[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

X-Ray Induced Tl^{+++}–Tl^{+} Exchange in 0.8 *N* $\mathrm{H_2SO_4}$[1]

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A study has been made of the Tl^{+}–Tl^{+++} isotopic exchange reaction in 0.8 *N* $\mathrm{H_2SO_4}$ solutions undergoing irradiation with 50 kvp. X-rays. Throughout the range of the measurements, the radiation-induced exchange rate was found to be independent of thallous concentration, 0.503-order dependent upon thallic concentration, and 0.670-order dependent upon irradiation intensity. The results are explained in terms of a proposed mechanism involving the formation of the intermediate species Tl^{++} at an appreciable steady-state concentration in the irradiated solutions. The Tl^{++} intermediate is presumed to exchange rapidly with Tl^{+} and somewhat less readily with Tl^{+++}. In the absence of radiation, ferrocyanide ion was found to induce an exchange in Tl^{+}–Tl^{+++} solutions, indicating that Tl^{++} may be an important intermediate in the Tl^{+++}–$\mathrm{Fe(CN)_6^{\equiv}}$ oxidation–reduction reaction. In order to study the X-ray induced exchange, it was necessary to measure the "thermal" electron exchange rate in these solutions. The "thermal" rate was found to be first order both in $[\mathrm{Tl}^{+}]$ and in $[\mathrm{Tl}^{+++}]$. A bimolecular rate constant of 1.19 liter-mole^{-1} min.$^{-1}$ at 25° was measured. The energy of activation was found to be 13.8 kcal. mole^{-1}, and the entropy of activation, -22 e.u.

Introduction

In a recent paper the authors[2] have reported that Ce^{+++}–Ce^{++++} solutions irradiated by X-rays undergo an apparent exchange reaction in addition to the ordinary electron ("thermal") exchange. This they attributed to the reaction $\mathrm{Ce}^{+++} + \mathrm{OH} \rightarrow \mathrm{Ce}^{++++} + \mathrm{OH}^-$ opposing the over-all X-ray reduction of Ce^{++++}, since the observed rate of radiation-induced exchange was approximately equal to the expected rate of formation of OH radicals. Unfortunately, in the cerium system it was found necessary to work at 0° in order to minimize the "thermal" exchange contribution.

The "thermal" exchange rate of Tl^{+++} with Tl^{+} in $\mathrm{HClO_4}$ is quite slow,[3,4] and although preliminary work indicated that this exchange is considerably faster in 0.8 *N* $\mathrm{H_2SO_4}$, it is still slow enough so that radiation-induced exchange studies can be carried out at 25°. Furthermore, little is known of the radiation chemistry of thallium solutions, except for the recent communication of Sworski.[5] Also, the behavior of thallium in oxidizing–reducing systems is not completely understood, particularly in regard to the role of Tl^{++}.[6,7] Consequently, it was thought that a study of the radiation-induced Tl^{+++}–Tl^{+} exchange would be of interest for its own sake as well as to serve as a check on the radiation-induced Ce^{++++}–Ce^{+++} exchange.

Experimental

X-Ray Source.—A G. E. 50 kvp. X-ray machine with a beryllium window tube, a tungsten target and an unfiltered full wave rectifier was used as a radiation source. The spectral distribution for this particular instrument has been reported.[8] For the experiments reported in this paper, the tube current of the machine was varied from about 2 to 50 ma., and was measured with a calibrated milliammeter accurate to about 1–2%.

Irradiation Cell.—The irradiation cell consisted of a 50-ml. beaker provided with a machined and carefully fitted Lucite top which was also threaded to fit the output port of the X-ray machine in an easily reproducible position. The Lucite top was fitted with a 2-mil mica window, designed to protect the X-ray machine and the irradiated solution from mutual contamination. The collimated beam leaving the X-ray tube port passed vertically downward through the mica window, as well as through a total one-inch air path, before entering the upper surface of the solution to be irradiated. Absorption of X-rays by the mica window and air path was negligible. It is estimated that the solutions absorbed about 70% of the incident radiation energy. Because complete absorption was not obtained, considerable care was taken not only to reproduce the position of the cell for each run, but also to use the same amount of solution (30 ml.) in each irradiation. All solutions were stirred continuously during irradiations by means of a $^1/_4''$ Pyrex-covered magnetic stirring bar.

Ferrous Dosimeter.—Energy absorption was determined by measuring the rate of radiation-induced oxidation of air-saturated $\mathrm{FeSO_4}$ in 0.8 *N* $\mathrm{H_2SO_4}$. The value $G_{\mathrm{Fe}^{+++}} = 14.0$ ions oxidized per 100 e.v. absorbed, obtained by combining Hardwick's low energy X-ray irradiation data[9] with the value of $G_{\mathrm{Fe}^{+++}} = 15.6$ ions/100 e.v. for fast electrons, was used to compute the number of electron volts per liter per minute absorbed by the solution in the irradiation cell.

Temperature Control.—The lower portion of the irradiation cell was submerged in a thermostated water-bath (or crushed ice, in the case of the 0° runs) in order to maintain the temperature of the irradiated solution to within 0.1° of the desired temperature. "Thermal" exchange solutions were similarly thermostated.

In the case of the irradiated runs, the possibility of local heating of the solution by X-rays or by the X-ray tube was investigated. A thermocouple was placed within the thermostated absorption cell containing the solution to be irradiated, the X-ray machine was turned on, and the temperature of the thermocouple was followed as a function of time. The maximum heating was found to be less than 0.1°.

Reagents and Solutions.—All water used in these experiments was redistilled from alkaline permanganate.

Sulfuric acid was reagent grade redistilled from $\mathrm{K_2Cr_2O_7}$.

