391. *Tracer Studies in Carboxylic Acids. Part III.*[1] *Oxalic Acid*

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The rate of oxygen exchange of oxalic acid with water varies with hydrogen-ion concentration. Four paths are postulated for this exchange, of which three are major contributors. The activation energies, frequency factors, and entropies of activation have been calculated.

The exchange of the oxygen atoms of oxalic acid with water has been studied kinetically previously but only over a limited concentration of hydrogen ions. It was found that in the range $0{\cdot}3\text{M} \leqslant [H^+] \leqslant 4\text{M}$ the rate of exchange was dependent on the first power of stoicheiometric acidity.[2] The rate law suggested was

$$R = k[(CO_2H)_2][H^+][H_2O].$$

Milburn and Taube [3] extended the earlier study [2a] to pH 3 and found that the results could be accounted for if a two-term rate law were used, *viz.*

$$R = k_1[(CO_2H)_2][H_2O] + k_2[(CO_2H)_2][H^+][H_2O],$$

but not by a single-term rate law.

This Paper describes the exchange of the oxygen atoms of oxalic acid with water over the hydrogen-ion concentrations 4—10^{-12}M and in the temperature range 0—123°.

Mechanism of Oxygen Exchange.—In an aqueous solution of oxalic acid the following rapid equilibria occur:

$$HO_2C{\cdot}CO_2H \overset{K_1}{\rightleftharpoons} {}^-O_2C{\cdot}CO_2H + H^+$$

$$^-O_2C{\cdot}CO_2H \overset{K_2}{\rightleftharpoons} {}^-O_2C{\cdot}CO_2{}^- + H^+$$

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[1] Part II, D. R. Llewellyn and C. O'Connor. *J.* 1964. 4400.

[2] (*a*) C. A. Bunton, C. J. Bishop, J. H. Carter, D. R. Llewellyn, A. L. Odell, R. W. Olliff, and S. Y. Yih, *Australian Atomic Energy Symposium,* 623 (1958); (*b*) C. A. Bunton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J.*, 1964, 4615.

[3] R. M. Milburn and H. Taube, *J. Amer. Chem. Soc.*, 1959, **81**, 3515.

Since these equilibria are rapid it can be assumed that there are only four paths for the three species shown to exchange oxygen atoms with water.

(1) $HO_2C{\cdot}CO_2H + H^+ + H_2O$
(2) $HO_2C{\cdot}CO_2H + H_2O$ or $^-O_2C{\cdot}CO_2H + H^+ + H_2O$
(3) $^-O_2C{\cdot}CO_2H + OH^-$ or $^-O_2C{\cdot}CO_2{}^- + H_2O$
(4) $^-O_2C{\cdot}CO_2H + H_2O$ or $HO_2C{\cdot}CO_2H + OH^-$

The alternatives in reactions (2—4) are mechanistically different but cannot be distinguished chemically at the present time. This treatment neglects exchange due to attack on an oxalate ion by a hydroxyl ion, because it was shown experimentally that even at pH $> 8{\cdot}7$ where $(CO_2{}^-)_2$ is the only species present, an increase in hydroxyl ion concentration did not increase the rate. It also neglects any second-order terms in $(CO_2H)_2$ [*i.e.*, catalysis of reaction (1) by $(CO_2H)_2$ instead of by H^+] because the rate is found to be independent of the stoicheiometric concentration, C, of total oxalic acid added.

Up to the first "neutralisation" point of oxalic acid, the only species present are $(CO_2H)_2$ and $^-O_2C{\cdot}CO_2H$. If f is the fraction of the stoicheiometric concentration present as $(CO_2H)_2$, then $(1 - f)$ is the fraction present as $^-O_2C{\cdot}CO_2H$, and the rate of exchange is:

$$R = [H_2O]C\{k_1f\,.\,[H^+] + k_2(1-f)\,.\,[H^+] + k_4(1-f)\}.$$

Let $R/[H_2O]C = R^*$

then
$$R^* = k_1f[H^+] + k_2(1-f)[H^+] + k_4(1-f).$$

From the first to second "neutralisation" points the only species present are $^-O_2C{\cdot}CO_2H$ and $(CO_2{}^-)_2$. If f' is the fraction of total molecules present as $^-O_2C{\cdot}CO_2H$, and $(1 - f')$ is the fraction of total molecules present as $(CO_2{}^-)_2$, the rate equation may be derived as

$$R^* = k_2\,.\,f'[H^+] + k_3\,.\,(1-f') + k_4\,.\,f'.$$

Beyond the second "neutralisation" point $(CO_2{}^-)_2$ is the only species present and $R^* = k_3$.

