

SALT EFFECTS ON THE RATE OF EXCHANGE OF THALLOUS AND THALLIC IONS IN WATER AND HEAVY WATER

PART 2.—THE EFFECT OF CHLORIDE ON THE SOLVENT REACTION *

BY S. GILKS, T. E. ROGERS AND GWYNETH M. WAIND †
Queen Mary College, University of London, London, E.1

Received 13th February, 1961

The chloride inhibition and catalysis of the thallos-thallic electron-exchange reaction in concentrated perchlorate solutions has been measured in water and in heavy water. In the range of chloride ion concentration in which this ion is a catalyst for the exchange reaction, there is no kinetic deuterium isotope effect. From spectroscopic observations it is concluded that chloride and bromide ions form inner-sphere co-ordination complexes with thallic ions, whereas the sulphate ion forms an outer-sphere complex. The inner-sphere complex TlCl^{2+} does not undergo electron exchange with the thallos ion whereas the sulphate outer-sphere complex does so. The opposite kinetic effects of sulphate and of perchlorate ions are also discussed. It is suggested that polyvalent oxy-anions may function as proton acceptors in reactive ion-pairs.

The rate of the thallos-thallic electron-transfer reaction in perchlorate solutions is first-order in each of the ions and also depends on the availability of solvent (water) molecules.^{1, 2} Large changes in the rate are, however, found in solutions containing other anions.² The present study is an attempt to use either the presence or absence of a kinetic deuterium isotope effect, or the tendency of anions to form either covalent complexes or ion-pairs with the thallic ion, as a means of deciding in which systems water molecules are an important constituent of the activated complex.

EXPERIMENTAL

MATERIALS

These were obtained, purified and standardized, as described elsewhere.^{1, 3}

RATES OF EXCHANGE

Rates of exchange were followed (using ^{204}Tl) at $25 \pm 0.01^\circ\text{C}$ by precipitating thallos ion as the chloroplatinate. Details of the apparatus and procedure are given in part 1.¹ Bimolecular rate constants were calculated in the usual way.⁴ The ionic strengths of the solutions were adjusted with sodium perchlorate. Chloride ion was added as sodium chloride.

SPECTROPHOTOMETRIC MEASUREMENTS

These were made with an Optica spectrophotometer fitted with a thermostatted cell-carriage.³

RESULTS

EXCHANGE RATES

The effect of chloride on the exchange rate in water and in 80 % heavy water is shown in fig. 1*a*, 1*b* and 2. Fig. 2 includes unpublished results of other workers⁵

* part 1, Gilks and Waind, *Disc. Faraday Soc.*, 1960, **29**, 102.

† present and permanent address: Department of Inorganic Chemistry, University of Copenhagen, at. Chemistry Department A, Sølvgade 83, Copenhagen K, Denmark.

