an extrapolation of $k_{obs.}$ *vs.* $\alpha_2$ gave $k_{obs.}$ at $\alpha_2 = 1.0$. This value of $k_2$ was used to analyse the data obtained with solutions (**B**) by applying linear least mean squares with[2] equations (21) and (22). The 'intercept'

$$X = \alpha_1 \qquad (21)$$

$$Y = k_{obs.} - (k_2 - k'_0) \qquad (22)$$

gives $k'_0$ and the 'slope' plus $k'_0$ gives $k_1$; $k'_0$ is a preliminary value of $k_0$. The process was continued with $k_0$ replacing $k'_0$ until $|k'_0 - k_0|$ was $<10^{-6}$ s$^{-1}$.

Rates of decarboxylation in the presence of metal(II) ions were also obtained from timed u.v. absorptions and from timed e.m.f. measurements $E$ of a pressure-sensitive transducer, DVM microcomputer system described in the Experimental section. The calculations were based on the previously mentioned method of Moore,[8] starting in the case of the transducer method with estimates of $E$ at $t = 0$ and $t = \alpha$, and setting the conditions in the program to adjust these until $E$ at $t = 0$ was constant to $<0.01$ mV. The transducer method was unsatisfactory on introducing the copper(II) ion. This is discussed later.

**Table 5.** Summary of stability constants and rate coefficients of oxalacetic acid and some metal oxalacetates

(*a*) Stability constants of oxalacetic acid

| Temp./°C | $I$/mol dm$^{-3}$ | $10^{-3}\beta_{021}$ | $10^{-5}\beta_{011}$ | Ref. |
|---|---|---|---|---|
| 25 | 0.5 | 5.40 + 0.9% | 8.63 + 1.3% | Present work |
| 25 | 0.5 | 5.25 | 8.63 | 1[a] |
| 25 | 0.2 | 5.65 + 0.6% | 10.11 + 0.8% | 1[b] |
| 25 | 0.2 | 6.00 | 10.72 | 1[a] |
| 25 | 0.1 | 7.30 | 11.78 | 1 |
| 30 | 0.5 | 4.96 + 1.9% | 6.90 + 1.1% | Present work |
| 37 | 0.5 | 5.00 + 1.1% | 7.09 + 3.2% | Present work |
| 37 | 0.5 | 4.97 | 6.95 | 1[a] |
| 37 | 0.2 | 5.66 | 8.14 | 1[a] |

(*b*) Stability constants $\beta_{101}$ of metal oxalacetates

| Temp./°C | $I$/mol dm$^{-3}$ | Cu$^{II}$ | Zn$^{II}$ | Ni$^{II}$ | Co$^{II}$ | Mn$^{II}$ | Ref. |
|---|---|---|---|---|---|---|---|
| 25 | 0.5 | 6 510 ± 2.5% | 101 ± 4% | 156 ± 1% | 65.8 ± 1.4% | 16.3 ± 2.5% | Present work |
| 25 | 0.5 | | 98 | | | 17.4 | Ref. 6 |
| 30 | 0.5 | 5 570 | 94 | 149 | 70.7 | 13.7 | Present work |
| 25 | 0.1 | 16 500 ± 3% | 245 ± 2.9% | 360 ± 2.2% | 168 ± 0.6% | 43.4 ± 0.5% | Present work |
| 25 | 0.1 | 8 730 ± 10% | 300 ± 19% | 662 ± 22% | 253 ± 24% | 91 ± 20% | Ref. 4, recalc. |
| 25 | 0.1 | | 219 | | | 38 | Ref. 7 |
| 25 | 0.2 | 9 550 | 168 ± 0.6% | | | | Present work |

(*c*) Rate coefficients at 37 °C for oxalacetic acid species (s$^{-1}$)

| $I$/mol dm$^{-3}$ | $10^6 k_0$ | $10^4 k_1$ | $10^5 k_2$ | Ref. |
|---|---|---|---|---|
| 0.5 | 6.67 + 5% | 2.35 + 1.5% | 6.7 | Present work |
| 0.2 | 5.87 | 2.52 | 6.9 | 2 |
| 0.1 | 5.68 | 2.51 | 6.9 | 2 |
| 0.5 | 6.1 | 2.54 | 6.9 | Ref. 2, extrap. |

