It would appear, however, that the absence of rings and quaternary carbons in phthioic acid has hardly been demonstrated.

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THE EXCHANGE REACTION BETWEEN THE TWO OXIDATION STATES OF THALLIUM IN PERCHLORIC ACID SOLUTIONS

Sir:

We have studied the exchange reaction between thallous and thallic ions in aqueous perchloric acid and wish to make a preliminary report of the results. This reaction is of interest in that it involves transfer of two electrons between the reacting species and in that it is found to proceed at a slow and measurable rate, in contrast to the several other electron-transfer exchange reactions which have been reported to be fast.[1] Earlier studies of this reaction[2,3] were handicapped by the short half-life of the radioactive tracer used (ThC″, half-life 3.1 min.) and gave results which are difficult to interpret.

Using $Tl^{204,206}$ (half-life *ca.* 3 years), we have observed the exchange reaction and have investigated the dependence of the rate of exchange on the concentrations of thallous and thallic perchlorates, on the acid concentration, and on the temperature. The thallous perchlorate concentration was varied from 0.003 f. to 0.015 f., that of thallic perchlorate from 0.0006 f. to 0.003 f.

The method employed was to mix stock solutions of active thallic perchlorate and inactive thallous perchlorate in a stoppered flask immersed in a constant temperature bath, to withdraw samples at intervals, and to determine the distribution of activity between the two oxidation states of thallium. Thallous chromate was precipitated from the sample by the addition of a mixture containing chromate, cyanide, ethanol and excess ammonia. This method was found to give a reasonably clean separation, and not to induce a significant amount of exchange during precipitation.

The activity in the thallous fraction was found to vary with time in the simple exponential manner expected for an exchange reaction occurring at chemical equilibrium.[4,5] The rate of exchange was found to be proportional to the first power of the concentration of each reactant. The specific rate constant is 2.0 moles^{-1} liter hours^{-1} at 49.5° (perchloric acid 0.4 f.). The experimental activation energy is 12 kcal./mole. The addition of a neutral salt ($LiClO_4$ 0.6 f.) increased the rate, suggesting that ions of like sign participate in the exchange.

When the acid concentration was varied, the rate constant showed a maximum at about 1 f. ($k = 2.5$) and decreased to 0.9 at 3.9 f. This behavior doubtless results from the combined effects of ionic strength and hydrolysis of thallic ion.

We have also observed the exchange in 0.2 f. hydrochloric acid and find that the rate is markedly greater than in perchloric acid.

We are continuing these studies.

We are grateful to the Los Alamos Laboratory, in particular to Mr. J. W. Starner and Mr. E. L. Bentzen, for neutron irradiation of the thallium. We also are indebted to Dr. Norman Davidson for his interest and helpful advice.

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(1) See for example G. T. Seaborg, *Chem. Rev.*, **27**, 199 (1940).

(2) J. Zirkler, *Z. Physik*, **99**, 669 (1936), *et al.*

(3) V. Majer, *Z. physik Chem.*, **A179**, 51 (1937).

(4) H. A. C. McKay, *Nature*, **142**, 997 (1938).

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

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EXCHANGE REACTION BETWEEN THALLIUM (I) AND THALLIUM (III) IONS IN PERCHLORIC AND NITRIC ACID SOLUTIONS

Sir:

We have measured the rate of the exchange reaction between thallium(I) and thallium(III) ions in aqueous solutions of perchloric and nitric acid and have found it to be slow and measurable. The data from earlier work[1,2] on this reaction are difficult to interpret because the short lived tracer, ThC″ (3.1 m.), limited the duration of the experiments.

Part of the $Tl^{204,206}$ (*ca.* 3.5 y) used as tracer in our experiments was prepared by the $Tl(d, p)$ reaction in the Washington University cyclotron, the rest by the $Tl(n,\gamma)$ reaction in the Oak Ridge pile. Our procedure was to mix acid solutions of thallium (I) perchlorate (nitrate) and active thallium (III) perchlorate (nitrate), remove aliquots at definite intervals of time, separate the two oxidation states, and assay and count the two fractions. Two methods of separation were used. (1) Thallium (III) hydroxide was precipitated with ammonium hydroxide; both fractions being subsequently weighed and counted as thallium (I) chromate. (2) Thallium (I) bromide was precipitated with sodium bromide solution, both fractions being weighed and counted as thallium (I) bromide.

A fast, incomplete, but reproducible exchange was induced at the time of separation. The induced exchange (exchange measured at zero time) could be varied from 45 to 70% for the hydroxide separation and from 8 to 13% for the bromide separation by adding the reagents in a different

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(1) J. Zirkler, *Z. Physik*, **87**, 410 (1934); **98**, 75 (1935); **99**, 669 (1936); *Z. physik Chem.*, **A187**, 103 (1940).

(2) V. Majer, *ibid.*, **A179**, 51 (1937).