Thallous sulfate stock solution was made by dissolving A. D. Mackay $\mathrm{Tl_2SO_4}$ in purified $\mathrm{H_2SO_4}$, then adding enough water so that the final solution was 0.0204 *M* in Tl^{+} and 0.800 *N* in $\mathrm{H_2SO_4}$.

Thallic sulfate stock solution was made by oxidizing thallous sulfate stock with ozone. Excess ozone was removed by bubbling air through the solution until no odor of $\mathrm{O_3}$ could be detected, and a negative starch–iodide test was obtained from the effluent gases. The thallic stock solution was periodically tested for thallous ion by adding a small portion to chloroplatinate solution. No precipitate of thallous chloroplatinate was ever detected. Titration of the stock solution with standardized Ce^{++++} in >3 *N* HCl using ICl as a catalyst and ferrous orthophenanthroline indicator also affirmed the conclusion that no detectable amount of thallous ion was present. The solution remained apparently unchanged over the period of several months during which the experiments were performed.

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[1] The work was performed under the auspices of the United States Atomic Energy Commission.

[2] G. E. Challenger and B. J. Masters, THIS JOURNAL, **77**, 1063 (1955).

[3] R. J. Prestwood and A. C. Wahl, *ibid.*, **71**, 3137 (1949).

[4] G. Harbottle and R. W. Dodson, *ibid.*, **73**, 2442 (1951).

[5] T. J. Sworski, *ibid.*, **77**, 4689 (1955).

[6] Carl E. Johnson, Jr., *ibid.*, **74**, 959 (1952).

[7] K. G. Ashurst and W. C. E. Higginson, *J. Chem. Soc.*, 3044 (1953).

[8] C. R. Emigh and L. R. Megill, *Nondestructive Testing*, **11**, 30 (1953).

[9] T. J. Hardwick, *Disc. Faraday Soc.*, No. 12, 203 (1952).

Portions of both thallium stock solutions were labeled[10] with Tl^{204}.

Ferrous solutions used for dosimetry were made from J. T. Baker special ferrous ammonium sulfate Lot No. 111749.

Ceric solutions used for titration were made from G. Frederick Smith ceric ammonium sulfate. Solutions used for irradiation experiments were made from G. Frederick Smith ceric sulfate. All ceric solutions were standardized relative to permanganate and ferrous.

All other chemicals were of reagent quality and were used without further purification.

Reduction Yields.—The radiation-induced reduction of Tl^{+++} proved, in preliminary experiments, to be slow compared to the radiation-induced exchange. Reduction yields were therefore determined independently of the exchange measurements. Solutions containing varying amounts of thallic and thallous ions were irradiated for periods of time up to two hours, and with various X-ray intensities. The amount of thallic reduced to the thallous state was determined by titration with standardized Ce^{++++} as described earlier. The yield in terms of Tl^{+} ions produced per 100 e.v. absorbed (G_{Tl^+}) was calculated by comparing the reduction rate with the results obtained from the ferrous dosimeter.

"Thermal" Exchange Runs.—The solutions were made up from stock solutions of thallic sulfate, thallous sulfate and 0.8 *N* H_2SO_4. Calculated amounts of 0.8 *N* H_2SO_4 and one of the thallium fractions were mixed and allowed to come to temperature in the thermostat. The other fraction, also at the correct temperature, was then added. The first, or "zero time" sample was taken after the exchange solution was thoroughly mixed and equilibrated. Stirring was continued throughout the run. Five samples were taken at predetermined time intervals. In addition, a "complete exchange" sample was obtained by reducing a sample of solution completely to the Tl^{+} state with SO_2.

The thallium oxidation states were separated by the addition of chloroplatinic acid to the exchange solution samples. Insoluble thallous chloroplatinate was essentially quantitatively precipitated. The precipitate was collected on a tared filter paper, which was subsequently washed, dried, weighed and mounted on an aluminum plate. The Tl^{204} activity was determined with a β-γ proportional counter and an empirical self-absorption correction was applied. If the thallic fraction was to be counted, the supernatant liquid from the original precipitation was treated with SO_2, the excess of which was removed by boiling. The thallous ion produced by this treatment was precipitated as the chloroplatinate, then collected and counted as described above. The separation-induced exchange amounted to 2–3% at most, irrespective of which fraction was counted. No exchange was found between the supernatant Tl^{+++} and the precipitated thallous chloroplatinate, even after many hours.

Radiation-induced Exchange Runs.—In this case, the exchange solutions containing everything but the tagged thallium fraction were placed in the irradiation cell and allowed to equilibrate. Each run was started by adding the tagged constituent and turning on the X-ray machine after allowing 10–15 seconds for the solution to become thoroughly mixed by the magnetic stirrer. The X-ray machine was permitted to run for a carefully timed interval, usually from 2 to 10 minutes. After the machine was turned off, the thallous fraction was immediately precipitated with chloroplatinic acid, and the specific activity of the resulting thallous chloroplatinate sample was determined in the same manner as for the "thermal" exchange experiments. The radiation-induced exchange rate was calculated, applying corrections for the independently determined thallic reduction rate and for the "thermal" exchange rate contribution. The details are given in the following section.