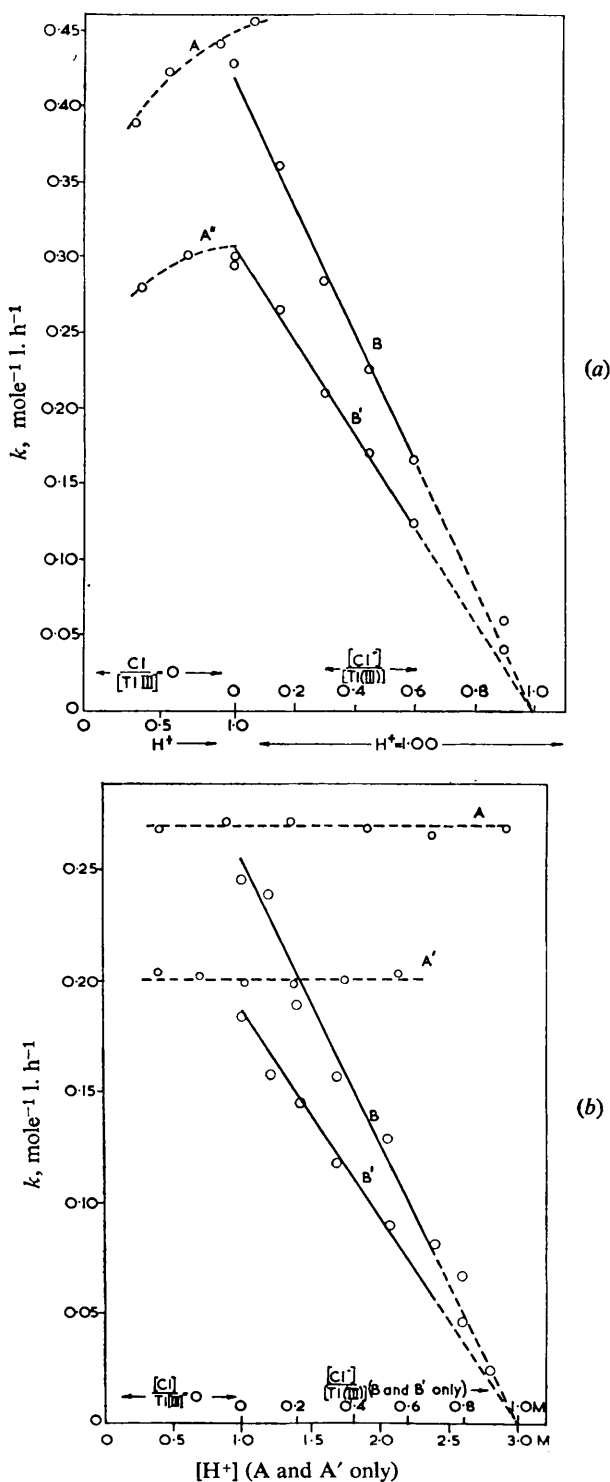


FIG. 1a.—The effect of small concentrations of chloride ions on the rate of thallic-thallos exchange in water (A and B) and in 80 % heavy water (A' and B'); 25°C $[\text{Tl(III)}]_{\text{formal}} = 7.70 \times 10^{-3}$; $[\text{Tl(I)}]_{\text{formal}} = 2.01 \times 10^{-2}$. Fig. 1a: ionic strength 1.2 with sodium perchlorate. Fig. 1b: ionic strength 3.0 with sodium perchlorate.

which were obtained by a different experimental technique. The initial inhibition at low chloride concentrations followed by the large increase at higher chloride concentrations has been previously found both in perchloric⁶ and in sulphuric acid⁷ solutions. Fig. 1*a* and 1*b* show that in water and in the heavy-water mixture, the effect of small concentrations of chloride is to quantitatively (i.e., within the experimental error of about $\pm 2\%$) remove thallic ions from the reaction. Above a ratio of about 1.5 of [chloride]/[thallium(III)], the reaction rate increases steeply and in a manner which has been attributed⁶ to reaction between chloride complexes of Tl(III) and Tl(I) which rearrange on contact forming symmetrical chloride bridged reaction intermediates. Fig. 2 shows clearly that in this range there is no kinetic deuterium isotope effect.

