845. *Tracer Studies of Carboxylic Acids. Part II.[1] Trifluoro-
acetic Acid and Trichloroacetic Acid.*

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The rate of oxygen exchange of trifluoroacetic and trichloroacetic acid
with solvent 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.

In Part I,[1] it was shown that the oxygen exchange of acetic and pivalic acid with solvent
water could take place along three different paths. This Paper describes the exchange
of the oxygen atoms of trifluoroacetic and trichloroacetic acid with solvent water over the
ranges of hydrogen-ion concentration 4—10^{-2}M and 10^{-11}—10^{-14}M, and over the temper-
ature range 0—55°.

Mechanism of Oxygen Exchange.—In an aqueous solution of trifluoroacetic or trichloro
aceticacid, the following equilibrium occurs:

$$R \cdot CO_2H \underset{}{\overset{K_a}{\rightleftharpoons}} R \cdot CO_2^- + H^+$$

At 25°: $K(CF_3 \cdot CO_2H) = 0.588$ (ref. 2); $K(CCl_3 \cdot CO_2H) = 0.25$ (ref. 3).
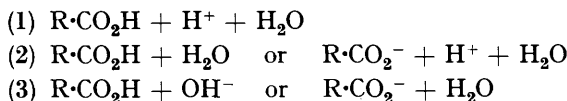
[1] Part I, Llewellyn and O'Connor, *J.*, 1964, 545.
[2] Henne and Fox, *J. Amer. Chem. Soc.*, 1951, **73**, 2323.
[3] Drucker, *Z. phys. Chem.*, 1920, **96**, 381.

There are insufficient data in the literature to enable one to make an allowance for the variation of K_a with temperature, but in the temperature range used here, this variation is not expected to be large.

It can be assumed that the three paths postulated for the exchange of the oxygen atoms of acetic acid with water also apply for the species present in this equilibrium, *i.e.*,

(1) $R \cdot CO_2H + H^+ + H_2O$

(2) $R \cdot CO_2H + H_2O$ or $R \cdot CO_2^- + H^+ + H_2O$

(3) $R \cdot CO_2H + OH^-$ or $R \cdot CO_2^- + H_2O$

In addition, because of the strong inductive effect of three fluorine or three chlorine atoms, a further path, which could be neglected in the case of acetic acid, now becomes significant:

(4) $R \cdot CO_2^- + OH^-$
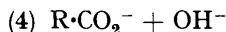
This treatment neglects any second-order term in $R \cdot CO_2H$ [*i.e.*, catalysis of reaction (1) by $R \cdot CO_2H$ instead of by H^+] because the rate is found to be independent of the stoicheiometric concentration, C, of total carboxylic acid added.

If x is the fraction of the stoicheiometric concentration present as $R \cdot CO_2H$, then the rate of exchange is:

$$R = xC(k_1[H^+][H_2O] + k_2[H_2O] + k_3[OH^-]) + (1 - x)Ck_4[OH^-].$$

Beyond the equivalence point, where the predominating species is the ion $R \cdot CO_2^-$, the rate is found to be dependent on the first power of the hydroxyl-ion concentration, *i.e.*, path (4) is occurring. Since in the pH range studied, 11—14, there is no departure from linearity when $-\log R$ is plotted against pH, path (3), if it occurs at all, must make a very small contribution and can be ignored.

Thus $R = k_4C[OH^-].$

Let $R/C =$ " R "; then " R " $= k_4[OH^-].$

Also at $[H^+] > 10^{-2}$M, $[OH^-]$ is very small, and paths (3) and (4), both of which involve $[OH^-]$, will make only relatively small contributions, and can be ignored. At pH < 2, therefore, we need consider only paths (1) and (2).

Let $R/[H_2O]C = R^*$; then $R^*/x = k_1[H^+] + k_2.$

The values of $[H^+]$ and x (Tables 1 and 2) are calculated from the classical equilibrium constant, K_a, for trifluoroacetic and trichloroacetic acid, using the known weight of tri-fluoroacetic or trichloroacetic acid and the known volume of standardised perchloric acid or lithium hydroxide added. This procedure may not be fully justified because $K_a = a_{H^+}[A^-]f_{A^-}/[HA]f_{HA}$, and the term $f_{H^+}f_{A^-}/f_{HA}$ could change very much with acidity, even at constant ionic strength. This uncertainty in interpretation will reflect on the significance of the Arrhenius parameters.

The position has been clarified a little by using two different salts, silver perchlorate and lithium perchlorate, to adjust the ionic strength. The observed rate of exchange was independent of the salt medium. The specific salt effect of Ag^+ is therefore the same as for Li^+, and this latter ion is known [4] to be reasonably similar to H^+. It can therefore be argued that $f_{H^+}f_{A^-}/f_{HA}$ is constant, though it may not equal 1, and the value of K_a used may be wrong, but to the same extent for each reaction.