Allowance has been made for variation of the acid dissociation constants K_1 and K_2, of oxalic acid with temperature, by using the empirical relation [4a]

$$\log K = -A_1/T + A_2 - A_3T.$$

For K_1, the constants A_1, A_2, and A_3 may be calculated from known [5] variations of pK_1 with temperature, $A_1 = 9100$, $A_2 = 61{\cdot}1$, $A_3 = 0{\cdot}1066$. At 25° $K_1 = 5{\cdot}4 \times 10^{-2}$. For K_2 the known values [4b] are $A_1 = 1424$, $A_2 = 6{\cdot}50$, $A_3 = 0{\cdot}0201$. The value of K_2 has been determined by a number of workers [6] and at 25° is equal to $5{\cdot}5 \times 10^{-5}$.

The values of f and f' can be calculated from these dissociation constants and from the measured hydrogen-ion concentration, thus

$$f = [H^+]/([H^+] + K_1),$$

and
$$f' = [H^+]/([H^+] + K_2).$$

The McKay plots [7] for exchange were linear over the range studied, which was up to 92% of complete exchange.

The experimental values of R^* are shown in Table 1. Results previously published [2]

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[4] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, (*a*) p. 357, (*b*) p. 520.

[5] L. S. Darken, *J. Amer. Chem. Soc.*, 1941, **63**, 1007; H. N. Parton and A. J. C. Nicholson, *Trans. Faraday Soc.*, 1939, **35**, 546.

[6] G. D. Pinching and R. G. Bates, *J. Res. Nat. Bur. Stand.*, 1948, **40**, 405; Harned, H. S. and L. D. Fallon, *J. Amer. Chem. Soc.*, 1939, **61**, 3111; H. N. Parton and R. C. Gibbons, *Trans. Faraday Soc.*, 1939, **35**, 542.

[7] H A. C. McKay, *Nature*, 1938, **142**, 997.

TABLE 1

Exchange for 0·15M-oxalic acid–$H_2{}^{18}O$ (R^* in l. mole^{-1} sec.$^{-1}$)

At $I = 4$.								
Temp.	0·0°	0·0°	0·0°	0·0°	25·0°	25·0°	25·0°	25·0°
$[H^+]$.........	3·70	2·77	1·85	0·92	3·70	2·77	1·85	0·92
10^7R *	27·4	20·2	13·4	6·87	338	252	176	90·5
$10^7R^*_{\text{calc.}}$ ...	26·8	20·0	13·4	6·65	339	257	172	86·4
Temp.	25·0°	25·0°	25·0°	44·9°	44·9°	44·9°	44·9°	
$[H^+]$.........	0·48	0·26	0·099	0·92	0·48	0·26	0·099	
10^7R^*	45·6	28·1	9·00	448	249	150	45·6	
$10^7R^*_{\text{calci}}$ ...	45·4	25·2	9·85	448	234	129	48·8	
At $I = 1$.								
Temp.	55·0°	55·0°	55·0°	55·0°	80·0°	80·0°	80·0° †	80·0
pH	1·57	2·01	2·56	2·97	2·01	2·56	2·59	2·97
10^8R^*	361	117	26·0	9·15	567	132	292	42·2
$10^8R^*_{\text{calc.}}$ ...	355	111	27·7	10·0	566	135		44·9
Temp.	80·0°	101·0°	101·0°	101·0°	101·0°	101·0°	101·0°	101·0°
pH	3·50	1·51	2·05	2·56	2·97	3·50	3·95	4·52
10^8R^*	10·8	7310	2570	925	168	38·1	11·1	4·75
$10^8R^*_{\text{calc.}}$ ...	12·1	7010	2220	942	161	37·8	10·8	
Temp.	101·0°	101·0°	101·0°	101·0°	101·0°	123·0°	123·0°	123·0°
pH	5·06	6·30	9·92	10·98	12·20	2·06	2·34	2·93
10^8R^*	4·81	4·67	4·62	4·67	4·80	5370	1610	778
$10^8R^*_{\text{calc.}}$ ...			4·72	4·72	4·72	5170	1772	788
Temp.	123·0°	123·0°	123·0°	123·0°	123·0°	123·0°	123·0°	
pH	3·50	3·95	4·52	5·06	6·61	9·92	10·98	
10^8R^*	206	43·3	37·8	36·7	37·5	36·7	37·0	
$10^8R^*_{\text{calc.}}$ ...	282					36·9	36·9	