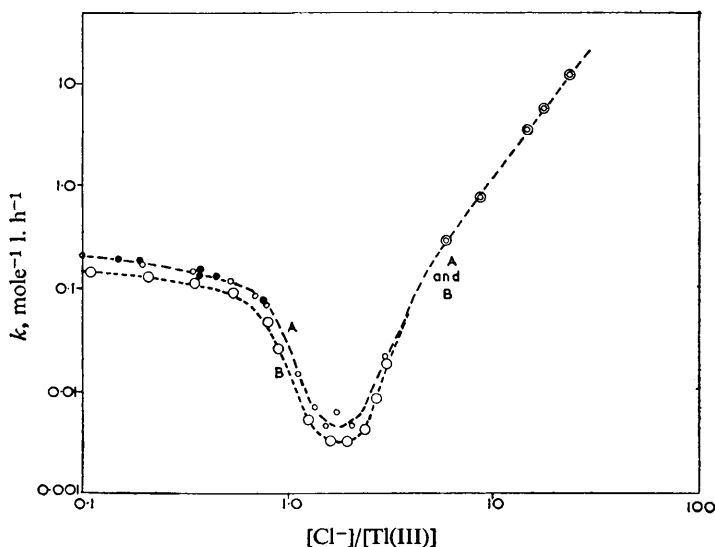


FIG. 2.—The effect of sodium chloride on the rate of thallos-thallic exchange in water (A) and in 80 % heavy water (B); 25°C, HClO_4 or $\text{DClO}_4 = 1.00 \text{ M}$; ionic strength 3.00 with sodium perchlorate. $[\text{Cl}]_{\text{total}}/[\text{Tl(III)}]_{\text{total}} < 2.0$; $[\text{Tl(III)}]_{\text{total}} = 7.70 \times 10^{-3}$; $[\text{Tl(I)}]_{\text{total}} = 2.01 \times 10^{-2} \text{ M}$. $[\text{Cl}]_{\text{total}}/[\text{Tl(III)}]_{\text{total}} > 2.0$; $[\text{Tl(III)}]_{\text{total}} = 5.38 \times 10^{-3}$; $[\text{Tl(I)}]_{\text{total}} = 1.00 \times 10^{-3} \text{ M}$.

● Roig and Dodson

ABSORPTION SPECTRA

Fig. 3 shows that addition of sodium chloride to a solution of thallic perchlorate markedly affects the absorption. This has been detected at the long wave-length edge of the bands by earlier workers.^{6, 8} As the absorbance of the solutions increased linearly with [chloride]/[thallium(III)] ratios below 1.0, and as the association constant for TlCl_2^+ is very large,⁸ the concentrations of free chloride could be neglected and the extinction curve for TlCl_2^+ ($\epsilon_{\text{max}} = 7.28 \times 10^3$, $\lambda_{\text{max}} = 210 \text{ m}\mu$) was therefore calculated. At 230 $\text{m}\mu$ the value calculated for $\epsilon_{\text{TlCl}_2^+}$ is $2.2 \times 10^3 \text{ l. cm}^{-1} \text{ moles}^{-1}$ which is in reasonable agreement with the figure of 2.46×10^3 quoted by Peschanski⁸ for this wavelength at 21°C. Small concentrations of sodium bromide produced a similar effect which was attributed to the absorbance of TlBr_2^+ ($\lambda_{\text{max}} 217 \text{ m}\mu$, $\epsilon_{\text{max}} 1 \times 10^4$). The addition of sodium fluoride to thallic perchlorate solutions produced no effect on the absorbance over the range of wavelengths studied (185 to 230 $\text{m}\mu$).

Although the order of decreasing bathochromic shift with bromide and chloride ions is that expected from the effect of the decrease in the electron affinity of the

anion on the energy for a transition in which an electron is transferred from the anion to the cation, the correlation between the maxima reported here and the calculated values using the treatment that has been successfully applied to ferric-halide complexes,⁹ is not quantitative. This gives support to the suggestion of Leden and Chatt¹⁰ that in thallic-halide complexes, as also in halide complexes of ions of other metals near the end of the transition series, the bonds have appreciable covalent character. The differences in the absorption of these complexes is therefore that expected if their formation involves substitution in the first co-ordinated sphere of water molecules of the thallic aquo ions.

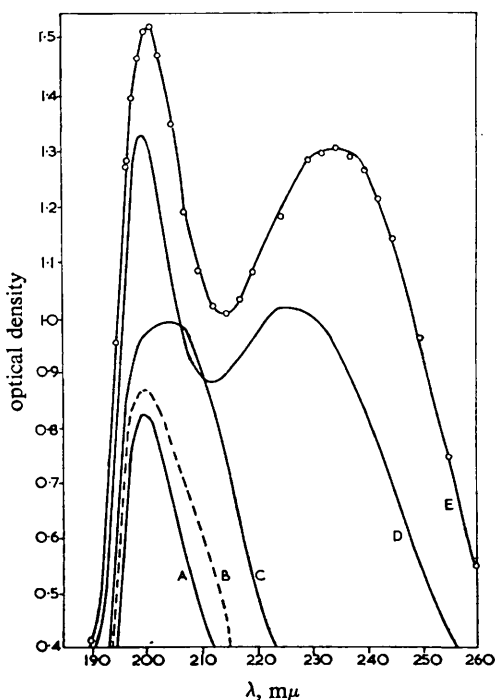


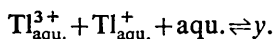
FIG. 3.—The effect of sodium chloride on the ultra-violet absorption of thallic perchlorate in 3.00 M perchloric acid at 25°C. $[\text{Cl}]_{\text{total}}/[\text{Tl(III)}]_{\text{total}} = 0$ (A); $= 0.115$ (B); $= 0.461$ (C); $= 2.77$ (D); $= 4.60$ (E). $[\text{Tl(III)}]_{\text{total}} = 2.16 \times 10^{-4}$ M.