The McKay plots [5] for exchange were found to be linear over the range studied, which was up to 89% of complete exchange.

[4] Long and King, *J. Amer. Chem. Soc.*, 1953, **75**, 6180.
[5] McKay, *Nature*, 1938, **142**, 997.

TABLE 1.

Exchange for [^{18}O]trifluoroacetic acid–H_2O at an ionic strength of 4.

Temp. = 0°.

C (M)	1·058	0·694	0·851	0·689	0·887	1·081	0·537	0·494	0·494	0·563	0·241
[HClO$_4$] (M)	1·848	1·848	0·924	0·924	0·471	—	—	—	—	—	—
[LiOH] (M)	—	—	—	—	—	—	0·128	0·202	0·323	0·404	0·216
[H$^+$] (M)	2·081	2·006	1·203	1·158	0·838	0·556	0·250	0·178	0·099	0·087	0·018
x	0·780	0·773	0·657	0·660	0·586	0·486	0·296	0·231	0·146	0·128	0·029
$10^7 R^*$	58·1	56·2	36·4	35·6	25·8	16·5	6·53	4·33	2·03	1·98	0·361
$10^7 R^*_{calc.}$	67·5	64·7	36·4	35·4	24·8	15·6	6·31	4·33	2·33	1·98	0·378

Temp. = 25·0°.

C (M)	0·660†	0·560	0·592	0·840	0·522	0·496	0·193	0·517	0·501	0·451
[HClO$_4$] (M)	0·924	0·924	0·462	—	—	—	—	—	—	—
[LiOH] (M)	—	—	—	—	—	0·128	—	0·257	0·385	0·404
[H$^+$] (M)	1·147	1·117	0·727	0·468	0·334	0·230	0·154	0·154	0·066	0·027
x	0·663	0·655	0·553	0·443	0·361	0·279	0·202	0·204	0·100	0·044
$10^7 R^*$	282	277	173	117	89·5	63·9	34·8	32·3	16·4	6·48
$10^7 R^*_{calc.}$	285	275	179	115	81·0	55·2	36·1	36·5	15·7	6·45

Temp. = 45·3°.

C (M)	0·603	0·199	0·516	0·224
[HClO$_4$] (M)	—	—	—	—
[LiOH] [M]	—	—	0·363	0·208
[H$^+$] (M)	0·376	0·157	0·086	0·012
x	0·379	0·211	0·130	0·018
$10^7 R^*$	442	177	91·5	8·69
$10^7 R^*_{calc.}$	443	161	81·0	8·69

Temp.	0·0°	0·0	0·0	0·0	25·0	25·0	25·0	25·0	45·3	45·3	45·3
pH	11·56	12·24	13·01	13·62	11·56	11·86	13·01	13·46	10·98	11·76	12·92
10^7 " R "	0·725	3·61	23·3	85·8	5·31	9·79	131	342	5·22	23·7	351

R^* in l. mole^{-1} sec.$^{-1}$. " R " in sec.$^{-1}$.

† In this run the ionic strength was adjusted with lithium perchlorate. In the other runs silver perchlorate was used.

TABLE 2.

Exchange for trichloroacetic acid–H_2 ^{18}O at an ionic strength of 4.

Temp. = 25·5°.

C (M)	0·454	0·476	0·425	0·464	0·447	0·485
[HClO$_4$] (M)	3·696	2·772	1·680	0·924	—	—
[LiOH] (M)	—	—	—	—	0·202	0·387
[H$^+$] (M)	3·724	2·811	1·734	1·016	0·109	0·037
x	0·939	0·920	0·873	0·800	0·305	0·127
$10^7 R^*$	78·9	59·4	45·8	27·3	4·66	1·52
$10^7 R^*_{calc.}$	80·3	62·6	41·4	27·0	4·87	1·89

Temp. = 55·0°.

C (M)	0·475	0·506	0·483	0·472	0·473	0·480	0·587	0·465	0·481	0·460
[HClO$_4$] (M)	3·696	2·772	1·895	0·924	0·462	—	—	—	—	—
[LiOH] (M)	—	—	—	—	—	—	0·202	0·202	0·303	0·437
[H$^+$] (M)	3·727	2·813	1·950	1·017	0·601	0·243	0·158	0·116	0·072	0·009
x	0·936	0·919	0·888	0·803	0·707	0·489	0·387	0·317	0·221	0·031
$10^7 R^*$	678	564	450	231	166	71·2	57·5	41·4	28·1	4·42
$10^7 R^*_{calc.}$	810	625	449	254	164	77·8	54·9	42·5	27·6	3·47

Temp.	25·5°	25·5	25·5	55·0	55·0	55·0
pH	12·36	12·92	13·59	12·36	12·92	13·55
10^6 " R "	7·44	24·3	120	63·8	276	960

R^* in l. mole^{-1} sec.$^{-1}$. " R " in sec.$^{-1}$.