Mathematical Treatment of Exchange Results.—The classical isotopic exchange law[11,12] may be written

$$R = -\frac{1}{v} \times \frac{ab}{a+b} \times \frac{\ln(1-F)}{t} \qquad (1)$$

in which R is the rate of the exchange reaction, a and b represent constant amounts of the two exchanging species homogeneously distributed throughout the constant volume v, and F is the fraction of complete exchange occurring in time t. Although this equation suffices for the "thermal" exchange runs, it is inadequate in the case of the irradiated exchange experiments because during the irradiations thallic ion is converted to thallous ion, so that the quantities a and b are not constant. The situation is further complicated by the fact that the radiation-induced exchange follows different kinetics from the "thermal" exchange, so that variations in a and b affect the two exchange paths in different ways. Recently, the mathematics of systems such as this have been investigated,[13] and two equations have been derived which are applicable to the radiation-induced exchange experiments. These equations are

$$\ln(1 - F_{Tl^{+++}}) = -kt([Tl^+]_0 + [Tl^{+++}]_0) + \frac{R_{xg}}{r} \ln \frac{[Tl^+]_0([Tl^{+++}]_0 - rt)}{[Tl^{+++}]_0([Tl^+]_0 + rt)} \qquad (2)$$

$$\ln(1 - F_{Tl^{+}}) = -kt([Tl^+]_0 + [Tl^{+++}]_0) + \left(\frac{R_{xg}}{r} + 1\right) \ln \frac{[Tl^+]_0([Tl^{+++}]_0 - rt)}{[Tl^{+++}]_0([Tl^+]_0 + rt)} \qquad (3)$$

The zero subscripts denote the initial concentrations of the two exchanging species; k is the independently determined bimolecular rate constant for the "thermal" exchange contribution; r is the net rate of reduction of Tl^{+++} to Tl^{+} occurring during the irradiation as measured in the reduction yield experiments previously mentioned. Either of these equations could be applied to the experimental data in order to calculate R_{xg}, which is defined here as the radiation-induced exchange rate. Equation 2 was applied whenever the change in specific activity of the Tl^{+++} component was the experimentally measured quantity, in which case $F_{Tl^{+++}}$ represented the fraction of complete exchange specific activity attained by the Tl^{+++} component at the time t. Alternatively, whenever the Tl^{+} component was counted, equation 3 was employed and $F_{Tl^{+}}$ represented the fraction of complete exchange specific activity attained by this component at the time t. Since it was experimentally simpler to count the Tl^{+} component, equation 3 was generally used in this work.

Note that R_{xg} was assumed to be constant throughout a given irradiation run. Although R_{xg} was subsequently found to vary approximately as the square root of the Tl^{+++} concentration, the variation during any given irradiated exchange run was so small (<1%) that this assumption is an excellent approximation.

Results and Discussion

Thallous Yield, G_{Tl^+}.—The determination of the reduction yields in X-ray irradiated thallium sulfate solutions proved to be more difficult than anticipated. In the first place, the rate of thallic ion reduction is quite slow at the irradiation intensities used in this study. Secondly, the reduction yield is, under certain conditions, somewhat dependent upon the irradiation intensity and upon the thallic and thallous concentrations. Fortunately, the exchange experiments were carried out in the range where the thallous yield dependence upon both dosage rate and solution composition was relatively small. Thus, for the conditions prevailing during these exchange studies, the thallous yield at 25° can be represented by the value of $G_{Tl^+} = 1.34 \pm 0.08$ ions/100 e.v. while for 0° irradiations a yield about 7% lower than this value was observed. Within experimental error, the thallic sulfate reduction yield in these solutions was approximately one-half the ceric sulfate reduction yield value of $G_{Ce^{+++}} = 2.93 \pm 0.15$ observed for identical irradiations of 0.8 *N* H_2SO_4 cerium solutions at 25°.

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[10] The authors are indebted to R. J. Prestwood of this Laboratory for supplying the Tl^{204} used in this work, and for suggesting the radiochemical procedures used for separation of the thallium oxidation states and for counting.

[11] H. A. C. McKay, *Nature*, **142**, 997 (1938).

[12] R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

[13] C. P. Luehr, C. E. Challenger and B. J. Masters, *ibid.*, **78**, 1314 (1956).

There is considerable evidence[14] that the radiation-induced reduction of ceric sulfate proceeds through some such mechanism as

$$2\mathrm{Ce}^{++++} + \mathrm{H_2O_2} \longrightarrow 2\mathrm{Ce}^{+++} + 2\mathrm{H}^+ + \mathrm{O_2} \qquad (4)$$
$$\mathrm{Ce}^{++++} + \mathrm{H} \longrightarrow \mathrm{Ce}^{+++} + \mathrm{H}^+ \qquad (5)$$
$$\mathrm{Ce}^{+++} + \mathrm{OH} \longrightarrow \mathrm{Ce}^{++++} + \mathrm{OH}^- \qquad (6)$$

The fact that a thallic sulfate reduction yield value very close to one-half the ceric sulfate reduction yield was observed in this study, suggests that perhaps a similar mechanism may be written to describe the thallic reduction process in these solutions for which G_{Tl^+} is relatively independent of variations in the thallium concentrations and in dosage rate. In the following equations, and throughout the rest of this paper, no attempt shall be made to differentiate between the various hydrolyzed and sulfate-complexed thallium species. Each oxidation state shall be represented simply as the free ion.

$$\mathrm{Tl}^{+++} + \mathrm{H_2O_2} \longrightarrow \mathrm{Tl}^+ + 2\mathrm{H}^+ + \mathrm{O_2} \qquad (7)$$
$$\mathrm{Tl}^{+++} + \mathrm{H} \longrightarrow \mathrm{Tl}^{++} + \mathrm{H}^+ \qquad (8)$$
$$\mathrm{Tl}^{++} + \mathrm{H} \longrightarrow \mathrm{Tl}^+ + \mathrm{H}^+ \qquad (9)$$
$$\mathrm{Tl}^+ + \mathrm{OH} \longrightarrow \mathrm{Tl}^{++} + \mathrm{OH}^- \qquad (10)$$
$$\mathrm{Tl}^{++} + \mathrm{OH} \longrightarrow \mathrm{Tl}^{+++} + \mathrm{OH}^- \qquad (11)$$