Fig. 4 shows that the addition of sodium sulphate to thallium perchlorate in perchloric acid has little effect on the absorption. The concentration of "free" sulphate ions was calculated by combining the results of Ashurst and Higginson¹¹ for the first dissociation constant of HSO_4^- with those of earlier workers.¹² It is relevant here that in solutions in which the ratio $[\text{SO}_4^{2-}]_{\text{free}}/[\text{Tl(III)}]$ is one (ionic strength = 3.3) the rate of the thallos-thallic exchange is about 20 times that in the absence of sulphate,¹³ and that both electrometric titrations¹⁴ and the increased solubility of thallic hydroxide in sodium sulphate solutions^{15, 16} have been interpreted in terms of thallic sulphate complexing. It was also found that the absorbance of a solution of 2.16×10^{-4} M thallic perchlorate in 3 M perchloric acid containing 0.99×10^{-4} M thallos ions and with a formal concentration of SO_4^{2-} of 2.16×10^{-4} M, equalled that of the sum of the absorbances of solutions containing the same concentration of thallos and thallic salts measured separately. It was therefore concluded that the mono-sulphato thallium(III) complex has an absorption profile similar to that of the uncomplexed metal aquo ion and that there is no evidence for interaction absorption in these solutions.

DISCUSSION

The absence of a kinetic deuterium isotope effect at high chloride concentrations supports the suggestion of earlier workers, that in these solutions electron exchange occurs between thalious and thallic chloride complexes. The results of the spectrophotometric measurements are consistent with this.

In perchlorate solutions, however, it has been previously shown¹⁷ that not only is the rate of exchange slower in heavy water but also that the reaction between the aquo ions can be represented by



The deuterium isotope effect on the sulphate-catalyzed paths is not known, but the lack of modification of the absorption band of the thallic aquo ion, together with the catalysis of the exchange reaction at low sulphate concentrations, suggests

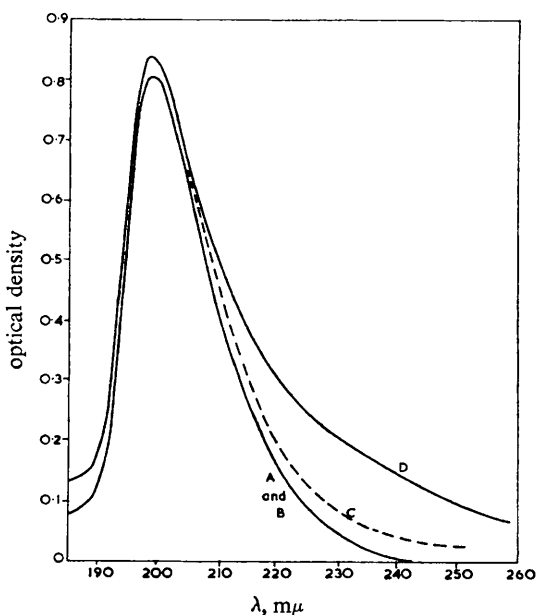


FIG. 4.—The effect of sodium sulphate on the ultra-violet absorption of thallic perchlorate in 3.00 M perchloric acid at 25°C. $[\text{SO}_4^{2-}]_{\text{free}}/[\text{Ti(III)}]_{\text{total}} = 0.01$ (A); $= 0.15$ (B); $= 1.0$ (C); $= 7.0$ (D). $[\text{Ti(III)}]_{\text{total}} = 2.16 \times 10^{-4}$ M.