The experimental values of R^* and " R " are shown in Tables 1 and 2. In the experiments with trifluoroacetic acid, the concentration C was varied from 0·2M to 1M. When $-\log R^*$ is plotted against $-\log$ [H$^+$], a smooth curve is obtained, showing that the rate of exchange is dependent on the hydrogen-ion concentration and is independent of the

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original composition of the solution. This shows that, at a given hydrogen-ion concentration, the rate of oxygen-18 exchange is solely dependent upon the difference in isotopic abundance of the two species trifluoroacetic acid and water, and is independent of the concentration of trifluoroacetic acid. Thus the possibility of catalysis of the exchange by carboxylic acid molecules can be discounted.

The values of k_1, k_2, and k_4 are given in Tables 3 and 4. In order to demonstrate the

TABLE 3.

Rate constants for oxygen-18 exchange of trifluoroacetic acid at an ionic strength of 4.

Temp.	$10^6 k_1$ (l.^{2} mole^{-2} sec.$^{-1}$)	$10^6 k_2$ (l. mole^{-1} sec.$^{-1}$)	$10^2 k_4$ (l. mole^{-1} sec.$^{-1}$)
0·0°	3·57	1·24	1·12
25·0	25·3	14·0	7·39
45·3	189	46·0	23·7

TABLE 4.

Rate constants for oxygen-18 exchange of trichloroacetic acid of an ionic strength of 4.

Temp.	$10^6 k_1$ (l.^{2} mole^{-2} sec.$^{-1}$)	$10^6 k_2$ (l. mole^{-1} sec.$^{-1}$)	$10^4 k_4$ (l. mole^{-1} sec.$^{-1}$)
25·5°	1·92	1·42	3·11
55·0	20·3	11·0	27·8

adequacy of the analysis, values of R^* calculated from the tabulated values of k_1 and k_2, *i.e.*, $R^*_{\text{calc.}}$, are given in Tables 1 and 2.

It is clear that path (2), which had almost no significance in the exchange of the oxygen atoms of acetic and pivalic acid with water, has become a major contributor to the rate of exchange of trifluoroacetic and trichloroacetic acid with water.

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

TABLE 5.

Arrhenius parameters.

Acid	Rate constant	E (kcal. mole^{-1})	log A	ΔS^* (cal. deg.$^{-1}$ mole^{-1})
Trifluoroacetic	k_1'	15	8	−23
Trifluoroacetic	k_2'	14	7	−26
Trifluoroacetic	k_4	12	7	−29
Trichloroacetic	k_1'	15	7	−27
Trichloroacetic	k_2'	13	5	−35
Trichloroacetic	k_4	14	7	−29

For convenience, the rate constants k_1 and k_2 (Tables 3 and 4) were calculated so that they did not include [H$_2$O], but the Arrhenius parameters (see Table 5) are calculated on the conventional rate constants k_1' and k_2', where $k' = k[\text{H}_2\text{O}] = 55·5k$.

EXPERIMENTAL

Materials.—The solvent for the experiments with enriched trifluoroacetic acid was normal water, and that for the experiments with trichloroacetic acid was water containing *ca.* 1 atom % abundance of oxygen-18.

Trifluoroacetic anhydride (Eastman Kodak) was distilled, and the fraction boiling at 40·0° was added to water, *ca.* 3 atom % enriched in oxygen-18. This mixture was then distilled and trifluoroacetic acid, enriched in oxygen-18, was collected at 68·5—69·0°.

Trichloroacetic acid May and Baker was recrystallised from water; it had m. p. 57°.

Recrystallised silver perchlorate and lithium perchlorate were used to adjust the ionic strength.

The pH values of alkaline solutions were measured on a Doran pH-meter.

Kinetics of Oxygen Exchange.—Weighed samples of the carboxylic acid were dissolved by

shaking them in solvent containing perchloric acid or lithium hydroxide, and perchlorate salt, the solvent being at the temperature of the thermostat bath. Samples were removed at intervals and cooled rapidly in liquid nitrogen.

Solutions of trifluoroacetic acid which contained no silver perchlorate were made just acid by the addition of perchloric acid, and then a few drops of 5M-silver perchlorate were added. Then the samples of trifluoroacetic acid were shaken for 30 sec. with 3 ml. of benzene, which extracted the silver trifluoroacetate. The benzene extract was removed and evaporated nearly to dryness on a hot plate. Final drying was carried out under a vacuum.

Samples of trichloroacetic acid were made just acid. A few drops of mercurous nitrate were added, and the precipitate of mercurous trichloroactate filtered off, washed with alcohol, and dried under a vacuum.

Silver trifluoroacetate was pyrolysed on heated carbon, and mercurous trichloroacetate by gentle heating under a vacuum; the carbon dioxide produced was analysed on an A.E.I.M.S.3. mass spectrometer.

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