TABLE III

Molality	9-Tungstophosphoric acid			12-Tungstophosphoric acid		
	c	(d ln a_0/dc)	$H \times 10^6$	c	(d ln a_0/dc)	$H \times 10^6$
0.02	0.086	−0.020	3.93	0.058	−0.011	2.96
.04	.170	.022	3.96	.115	.013	2.98
.06	.251	.023	3.99	.171	.014	2.99
.08	.328	.026	4.01	.227	.016	3.00
.10	.407	.028	4.04	.283	.017	3.02
.15	.597	.035	4.11	.418	.020	3.04
.20	.769	.042	4.17	.550	.023	3.07
.30	1.078	.059	4.25	.770	.029	3.13
.40	1.36	.080	4.39	1.029	.034	3.18
.50				1.26	.038	3.23
.60				1.47	.042	3.29
.70				1.88	.044	3.34

solutions, this is not the case for concentrated solutions. The turbidities were calculated from the tabulated quantities using equation 2. They are plotted together with the experimental turbidities obtained previously[2,4] in Figs. 1 and 2. Also shown in these figures are the turbidities calculated on the assumption of ideal behavior, from

$$\tau = \frac{8\pi^3}{3\lambda^4 N}\, cm \left(\frac{\mathrm{d}n^2}{\mathrm{d}c}\right)^2 = HcM \qquad (4)$$

where M is the molecular weight of the solute.

The agreement between the experimental turbidities and those calculated from activity data is quite satisfactory. In the concentration range where the results by the two methods overlap, the agreement is within 10%, which is approximately the combined uncertainty in determining (d ln a_0/dc) at these very low molalities and the experimental turbidity. The difference between the experimental turbidities and those calculated from equation 4 is quite striking, indicating the failure of the approximations based on ideal behavior for these systems.

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The Effects of Some Organic Oxy-acids on the Electron Exchange Reaction between Thallium(I) and (III) in Aqueous Perchloric Acid

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The effects of these various oxy-acids: oxalic, acetic, malonic, succinic, malic and tartaric, on the Tl(I)–Tl(III) exchange in 3.50 *M* $HClO_4$ were studied. With oxalic, malonic, malic and tartaric, reduction of Tl(III) proceeded at a rate comparable to or faster than the exchange. Acetic and succinic acids retard the exchange; the exchange rate reflects the loss of exchangeable species through competition of the acetate or succinate complexes.

The thallium(I)–(III) electron transfer reaction in perchloric acid has been studied by Dodson and co-workers,[2] Prestwood and Wahl[3] and Rossotti[4] and the effects of chloride, cyanide and sulfate have been examined by various workers.[5-7] In view of suggestions that anion bridges might accelerate exchange[6,7] and in view of the contrasting effects of various anions on the exchange, we decided to examine the exchange in perchloric acid in the presence of various added organic oxy-acids.

Experimental

Experimental procedures were the same as have been reported in earlier papers,[6] except that glass filters, with fritted discs and removable glass chimneys, replaced the steel models. The reactions were run at 25.0°.

Reagents, except for the Oak Ridge Tl 204, were from Merck and Company (Germany).

Since all the organic acids employed (oxalic, acetic, malonic, succinic, malic and tartaric) are weak acids, these were simply added to the $TlClO_4$, $Tl(ClO_4)_3$ and $HClO_4$ (3.50 *M*) and it was assumed the change in ionic strength caused by the addition was negligible compared to 3.68; *i.e.*, $\mu = {}^1/_2 [(Tl(I)) + 9(Tl(III)) + (Na^+) + (H^+) + (ClO_4^-)]$. $NaClO_4$ was used, when necessary, to maintain μ = 3.68 *M*.

Results

Exchange between thallium(I) (0.0104 *M*) and thallium(III) (0.0100 *M*) in 3.50 *M* perchloric acid was found to proceed with a half-life of 205 hours, which agrees reasonably well with previous experiments.[3,6]

There was some problem in keeping the $Tl^{204}(ClO_4)_3$ tracer. It was stored in 3.50 *M* perchloric acid, but was reduced slowly, so that apparent induced exchange rose from about 5%, when fresh tracer was used, to about 12% in two months. When enough reduction had occurred to give an apparent 12% induced exchange, a new tracer solution was prepared. Probably some trace of reducing agent in the distilled water or perchloric acid was responsible.