that in the transition state γ sulphate ions are separated from thallic ions by water molecules. Inclusion of sulphate ions may thus result in a transition state similar to that above but formed from a thallic ion-pair. It is also known that changes in hydrogen-ion concentration have no marked effect on the exchange rate except at very high perchlorate concentrations where there is also evidence for perchlorate association.³ This means that if the formation of a species in which electron transfer can occur requires acid dissociation of the thallic aquo ion, as has been suggested for other systems,¹⁸⁻²⁰ then such hydrolysis must be restricted to the transition state. It is relevant here that for the chromic-chromous electron-exchange reaction the suggestion has been made that the specific effects of anions which are co-ordinated to the water of the chromic aquo ion may be related to their basicities.²¹ This receives some support from the results of sound absorption measurements which have shown that for some bivalent sulphates not

only does the decomposition and formation of hydration shells occur in discrete stages but that intermediate hydrolysis may occur during these.²² The role of outer-sphere anions seems worthy of further discussion as the possibility that basic anions such as sulphate may react in the transition state through structures such as $\text{TlOH}^{2+}(\text{HOH})_n\text{HSO}_4^-$ (cf. ref. (23)) also suggests an experimentally verifiable relationship between their catalytic effects and the corresponding stability constants of the thallic ion-pairs. Only after allowance for differences in these, and if the extent of interaction is very little altered by the inclusion of the thallos ion, would a correlation between the specific catalytic constants and basicity be expected. Although a qualitative relation between the rate of electron exchange induced substitution of the chromium(III) aquo ion and the stability constants of the product complexes of Cr^{3+} has recently been reported²⁴ there is at present insufficient data to enable the above relationships to be tested quantitatively, either for this reaction or for the thallos-thallic exchange.

Two of us (T. E. R.) and (S. W. G.) wish to acknowledge maintenance grants from the D.S.I.R.)

- 1 Gilks and Waind, *Disc. Faraday Soc.*, 1960, **29**, 102.
- 2 Taube, *Adv. Inorg. Chemistry and Radio-activity*, ed. Emeleus and Sharpe (Academic Press, New York, 1959), p. 42.
- 3 Rogers and Waind, submitted for publication. Rogers, *Ph.D. Thesis* (London, 1960).
- 4 McKay, *Nature*, 1939, **142**, 997.
- 5 Dodson and Roig, unpublished work at Brookhaven National Laboratory.
- 6 Harbottle and Dodson, *J. Amer. Chem. Soc.*, 1951, **73**, 2442.
- 7 Brubaker, Groves, Michel and Knop, *J. Amer. Chem. Soc.*, 1957, **79**, 4641.
- 8 Peschanski and Valladas-Dubois, *Bull. Soc. Chim.*, 1956, 1170.
- 9 Evans and Uri, *Symp. Soc. Expt. Biol.*, 1951, **5**, 130.
- 10 Leden and Chatt, *J. Chem. Soc.*, 1955, 2936.
- 11 Ashurst and Higginson, *J. Chem. Soc.*, 1956, 343.
- 12 Brag and Liebhaufsky, *J. Amer. Chem. Soc.*, 1935, **57**, 51.
- 13 Wiles, *Can. J. Chem.*, 1958, **36**, 167.
- 14 Moeller, *J. Amer. Chem. Soc.*, 1953, **75**, 4852.
- 15 Sherrill and Haas, *J. Amer. Chem. Soc.*, 1936, **58**, 953.
- 16 Benoit, *Bull. Soc. Chim.*, 1949, 518.
- 17 Waind, *Disc. Faraday Soc.*, 1960, **29**, 136.
- 18 Dodson and Davidson, *J. Physic. Chem.*, 1952, **56**, 866. Hudis, *J. Physic. Chem.*, 1960, **11**, 1766.
- 19 Reynolds and Lumry, *J. Chem. Physics*, 1955, **23**, 2360.
- 20 Taube, ref. (2), and *Can. J. Chem.*, 1959, **37**, 135.
- 21 Connick, *J. Physic. Chem.*, 1942, **56**, 37.
- 22 Eigen, *Disc. Faraday Soc.*, 1957, **24**, 25.
- 23 Robinson and Harned, *Chem. Rev.*, 1941, **28**, 419.
- 24 Hunt and Early, *J. Amer. Chem. Soc.*, 1960, **20**, 5312.