(*d*) Rate coefficients for metal oxalacetates ($10^4 k_{ML}$/s$^{-1}$) at 37 °C

| $I$/mol dm$^{-3}$ | Cu$^{II}$ | Zn$^{II}$ | Ni$^{II}$ | Co$^{II}$ | Mn$^{II}$ | Ref. |
|---|---|---|---|---|---|---|
| 0.5 | 634 ± 1.3% | 349 ± 2.9% | 331 + 1.5% | 341 ± 3.8% | 189 + 2.1% | Present work |
| 0.2 | | 311 ± 2.6%[c] | | | | Ref. 2 |
| 0.1 | 660 | 310 | 230 | 240 | 65 | Ref. 4 |

[a] Calculated from equations (4) and (5) of ref. 1. [b] Recalculated by present method from data in Tables 4 and 7 of ref. 2. [c] Recalculated by present method using data in Table 5 of ref. 2 in which [HCl] = 0.05—0.005 mol dm$^{-3}$. For [HCl] = 0.1—0.18 mol dm$^{-3}$, $k_{ML}$ rises slightly. This may be due to MHL formation being significant but the evidence is too slight for a quantitative analysis.

To calculate values of $k_{ML}$ [equation (4)], equations (9) and (10) were used with a first estimate of [H] to get first estimates of [L] and [HL] and of [H$_2$L] from equation (13). One can also write equation (23) in which [ML] = 0 is used in the first cycle,

$$[HL] = c_1 - [L] - [H_2L] - [ML] \qquad (23)$$

and (24)—(26). The cycle starting at equation (9) was continued

$$[H] = 2c_1 + c_3 - c_2 - [HL] - 2[H_2L] \qquad (24)$$

$$[ML] = \beta_{101}[M][L] \qquad (25)$$

$$[M] = c_4 - [ML] \qquad (26)$$

until the two calculations of [HL] agreed to $< 10^{-7}$ mol dm$^{-3}$, whence from equation (4) one obtains equation (27). The results

$$k_{ML} = (k_{obs.}c_1 - k_0[H_2L] - k_1[HL] - k_2[L])/[ML] \qquad (27)$$

are shown in Table 4 and a summary is in Table 5.

Gelles and Salama[3] calculated $\beta_{101}$ values from pH measurements (to ± 0.001 pH) with a cell similar to (A). They used dilute solutions of varying ionic strengths (*ca.* 0.012 to *ca.* 0.029 mol dm$^{-3}$) and obtained $\beta_{101}$ values at $I = 0$ by a graphical method based on functions which included activity coefficients. Their plots were curved unless they allowed for M$_2$L formation.

The kinetics of the metal-ion catalysed decarboxylation were followed manometrically at $I = 0.1$ mol dm$^{-3}$ and the values of $k_{ML}\beta_{101}$ were derived by a plotting procedure involving functions which also incorporated $\beta_{111}$ values, namely from equation (28). A plot of the left-hand function against 1/[H]

$$(k_{obs.} - k_u)\beta_{011}/(\alpha_1 c_4) = k_{ML}\beta_{101}/[H] + k_{MHL}\beta_{111}\beta_{011} \qquad (28)$$

should be linear with a slope of $k_{ML}\beta_{101}$ and intercept of $k_{MHL}\beta_{111}\beta_{011}$. The evidence for $\beta_{111}$ is very slender since the intercept values were small or zero.

By calculating activity coefficients,[9] $\beta_{101}$ values at $I = 0.1$ mol dm$^{-3}$ were estimated to be those at $I = 0$ multiplied by 0.143 and approximate $k_{ML}$ values at $I = 0.1$ mol dm$^{-3}$ and 37 °C were also assessed. The corresponding data[3] have been recalculated by the present method and the outcome is shown in Table 5.