It was found that small amounts of acid [(acid)/(Tl^{III}) $\geq$ 0.5] caused reduction of thallium(III) when oxalic, malonic, malic and tartaric acids were added to the system. The reduction showed up not only in the MacKay plots log (1 − F) *vs.* time, where F is the fraction exchanged, but also in the increasing weights of the Tl_2CrO_4 precipitates. As an example, the data for one reaction with

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TABLE I

THE REACTION BETWEEN 0.010 M Tl^{I} AND 0.0108 M Tl^{III} IN 3.50 M $HClO_4$ WITH 0.0100 M TARTARIC ACID

Time (hr.)	Wt. Tl_2CrO_4 (mg.)	Spec. act. (c./m.-mg.)	$1 - F$
0.04	11.2	66.2	0.877
3.41	10.5	70.5	.868
23.6	14.6	73.5	.863
55.3	11.6	142	.735
77.5	12.5	170	.682
96.2	11.9	193	.640
151.2	13.0	228	.574
199.4	15.2	236	.559
264.1	14.9	279	.479
368.1	18.0	259	.516
∞	23.5	536	...

TABLE II

THE EFFECT OF VARYING THE CONCENTRATIONS OF Tl(I) AND Tl(III) IN 0.03 M ACETIC ACID, $[HClO_4]$ = 3.50 M

$a = [Tl^{I}]$ (molar × 10^3)	$b = C_{Tl}{}^{III}$ (molar × 10^3)	R/ab (l./mole hr.)	R (× 10^6)
5.5	10.0	0.124	6.96
10.4	10.0	.106	11.1
20.0	10.0	.121	24.4
29.6	10.0	.118	35.1
48.8	10.0	.119	58.4
10.0	5.0	.112	56.7
10.4	10.0	.106	11.1
11.1	20.1	.093	20.8
11.9	30.2	.083	29.7
13.4	50.3	.143	96.7

TABLE III

DEPENDENCE OF EXCHANGE RATE ON CONCENTRATION OF ACETIC ACID, $[HClO_4]$ = 3.50 M

$a = [Tl^{I}]$ (molar × 10^3)	$b = C_{Tl}{}^{III}$ (molar × 10^3)	$[HC_2H_3O_2]$ (molar × 10^3)	R/ab (l./mole hr.)	R (× 10^6)
10.2	10.0	5.0	0.131	13.4
10.1	10.8	10.0	.127	13.9
10.2	10.0	20.0	.114	11.8
10.2	10.6	30.0	.109	11.2
10.2	10.6	50.0	.094	9.7

TABLE IV

THE EFFECT OF VARYING THE CONCENTRATIONS OF Tl(I) AND Tl(III) IN 0.03 M SUCCINIC ACID, $[HClO_4]$ = 3.50 M

$a = [Tl^{I}]$ (molar × 10^3)	$b = C_{Tl}{}^{III}$ (molar × 10^3)	R/ab (l./mole-hr.)	R (× 10^6)
5.4	10.8	0.056	3.31
10.1	10.8	.080	8.81
19.6	10.8	.078	16.7
29.1	10.0	.067	19.6
47.9	10.0	.077	37.4
9.8	5.4	.082	4.34
10.1	10.8	.080	8.81
10.9	21.6	.095	22.5
11.6	32.5	.094	35.6
13.1	54.1	.091	64.8

tartaric acid are given in Table I and Fig. 1. Similar results were obtained in all experiments with the above four acids. However, if one estimates $t_{1/2}$ from early parts of the MacKay plots, retardation of the exchange is suggested for tartaric acid and acceleration for oxalic, malonic and malic.