Although the existence of Tl^{++} is moot, further evidence will be presented which indirectly supports the contention that an appreciable steady-state concentration of Tl^{++} is built up in thallium exchange solutions undergoing irradiation. Furthermore, T. J. Sworski[5] reports an increase in $G_{\mathrm{Ce}^{+++}}$ in irradiated ceric sulfate solutions containing small amounts of Tl^+. This he explains on the basis of the reactions

$$\mathrm{Tl}^+ + \mathrm{OH} \longrightarrow \mathrm{Tl}^{++} + \mathrm{OH}^- \qquad (10)$$
$$\mathrm{Tl}^{++} + \mathrm{Ce}^{++++} \longrightarrow \mathrm{Ce}^{+++} + \mathrm{Tl}^{+++} \qquad (12)$$

with reaction (10) being much faster than reaction (6), so that each OH radical effectively reduces one ceric ion rather than oxidizing one cerous ion. The contention that (10) is faster than (6) has been confirmed[15] by the present authors, who have found that the presence of a small amount of Tl^+ almost completely (>90%) suppresses the radiation-induced conversion[2] of tagged cerous ions to the ceric state.

It should be noted that only a cursory investigation of the thallic reduction process has been made here, since this paper is primarily concerned with the Tl^+–Tl^{+++} exchange process occurring in these irradiated systems. No great departure from the average G_{Tl^+} value of 1.34 ions/100 e.v. was ever observed throughout the range over which the thallium concentrations were varied in the exchange studies. However, it should be mentioned that when a solution originally containing only thallium in the thallic state is irradiated at particularly low dosage rates, the initial thallic reduction yield value observed may be as high as ~3.0 ion/100 e.v. A possible explanation may be that the reaction step

$$\mathrm{OH} + \mathrm{OH} \longrightarrow \mathrm{H_2O_2} \qquad (13)$$

followed by reaction (7) may be of importance at extremely low thallous ion concentrations.

"Thermal" Tl^+–Tl^{+++} Exchange.—The results of the "thermal" exchange experiments are summarized in Table I, and in Figs. 1 and 2. The linear plot obtained in Fig. 1 indicates that, as in the cases of the other thallium exchange studies,[3,4] the reaction is first order in both Tl^{+++} and Tl^+. However, the bimolecular rate constant of k = 1.19 liter-mole^{-1} min.$^{-1}$ at 25° is considerably higher than that reported for $\mathrm{HClO_4}$ solutions of corresponding hydrogen ion concentrations.

In agreement with Prestwood and Wahl,[3] platinum metal was found to have an appreciable catalytic affect on the rate.

The value of 13.8 kcal./mole found for the activation energy may be compared with Harbottle and Dodson's[4] 14.7 kcal./mole value for $\mathrm{HClO_4}$ solutions. Prestwood and Wahl[3] calculate 17.6 and 10.3 kcal./mole for $\mathrm{HClO_4}$ solutions on the basis of the exchange occurring along two separate paths, and 16.0 kcal./mole for a nitrate-dependent path. Assuming bimolecular exchange between the two exchanging species, the entropy of activation in 0.8 N $\mathrm{H_2SO_4}$ solutions may be calculated.[16] The value obtained is −22 e.u., and may be compared with the values of −20 e.u. and of −32 e.u. reported for $\mathrm{HClO_4}$ solutions of somewhat greater acid concentration by Prestwood and Wahl and by Harbottle and Dodson, respectively.

It may probably be said, then, that the mechanism for the exchange in sulfuric acid solutions is not too much different from that in perchloric acid solutions.

Radiation-induced Tl^+–Tl^{+++} Exchange.—In Table II are presented the radiation-induced exchange rates observed over tenfold variations in thallous and in thallic ion concentrations, and over a twenty-five fold range in irradiation intensities. These exchange rate values have been corrected for both the thermal exchange contribution and the X-ray reduction of Tl^{+++} to Tl^+ occurring during the measurement. The relative magnitudes of these corrections should be noted: for the solution containing 0.00136 M Tl^+ and 0.00204 M Tl^{+++} irradiated at maximum X-ray intensity, the radiation-induced exchange rate observed was 209 μM/min.$^{-1}$; the net rate of thallic ion reduction during this irradiation was 8.2 μM/min.$^{-1}$ and the rate of thermal exchange occurring simultaneously in the solution was 3.30 μM/min.$^{-1}$.

One set of exchange experiments was performed at 0°, and an exchange rate equal to only about one-third the corresponding 25° exchange rate was found. This observed temperature coefficient is orders of magnitude greater than the small temperature coefficients normally found for radiation chemistry phenomena, and suggests that the radiation-induced Tl^+–Tl^{+++} exchange is considerably removed from any *direct* radiation effect.

Figure 3[17] illustrates the magnitude of the radiation-induced exchange, at constant exchange solu-

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(14) A. O. Allen, *Radiation Research*, 1, 85 (1954).

(15) B. J. Masters and G. E. Challenger, unpublished results.

(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 417.

(17) For the purposes of this plot, equation 3 was expanded in series to give the approximate equation $-\ln(1 - F_{\mathrm{Tl}^+}) \cong t(R_{\mathrm{xg}} + k[\mathrm{Tl}^+]_0[\mathrm{Tl}^{+++}]_0 + r)([\mathrm{Tl}^+]_0 + [\mathrm{Tl}^{+++}]_0)/[\mathrm{Tl}^+]_0[\mathrm{Tl}^{+++}]_0$. This approximation is valid only when rt and $([\mathrm{Tl}^+]_0 - [\mathrm{Tl}^{+++}]_0)$ are small, and must be used with caution.