† No perchlorate salt added.

were for $T = 25·0°$ and were for exchange reactions carried out in the absence of added salt. These are higher than the comparable rates quoted here for $T = 25·0°$ and at ionic strength (I) of 4, indicating that the exchange is subject to a negative salt effect. This conclusion is confirmed by the fact that the observed rate for the exchange at 80·0° and pH 2·59, carried out without the addition of perchlorate salt, is faster than the corresponding rate at ionic strength 1. The result might seem surprising because the primary salt effect on the dissociation of oxalic acid should result in a positive salt effect, but this negative salt effect could be attributed perhaps to a decreased activity of water in the electrolytic solutions.

The values of k_1, k_2, and k_3 are shown in Table 2.

In order to show the adequacy of the analysis the values of R^* calculated from the tabulated values of k_1—k_4 ($R^*_{\text{calc.}}$) are given in Table 1.

There is uncertainty in the value of k_4, which is very small. This is because its evaluation depends upon small differences between large quantities, namely, the rates of more significant paths which may not be sufficiently accurate at high temperatures because of the uncertainties of the values of pH.

The Arrhenius plots of log k_1 and log k_2 against $1/T$ were linear. Hence the frequency factors, A, the activation energies, E, and entropies of activation, ΔS^*, could be evaluated.

For convenience the rate constants (Table 2) were calculated so that they did not include $[H_2O]$, but the Arrhenius parameters (see Tables 3 and 4) are calculated on the conventional rate contants k', where $k' = k[H_2O] = 55·5\ k$.

The Arrhenius parameters for paths (2) and (3) depend on whether the rate constant is calculated as k_2 and k_3 or k_2'' and k_3'' where

$$R_2 = k_2[^-O_2C{\cdot}CO_2H][H^+][H_2O] = k_2''[HO_2C{\cdot}CO_2H][H_2O]$$

and $$R_3 = k_3[^-O_2C{\cdot}CO_2{}^-][H_2O] = k_3''[^-O_2C{\cdot}CO_2H][OH^-].$$

It is extremely unlikely that k_2'' will be the operating rate constant in path (2) since water attack on the carboxylic acid group $\cdot CO_2H$ is less probable than water attack on the protonated acid group $\cdot CO_2H_2^+$. The rate constant for this latter reaction is measured by k_2 which is, in fact, large.

TABLE 2

Rate constants for ^{18}O exchange of oxalic acid

Temp.	10^4k_1 (l.^{2} mole^{-2} sec.$^{-1}$)	10^5k_2 (l.^{2} mole^{-2} sec.$^{-1}$)	10^8k_3 (l. mole^{-1} sec.$^{-1}$)	k_4 (l. mole^{-1} sec.$^{-1}$)	Conditions
0·0°	0·00734	—	—		$I = 4$
25·0	0·0925	1·14	—		,,
44·9	0·483	5·45	—		,,
55·0	1·62	9·02	—		$I = 1$
80·0	6·93	36·2	—		,,
101·0	20·1	81·2	4·72	$\sim 10^{-8}$	,,
123·0	57·5	216	36·9	$\sim 10^{-7}$	,,

TABLE 3

Arrhenius parameters for rate constants k_1' and k_2'

Rate constant	Condition	E (kcal. mole^{-1})	log A	ΔS^* (cal. deg.$^{-1}$ mole^{-1})
k_1'	$I = 1$ and $I = 4$	17	9	−18
k_2'	$I = 1$ and $I = 4$	13	6	−30

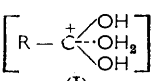
TABLE 4

Arrhenius parameters for rate constants k_3' and k_3''

Rate constant	Conditions	E (kcal. mole^{-1})	log A	ΔS^* (cal. deg.$^{-1}$ mole^{-1})
k_3'	$I = 1$	27	10	−13
k_3''	$I = 1$	21	14	+4

The transition states for reactions (1) and (2) will have very similar structures, *e.g.*, (I).