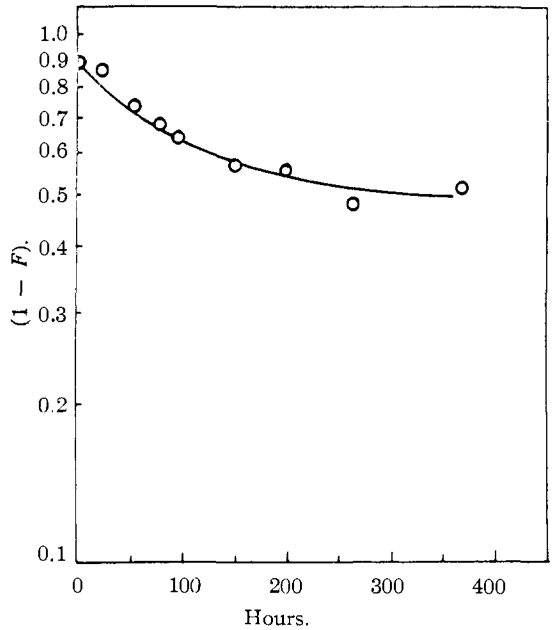

Fig. 1.—0.0101 M Tl(I) and 0.0108 M Tl(III) in 3.50 M $HClO_4$ with 0.0100 M tartaric acid (semilog scale).

In the several series of experiments, in which acetic or succinic acids were added to thallium(I) and (III) in 3.50 M perchloric acid, no evidence of reduction of thallium(III) was found. The results of these experiments are given in Tables II and III (acetic acid) and IV and V (succinic acid).

TABLE V

DEPENDENCE OF EXCHANGE RATE ON CONCENTRATION OF ADDED SUCCINIC ACID, $[Tl(I)]$ = 0.0102 M, $C_{Tl}{}^{III}$ = 0.0108, $[HClO_4]$ = 3.50 M

$[H_2C_4H_4O_4]$ (molar × 10^3)	R/ab (l./mole-hr.)	R (× 10^6)
3.0	0.124	13.7
5.0	.137	15.1
10.0	.121	13.3
15.0	.108	11.9
20.0	.111	12.2
30.0	.084	9.26
40.0	.061	6.69
50.0	.062	6.81

Discussion

It was found that the addition of acetic or succinic acid to the exchanging system in perchloric acid had the effect of depressing the rate of exchange. This suggests that the acetato- and succinato- complexes formed, probably with thallium(III), react slowly or not at all with the thallium(I) species.

It was found that, in the presence of 0.030 M acetic or succinic acid, the reactions were still first order in each of thallium(I) and (III). That is, if $R = k[Tl^{I}]^{\alpha}[C_{TL}]^{\beta}$, then in acetic acid, $\alpha = 1.00 \pm 0.03$, $\beta = 1.15 \pm 0.12$ and in succinic acid $\alpha = 1.06 \pm 0.07$, $\beta = 1.19 \pm 0.02$.

The results for both systems can be treated in the same way. If we assume that the complex species do not exchange with Tl(I) or exchange at a negligible rate and if we assume the existence of only the first complex, hereafter designated TlA, the following treatment will apply. [HA] is the con-