TABLE I

Tl^{+++}–Tl^{+} EXCHANGE IN 0.8 N H_2SO_4

T (°C.)	$[Tl^+]$ (M) × 10^3	$[Tl^{+++}]$ (M) × 10^3	$t_{1/2}$ (min.)	Exchange rate (μM/min.)	k (liter-mole^{-1} min.$^{-1}$)
25.0	1.700	1.700	173	3.40	1.18
25.0	1.700	3.400	116	6.75	1.17
25.0	1.700	0.850	226	1.74	1.20
25.0	0.850	0.850	338	0.871	1.21
25.0	8.50	0.850	63.0	8.49	1.18
					Av. = 1.19 ± 0.01
0.0	1.700	1.700	1506	0.391	0.135
44.3	1.700	1.700	43.9	13.4	4.64
25.0[a]	0.850	0.850	252	1.17	1.62

[a] 25 cm.^{2} Pt gauze present in 240 ml. exchange solution.

TABLE II

RADIATION-INDUCED THALLIUM EXCHANGE

50 kvp. X-rays; 0.800 N H_2SO_4; 25° except where noted.

$[Tl^+]_0$ (M)	$[Tl^{+++}]_0$ (M)	I (e.v./l.·min.) × 10^{-20}	R_{xg} (μM/min.)	G_{xg} (ions/100 e.v.)	$k' = R_{xg}/[Tl^{+++}]_0^{0.503} \cdot I^{0.670}$ (mols$^{0.497}$·l.$^{0.173}$/e.v.$^{0.67}$·min.$^{0.330}$) × 10^{17}
0.00136	0.00204	3.94	209	31.9	7.47
		2.41	161	40.3	7.99
		1.63	128	47.4	8.29
		0.839	70.8	50.8	7.12
		0.412	48.3	70.5	7.85
		0.173	29.0	101	8.40
	0.00544	3.94	327	49.9	7.14
		1.63	182	67.3	7.19
		0.839	122	87.5	7.49
		0.412	64.8	94.6	6.39
		0.173	33.7	117	5.54
0.00680	0.00204	3.94	227	34.6	8.11
		1.63	124	45.9	7.99
		0.839	77.7	55.7	7.81
		0.412	51.0	74.5	8.29
		0.173	25.9	90.1	7.51
	0.00680	3.94	469	71.6	9.09
		1.63	243	89.9	8.56
		0.839	151	108	8.27
		0.412	84.5	123	7.47
		0.173	47.6	166	7.51
0.00136	0.00068	3.94	110	16.8	6.82
		1.63	65.8	24.3	7.40
		0.839	41.3	29.6	7.21
		0.412	26.2	38.3	7.37
		0.173	15.4	53.6	7.74
0.00068	0.00204	3.94	207	31.6	7.40
		1.63	120	44.4	7.74
		0.839	81.2	58.2	8.15
		0.412	47.3	69.1	7.67
		0.173	23.6	82.1	6.85
				(av. all 25° runs	7.61 ± 0.51)
0.00136	0.00204	3.94	68.2 (0°)	10.4	2.44

tion composition, as a function of irradiation intensity. Note that even at the lowest irradiation intensity the radiation-induced exchange rate is about ten times the thermal exchange rate.

In Fig. 4, the induced-exchange dependencies upon $[Tl^+]_0$ and $[Tl^{+++}]_0$ are illustrated. Each point plotted in this figure represents an average of all values found over the entire range of irradiation intensity variation. The total spread of these values is illustrated by the vertical limits assigned to each point. A zero-order dependency of the induced exchange rate upon thallous concentration is indicated, while the 0.503-order dependency upon thallic concentration has been determined by the method of least squares.

In Fig. 5, the exchange rate dependence upon irradiation intensity is shown. The results obtained at each irradiation intensity for all variations

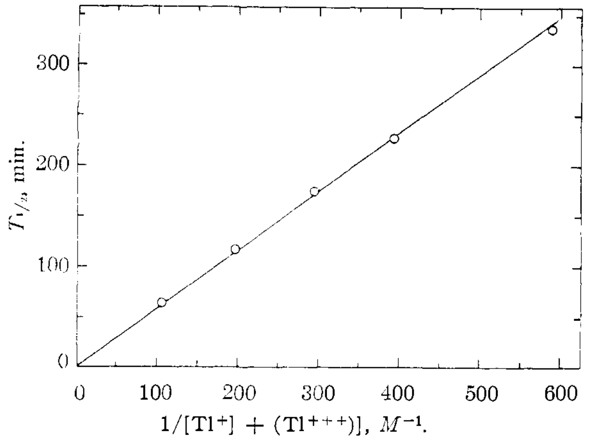

Fig. 1.—"Thermal" exchange half-time *versus* reciprocal total thallium concentration, 0.8 N H_2SO_4, 25°.

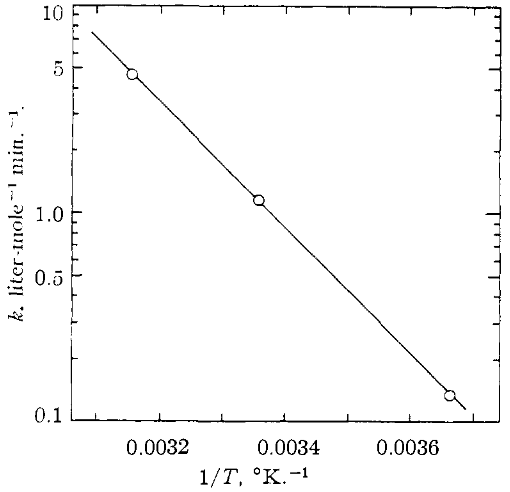

Fig. 2.—Temperature dependence of the "thermal" exchange, 0.8 N H_2SO_4: $[Tl^+] = [Tl^{+++}] = 0.00170$ M.