The orders of the stability constants $\beta_{101}$ and of the rate coefficients $k_{ML}$ of the ML species from the present work and from that of Gelles and Salama[4] are about the same but the present standard deviations in $\beta_{101}$ are much smaller. In closer detail, one would not expect marked ionic strength effects upon the $k_{ML}$ values and while this is found with $Cu^{II}$ and $Zn^{II}$, the present $k_{ML}$ values for the other metal oxalacetates are much higher than those of Gelles and Salama.[4] This may be due, to some extent, to the different methods of calculating $k_{ML}$. Their figures are based on one kinetic method (rate of gas evolution) whereas both this technique and spectrophotometry were used in the present studies and the answers are in good accord with one exception. It was mentioned earlier that satisfactory answers could not be obtained with the transducer method in the presence of $Cu^{II}$. The calculated value of $k_{obs.}$ varied with the proportion of reaction analysed, *i.e.* first-order kinetics were not followed. Gelles and Salama[4] did not report any kinetic work with $Cu^{II}$ and based their calculations upon the kinetic studies of Pedersen.[2] In this particular case the expression relating $k_{obs.}$ with the pressure readings had to be modified for the copper(II)–oxalacetate system. One possible explanation is that this is a consequence of the strong complexing ability of $Cu^{II}$. As the reaction proceeds, inert copper(II) pyruvate forms and this reduces the concentration of copper(II) oxalacetate that could exist so the rate of reaction is retarded. This effect was not apparent in the spectrophotometric work, possibly because the concentrations of reactants used (small $c_4$ and $c_4 \ll c_1$ and $c_3$) produced only low concentrations of these complexes.

One feature worth mentioning is that the rate coefficients $k_0$ of $H_2L$ and $k_{ML}$ of CuL have similar values.

## Experimental

Oxalacetic acid (Aldrich Chemical Co. Ltd., 96%) was recrystallised by dissolving it in hot acetone, precipitating by toluene, filtering on to a glass sinter, and air-drying to constant weight. The other reagents were either of AnalaR grade or were made from AnalaR perchloric acid and metal oxides. Stock solutions of the metal perchlorates were analysed by use of a hydrogen-ion exchange resin column and standard sodium hydroxide.

E.m.f. measurements were obtained with the DVM system described elsewhere[10] and UV measurements with a previously described[11] kinetic version of a Pye-Unicam SP8-200 spectrophotometer. Kinetic studies made by means of a transducer (Radio Spares, type 303-343) involved siting this near the top of a wide-necked vessel shaped like a graduated flask and with a bulb of about 60 cm$^3$ in capacity. The transducer output was fed into the DVM system mentioned above and the DVM output was recorded at selected time intervals by connecting it *via* a multiplexer into a BBC microcomputer. The readings could be followed by the monitor and at the same time printed out for use in the calculation programs.

The transducer flask was clamped in a thermostatted plastic tank of water sited on a magnetic stirrer so that the solution could be agitated by a 'flea' during a run. Stock solution (50 cm$^3$) containing 0.5 mol dm$^{-3}$ $NaClO_4$ and specific amounts of stock solutions of HCl and metal perchlorate were pipetted into the flask and when thermal equilibrium was reached about 0.15 g (weighed to 0.1 mg) of oxalacetic acid was tipped in *via* a narrow tube. The flask was sealed by a rubber bung and readings were taken at timed intervals (3—15 min, depending on the rate) until the e.m.f.s were almost unchanged with time.

For the determinations of the stability constants $\beta_{011}$ and $\beta_{021}$ of the acid by means of the e.m.f. cells (A) and (B), dilute HCl (*ca.* 0.0005 mol dm$^{-3}$, 150 cm$^3$) was equilibrated, about 0.3—0.5 g of solid oxalacetic acid (weighed to 0.01 mg) stirred in followed by sufficient standard NaOH to effect partial neutralisation. E.m.f. readings were taken at 0.5—1 min intervals and extrapolated to zero time to compensate for changes caused by decarboxylation. The same procedure was used for the $\beta_{101}$ values of the metal perchlorates except that only a small amount of standard NaOH was added so that the e.m.f. change with time was small and this was quickly followed by several cm$^3$ of stock metal perchlorate and sufficient timed readings were taken for extrapolation.

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