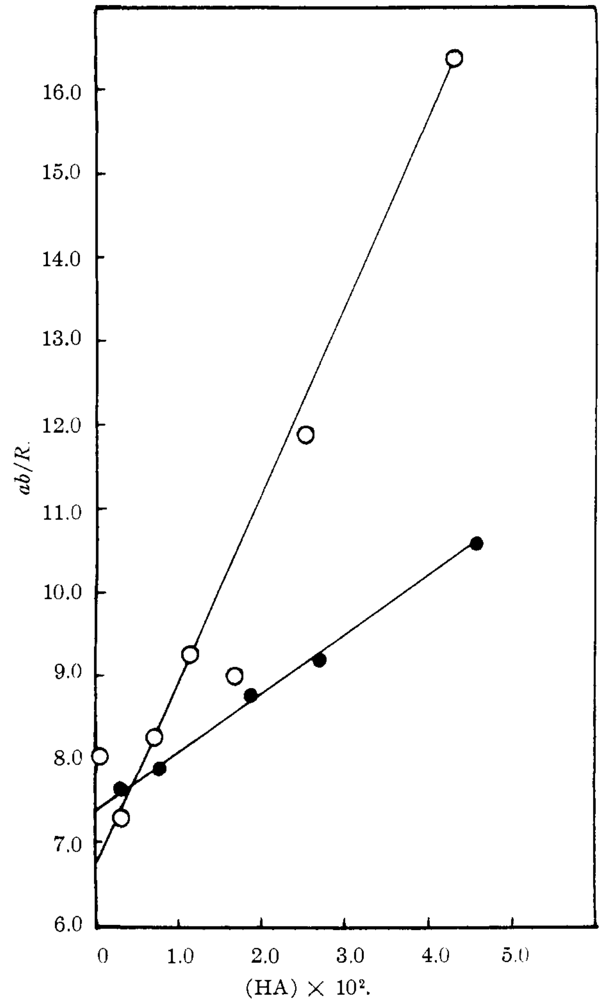

Fig. 2.—*ab/R vs.* (HA): open circles, succinic acid; solid circles, acetic acid.

centration of free acid, $[\mathrm{Tl^{III}}]$ of uncomplexed thallium(III), [TlA] of complex; C_{HA} the total organic acid concentration and C_{Tl} the total thallium(III).

Let $X = R/R^0$, the ratio of observed rate to that observed with no organic acid present. Then

$$X = \frac{R}{R^0} = \frac{[\mathrm{Tl^{III}}]}{C_{\mathrm{Tl}}} \qquad (1)$$

Then, if only the TlA complex is formed

$$[\mathrm{TlA}] = C_{\mathrm{Tl}}[1 - X] \qquad (2)$$
$$[\mathrm{Tl^{III}}] = XC_{\mathrm{Tl}}$$
$$[\mathrm{HA}] = C_{\mathrm{HA}} - [\mathrm{TlA}]$$

and

$$K^1 = \frac{K}{[\mathrm{H^+}]} = \frac{[\mathrm{TlA}]}{[\mathrm{Tl^{III}}][\mathrm{HA}]} \qquad (3)$$

If succinic acid serves as a chelate ligand, then for succinic acid, we use $[\mathrm{H_2A}]$ and

$$K^1 = K/[\mathrm{H^+}]^2$$

Then we can write, by substituting (2) in (1) and dividing by ab, $a = [\mathrm{Tl^I}]$, $b = C_{\mathrm{Tl}}$

$$\frac{R}{ab} = \frac{R^0}{ab} \times \frac{1}{[1 + K^1[\mathrm{HA}]]}$$

or

$$\frac{ab}{R} = \frac{ab}{R^0} + \frac{ab}{R^0K^1} \times [\mathrm{HA}]$$

Thus a graph (Fig. 2) of ab/R *versus* [HA] gives a straight line with intercept ab/R^0 and slope ab/R^0K^1.

For acetic acid, the ab/R^0 is 7.40 or $R^0/ab = 0.135$ and $K^1 = 9.5$. For succinic acid $ab/R^0 = 6.65$ or $R^0/ab = 0.150$ and $K^1 = 35$. The experimental R^0/ab is 0.165, so that these extrapolated values are a bit low. The 0.150 for succinic acid lies within the estimated ± 10% error. However, in view of the observed linearity of the graphs, especially for acetic acid, this deviation in R^0/ab is attributed to a compounding of experimental errors, especially in the calculation of [HA].

K can then be estimated, since $[\mathrm{H^+}] = 3.50\ M$ is known. For acetato-complexing $K = 33$ and for succinato-, $K = 1.2 \times 10^2$, if monodentate, or 4.3×10^2, if bidentate.

If the oxalic, malonic and malic acids actually do accelerate the exchange, their roles would be very interesting. It is hoped that a study of their effects in other systems can be evaluated. Probably the iron(II)–(III) exchange in perchloric acid will be the next studied with organic oxy-acids.

It seems possible to conclude that the effect of adding either acetic or succinic acid to solutions of thallium(I) and (III) in 3.50 M perchloric acid is to remove exchangeable thallium species, probably Tl(III), by complexing and thus to retard the electron exchange.

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