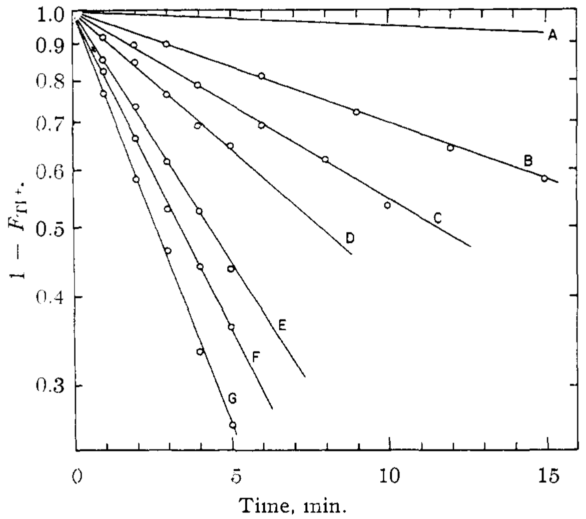

Fig. 3.—Effect of 50 kvp. X-rays upon Tl^+-Tl^{+++} exchange in 0.8 N H_2SO_4. $[Tl^+]_0 = 0.00136$ M; $[Tl^{+++}]_0 = 0.00204$ M; 25°. See footnote 17. Irradiation rates in e.v./l. min. are: A, non-irradiated ("thermal" exchange); B, 1.73 × 10^{19}; C, 4.12 × 10^{19}; D, 8.39 × 10^{19}; E, 1.63 × 10^{20}· F, 2.41 × 10^{20}; G, 3.94 × 10^{20}.

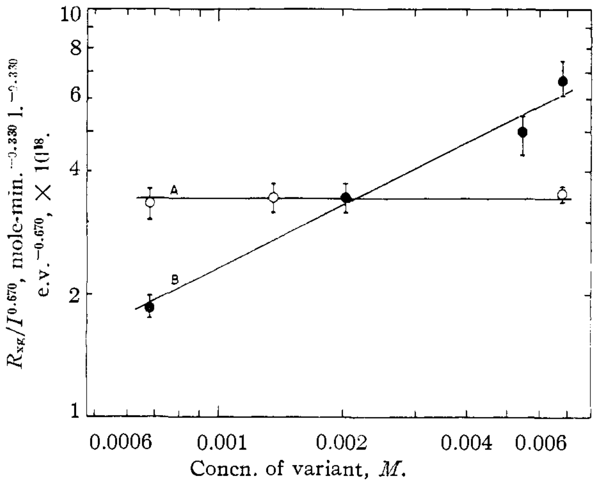

Fig. 4.—Induced exchange rate dependencies upon $[Tl^+]_0$ and $[Tl^{+++}]_0$, 25°: A, $[Tl^+]_0$ varied, $[Tl^{+++}]_0 = 0.00204$ M; B, $[Tl^{+++}]_0$ varied, $[Tl^+]_0 = 0.00136$ M.

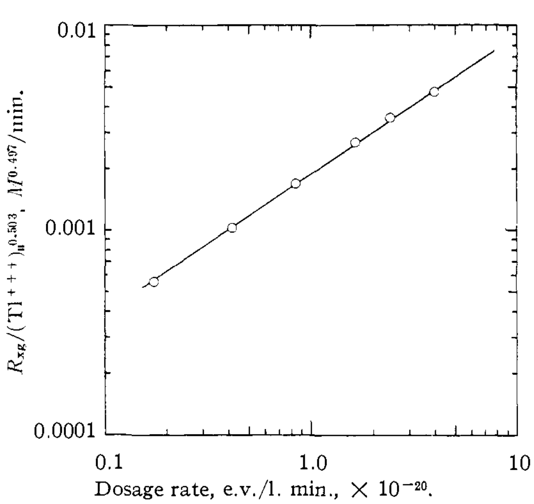

Fig. 5.—Induced exchange rate dependency upon irradiation intensity, 25°.

in $[Tl^+]_0$ and $[Tl^{+++}]_0$ have been averaged. The reaction order with respect to irradiation intensity has been found by the least squares method to be 0.670.

Referring again to Table II, it may be seen that, at least throughout the range of the present measurements, the radiation-induced exchange follows the empirical rate equation

$$R_{xg} = k'[Tl^{+++}]_0^{0.503} \times I^{0.670} \qquad (14)$$

with an average deviation less than 7%—about what we consider to be the experimental error.

It is believed that the close agreement between the observed reaction orders and the simple fractions $^1/_2$ and $^2/_3$ is fortuitous. In all probability, the exchange reaction proceeds through a very complex mechanism, possibly involving several parallel exchange paths, a number of radicals and intermediates, and various hydrolyzed and sulfate complexed thallium species. A quantitative interpretation of the present data cannot be undertaken without further information regarding the exact nature of the intermediate species possibly involved in the exchange mechanism.