The entropies of activation of A-2 ester hydrolysis reactions indicate that ΔS^* values lie between −15 and −30 e.u. It is suggested[8] that −18 e.u. is a reasonable value for the loss of translational and rotational feedom from incorporation of one water molecule in such a bimolecular process. In addition, the dissociation of oxalic acid to the dioxalate ion will result in an entropy decrease primarily associated with the orientation of the solvent molecule dipoles around the ions with an attendant loss of freedom. Each water molecule which is thus " frozen " accounts for a decrease in ΔS^* of −5 e.u.



(I)

The value of k_3'' ($= k_3K_2/K_W$) was 70·6 sec.$^{-1}$ at 101·0° and 329 sec.$^{-1}$ at 123·0°.

It is not possible to say whether path (3) is governed by k_3' or k_3''; the Arrhenius parameters for both rate constants are given in Table 4.

These parameters are only of doubtful significance because of the small temperature range over which they are evaluated. No attempt has been made to assess the effect, if any, of temperature on pH. Nor has any effort been made to assess the effect of added salt on the glass electrode or to take activity coefficients into account in the calculation of $[H^+]$, which has been determined directly from pH $= -\log_{10}[H^+]$. These assumptions and omissions are not necessarily valid but the division of the exchange rate between the various paths does not depend upon them quantitatively to any great extent. The value of k_3 is determined directly from a region of the pH profile where the rate of exchange is independent of pH. Its evaluation does not involve a term in $[H^+]$ and although the profiles might be slightly displaced from their true position, due to these assumptions, the absolute values of k_3 will be unaffected.

The calculated values of k_1 and k_2 at 0·0, 25·0, and 44·9° are based only on rate measurements where the hydrogen-ion concentration was checked by acid–base titration. The quoted values for k_1 and k_2 at higher temperatures seem to be justified by the fact that they fit the Arrhenius plots extrapolated from the lower temperatures very well.

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[8] L. L. Schaleger and F. A. Long, *Adv. Phys. Org. Chem.*, 1963, **1**, 1.

EXPERIMENTAL

Materials.—The solvent was water containing ~1 atom % abundance ^{18}O. AnalaR oxalic acid dihydrate was recrystallised from water. Recrystallised lithium perchlorate was used to adjust the ionic strength. Acid solutions with $[H^+] > 0{\cdot}1$M were made up by mixing 60% AnalaR perchloric acid with water. The acid concentration was checked by acid–base titration. The pH of other solutions was adjusted by adding a few drops of 60% AnalaR perchloric acid or of a solution of lithium hydroxide, and measured on a Doran pH meter.

Kinetics of Oxygen Exchange.—(*a*) Solutions of pH >1. Weighed samples of oxalic acid were dissolved by shaking them in solvent containing lithium perchlorate. After adjusting the pH, aliquot parts (0·5 ml.) sealed in ampoules, were placed in a constant-temperature bath.

(*b*) *Solutions of* $[H^+] > 0{\cdot}1$M. Weighed samples of oxalic acid were dissolved by shaking them in solvent, containing perchloric acid and lithium perchlorate, which was at the temperature of the thermostat-bath.

Samples were removed at intervals, cooled rapidly in liquid air, and brought to ~pH 7 (colourless to phenophthalein), by addition of dilute perchloric acid to basic solutions or dilute lithium hydroxide to acidic solutions. A few drops of silver nitrate were added, and the precipitate of silver oxalate filtered off, washed with alcohol, and dried *in vacuo*. The salt was then pyrolysed by gentle heating *in vacuo* to give carbon dioxide which was analysed on an A.E.I. M.S.3 mass spectrometer.

The initial abundance of ^{18}O in oxalic acid was measured on an unlabelled sample of silver salt, and excess abundances were calculated relative to this value. For the fast reactions the infinite-time value for complete exchange was measured after ~8—10 half-lives. If $t_{\frac{1}{2}}$ was greater than 4 days, the infinite-time abundance was measured on a sample of carbon dioxide which had been in equilibrium with a portion of the exchange solution for 36 hr. at 100°.

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