However, the observed exchange results may be accounted for, at least in a qualitative manner, by assuming the following reactions to be of major importance in the over-all exchange mechanism

$$Tl^{++} + \overset{*}{Tl}{}^{+} \longrightarrow Tl^{+} + \overset{*}{Tl}{}^{++} \text{ (very rapid)} \quad (15)$$

$$\overset{*}{Tl}{}^{++} + Tl^{+++} \longrightarrow \overset{*}{Tl}{}^{+++} + Tl^{++} \text{ (slow, rate determining)} \quad (16)$$

$$2Tl^{++} \longrightarrow Tl^{+} + Tl^{+++} \text{ (chain terminating)} \quad (17)$$

Such a reaction scheme is particularly attractive because it involves only single electron transfers. Furthermore, the chain type character of this sequence is of value in explaining the very high G_{xg} values observed. From a coulombic-repulsion viewpoint (neglecting effects of complexing), it appears likely that reaction (15) might indeed be very much faster than reaction (16), and this assumption is consistent with the observed zero-order dependency of the exchange rate upon thallous ion concentration. Finally, the reaction sequence (15) to (17) is compatible with the mechanism proposed in the previous section for the radiation-induced reduction of Tl^{+++}.

Although it is entirely possible that simple catalysis of the Tl^{+}–Tl^{+++} thermal exchange by excited molecules or ions, or by sub-excitation electrons[18] could produce the large induced-exchange yields observed, it is difficult to reconcile such a catalytic effect with the observed zero-order thallous concentration dependence.

The effect of oxidizing and reducing impurities upon the induced-exchange system was investigated by means of independent experiments. Solutions containing labeled Tl^{+}, unlabeled Tl^{+++} and an added oxidizing or reducing agent were irradiated for short time intervals, after which the Tl^{+++}-fraction radioactivities were measured. The observed radiation-induced exchange rates are given in Table III. Ferrous, ferric, cerous and ceric ions were chosen as the additives for these experiments because they react slowly or not at all with Tl^{+} and Tl^{+++} under the prevailing conditions. It is evident from Table III that all of these additives are very effective in interfering with the induced thallium exchange mechanism. It seems probable that the major effect of these inhibitors is to decrease the steady-state Tl^{++} concentration, either by reacting rapidly with H and OH in competition with equations 8 and 10, or by reacting with the Tl^{++} species itself to terminate the exchange chain.

TABLE III

RADIATION-INDUCED THALLIUM EXCHANGE WITH ADDITIVES PRESENT

$[Tl^{+}]_0$ = 0.00136 M, $[Tl^{+++}]_0$ = 0.00204 M, 0.800 N H_2SO_4; initial concentrations of all additives: 0.00167 M. All solutions irradiated at 25° with 50 kvp. X-rays, 3.94×10^{20} e.v. $l.^{-1}$ $min.^{-1}$.

Additive	R_{xg} (μM/min.)	G_{xg} (ions/100 e.v.)
None	210	32.0
Fe^{++}	1.3	0.2
Fe^{+++}	24.5	3.7
Ce^{++++}	11.6	1.8
Ce^{+++}	20.5	3.1

Chemically-induced Tl^{+}–Tl^{+++} Exchange.—The possibility that H_2O_2 simultaneously produced in the irradiated system might itself induce Tl^{+}–Tl^{+++} exchange was eliminated by independent experiments performed in the absence of external radiation. Solutions containing unlabeled Tl^{+++} and labeled Tl^{+}, originally in a concentration ratio of three to one, were titrated very slowly with dilute H_2O_2 until this ratio was approximately reversed. When the thallic fractions were subsequently counted, no active Tl^{+++} was found in excess of the amount to be expected from the ordinary thermal exchange contribution.

Several attempts were made to generate Tl^{++} chemically in unirradiated Tl^{+}–$\overset{*}{Tl}{}^{+++}$ solutions in order to determine whether induced exchange could be initiated in this manner. Very dilute solutions of one-electron oxidizing and reducing agents (Ce^{++++}, Fe^{++}, $Fe(CN)_6^{\equiv}$, Cr^{++}, Ti^{+++} and Co^{+++}) were run slowly into the thermally exchanging solutions and the effects upon the exchange rate were noted. In the case of the ceric, ferrous and cobaltic additions, no increase in the thermal exchange rate was noted. However, the reduction of Tl^{+++} by Fe^{++} and the oxidation of Tl^{+} by Ce^{++++} and by Co^{+++} proceed very slowly in 0.8 N H_2SO_4. It appears doubtful that an appreciable concentration of Tl^{++} could have been built up in these solutions containing relatively large amounts of unreacted oxidizing or reducing agent, particularly in view of the inhibiting action of Fe^{++} and Ce^{++++} noted in the foregoing radiation-induced exchange experiments. A very slight increase in the thermal $\overset{*}{Tl}{}^{+}$–Tl^{+++} exchange rate actually may have occurred during the experiments in which chromous and titanous salts were added to the exchange solutions; however, the observed effect only barely exceeded the estimated experimental error. Both Cr^{++} and Ti^{+++} appear to react fairly rapidly with Tl^{+++}, but there is no assurance that the reduction proceeds through the Tl^{++} state, so that the small induced-exchange effect found in these experiments neither confirms nor denies the validity of equations 15–17. On the other hand, a rapid reduction of Tl^{+++} was found to occur, accompanied by about a forty-fold increase in the thermal $\overset{*}{Tl}{}^{+}$–Tl^{+++} exchange rate, when an amount of ferrocyanide ion equivalent to about one-half of the Tl^{+++} present was added very slowly in the form of a dilute solution. This result is somewhat obscured by the possibility that complex ion formation in the system might have affected the thermal exchange rate, and by the fact that an insoluble precipitate (presumed to be thallic ferricyanide) was formed. However, when the same amount of ferrocyanide was added rapidly as a relatively concentrated solution, the observed increase in thermal exchange was only about ten-fold. This result appears to be consistent with the postulated induced exchange mechanism. Termination of the exchange chain *via* equation 17, or through removal of Tl^{++} by reaction with $Fe(CN)_6^{\equiv}$, presumably would occur earlier in the chain

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(18) R. L. Platzman, *Radiation Research*, **2**, 1 (1955).

sequence during the fast addition of concentrated ferrocyanide than in the case of slow addition of the dilute reducing agent.

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[Contribution from the Department of Chemistry of the State University of Iowa]

Praseodymium Oxides. III. The Heats of Formation of Several Oxides[1]

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Several stable oxides were prepared, including four of non-stoichiometric composition, and their heat of solution measured in an adiabatic microcalorimeter. The molal heats of reaction at 25° in 6.00 M HNO_3 of $PrO_{1.500}$ (A form), $PrO_{1.703}$, $PrO_{1.717}$, $PrO_{1.804}$ and $PrO_{1.833}$ were found to be -53.5 ± 0.1, -47.9 ± 0.1, -47.4 ± 0.4, -44.9 ± 0.1 and -43.8 ± 0.1 kcal., respectively. These values when combined with other data yielded the corresponding molal heats of formation for PrO_x of -217.9 ± 0.8, -223.5 ± 0.8, -224.0 ± 0.9, -226.5 ± 0.8 and -227.6 ± 0.8 kcal. mole^{-1}.

Ferguson, Guth and Eyring[2] have made a phase study of the praseodymium oxide system. This study was extended by Guth, Holden, Baenziger and Eyring[3] to include X-ray and differential thermal analyses. These studies revealed several stable oxides of non-stoichiometric composition intermediate to $PrO_{1.50}$ and $PrO_{2.00}$. The most interesting of these compounds have the empirical formulas $PrO_{1.703}$, $PrO_{1.717}$, $PrO_{1.804}$ and $PrO_{1.833}$.

It was desired to know the heat of formation and the integral heats of oxidation of these interesting non-stoichiometric oxide phases but the thermochemical data which would permit such calculations were not available.

Existing thermochemical data supplemented with the measured heats of reaction of these oxides with nitric acid solutions make possible the desired calculations. The heat of transition of $PrO_{1.50}$ from the hexagonal to the body centered cubic lattice is also calculable from the heat of reaction measurements.

The data were obtained using the adiabatic microcalorimeter described in a previous paper.[4]

Experimental Methods

Preparation and Properties of the Oxides.—The starting material for the preparation of all the samples was Pr_6O_{11} (99.9+ % pure) obtained from the Ames Laboratories, Ames, Iowa. The oxygen used was obtained from the thermal decomposition of $KMnO_4$ as previously described.[2] The atomic weight of praseodymium used was 140.92, and the defined calorie was assumed equal to 4.1840 absolute joules.

The conditions for preparation of the oxides and a full description of the apparatus used are given by Ferguson, Guth and Eyring.[2] Each oxide was quenched[3] after equilibrium was established at the predetermined pressure and temperature in order to freeze the oxide at a specific composition. The exact composition was determined by weight change. All the praseodymium oxides dissolve in nitric acid to produce the trivalent praseodymium ion in solution.

In general, the oxides prepared at low temperatures dissolved more readily than those prepared at higher temperatures, probably because of different particle size and degree of ordering in the crystal.

The composition of the calorimeter samples together with their color and lattice properties are tabulated in Table I.

Table I

Physical Properties of the Calorimeter Samples

Oxide	Color	Lattice	Lattice constants (Å.)
$PrO_{1.500}$	Yellow-green	Hexagonal	3.859 ± 0.003; 6.008 ± 0.003
$PrO_{1.703}$	Brown	Body centered cubic	11.055 ± 0.005
$PrO_{1.717}$	Brown	Rhombohedral	11.02; 89°40′[a]
$PrO_{1.804}$	Brown	Face centered cubic	5.482 ± 0.003
$PrO_{1.833}$	Black	Face centered cubic	5.468 ± 0.002

[a] Cell dimensions not determined by analytical extrapolation method.

Results

Heats of Reaction.—The enthalpy change upon reaction of the various oxides of praseodymium with oxygen saturated 6.00 M HNO_3 were determined in the microcalorimeter and are tabulated in Table II. It was apparent that a small concentration of Na_2SiF_6 did not significantly affect the heat of reaction of the oxides with 6.00 M HNO_3 as shown by the results obtained for $PrO_{1.703}$, Table II. The absence of a heat effect above experimental error upon addition of the complexing agent is probably due to a cancellation of terms.

The samples were weighed with an Ainsworth FDJ, Optical lever, microbalance (sensitivity: 2.5 micrograms per division). The enthalpy change was not corrected for the vaporization of water into the liberated oxygen because this correction (about 0.04 kilocalorie per mole for $PrO_{1.833}$) is small compared to the experimental error.

The reaction which occurred in the calorimeter may be represented by equation 1

$$PrO_x(c) + yHNO_3 \cdot zH_2O = Pr(NO_3)_3 \cdot (y - 3)HNO_3 \cdot (z + 3/2)H_2O + {}^1/_2(x - 3/2)O_2(g) \qquad (1)$$

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[1] These data were reported at the 126th meeting of the American Chemical Society at New York City in September, 1954, and were included in a dissertation submitted by C. T. Stubblefield to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree. The work was supported by the Atomic Energy Commission through the Research Contracts Division.

[2] R. Ferguson, E. Daniel Guth and L. Eyring, This Journal, **76**, 3890 (1954).

[3] E. Daniel Guth, J. R. Holden, N. C. Baenziger and L. Eyring, *ibid.*, **76**, 5239 (1954).

[4] G. Machlan, C. T. Stubblefield and L. Eyring, *ibid.*, **77**, 2975 (1955).