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Separation and Identification of Chlorocomplexes of Technetium(IV) formed in Hydrochloric Acid Solutions

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The chemical behavior of $TcCl_6^{2-}$ in HCl solutions of different concentrations has been investigated. It was confirmed that $TcCl_6^{2-}$ is sensitive to ultraviolet and visual light, giving a series of aquated species the quantities of which depend on the HCl concentration. Those technetium(IV) chlorocomplexes were isolated by means of ion-exchange and paper electrophoresis, and the composition of each species was determined by measuring the Cl/Tc ratio and the charge per species. The absorption spectra of isolated species were also measured.

A number of compounds of technetium are known for the valency states from +7 to −1.[1-3] In the field of the solution chemistry of technetium, the chemical behavior of pertechnetate(VII) ion has been investigated more extensively than the chemical species of any other valency state.

The lower oxidation states of technetium which result from the pertechnetate ion by the reduction have not been quantitatively investigated except for their reactions with special analytical reagents[4] and their magnetic properties.[5] The pertechnetate ion is gradually reduced to lower valency states by halides in acidic solution.[1] Lederer *et al.* have qualitatively investigated the reduction products of pertechnetate by chloride and bromide by separating them by means of paper chromatography.[6] In a previous communication[7] it was pointed out, on the basis of an analysis of the change of its absorption spectra, that hexachlorotechnetate(IV) underwent a photochemical aquation associated with a small quantity of oxidation in hydrochloric acid solution.

The present work will deal with the quantitative details of technetium(IV) chlorocomplex formation in hydrochloric acid solution. K_2TcCl_6 obtained by reducing the pertechnetate ion was dissolved in hydrochloric acid solutions of various concentrations. The experiments have proved that several new technetium chlorocomplexes are formed, step by step, during the aquation. These complexes were separated from each other by means of ion exchange, and the ratios of technetium to chloride were determined by analysing them. The electrical charges of the complex ions were determined by the ion-exchange equilibrium method.[8,9]

From the results obtained, the photo-aquation of $TcCl_6^{2-}$(1) is regarded as the main sequence in the formation of a variety of aquo-chlorocomplexes:

$$TcCl_6^{2-} + xH_2O \rightleftarrows TcCl_{6-x}(H_2O)_x^{(2-x)-} + xCl^- \quad (1)$$

The effects of light absorption were interpreted in terms of an equilibrium condition among the technetium chlorocomplex species in hydrochloric acid.

Experimental

Apparatus. All the absorption spectra were measured on a Shimadzu Recording Spectrophotometer, Model SV-50A, using quartz cells.

The radioactivities of technetium-99 were measured by a Osaka Dempa GM-Counter, Model GM-2.

Reagents. The technetium-99 had been obtained from Oak Ridge National Laboratory (U. S. A.). The chemical form was NH_4TcO_4 solution. The solution was standardized by gravimetry, using tetraphenylarsonium chloride as the precipitant.

The hydrochloric acid was a Koso Chemicals special grade reagent in which no impurities absorbing the

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UV light were detected.

K_2TcCl_6: Ammonium pertechnetate (100 mg) was mixed with 0.2 g of KCl and 10 ml of concentrated hydrochloric acid, and then the mixture was heated on a water bath while being refluxed for 20 hr. After evaporation to near dryness, the technetium residue was dissolved in concentrated hydrochloric acid. The absorption spectrum of the solution was identical with that of the K_2TcCl_6 solution obtained by the KI reduction of NH_4TcO_4.[10]

Formation of Other Chlorocomplexes of Technetium. K_2TcCl_6 was dissolved in 12 M, 8 M, 6 M, 3 M, 1 M, and 0.1 M HCl. One group of acid solutions was kept at room temperature in the dark, while another group was irradiated by luminescent lamps (Toshiba 10w×4) at 20°C in a thermostat. The absorption spectra of the two groups were measured at regular intervals.

In spite of the varied concentrations of the acid, the group kept in the dark showed the absorption spectrum of $TcCl_6^{2-}$ constantly, while the group irradiated with the luminescent lamps showed different absorption spectra according to the acid concentrations. This variation seemed to be caused by the formation of aquo-chlorocomplexes of technetium. Their spectra reached equilibria after two weeks under the experimental conditions.

Isolation of the Complexes by Ion-exchange Resin. Samples which had been irradiated for two weeks and had already been in equilibrium were subjected to ion-exchange separation.

The sample solutions were first passed through an anion exchange column (Dowex 2×8, 50—100 mesh, R-ClO_4 type, 15ϕ×200mm) in order to remove any anionic species. The cationic and neutral species were thoroughly washed with pure water and 0.1 M $HClO_4$.

The eluted fractions, containing cationic and neutral species, were again passed through a cationic exchanger column (Dowex 50×8, 100—200 mesh, R-H type, 15ϕ×200 mm). From the cation exchanger column, the neutral species was readily removed by 0.1 M $HClO_4$, while the cationic species were eluted by 1 M $HClO_4$. These species were eluted in discrete bands that could be detected by measuring their characteristic absorption spectra.

Analysis of Technetium. The technetium in the effluent was distilled as pertechnetate with concentrated sulfuric acid and was spectrophotometrically determined by measuring the absorbance at 244 mμ[1]; a molar extinction coefficient of 6220 was used for pertechnetate at this wavelength. It was also determined by the diphenylcarbazide method.[11]

Analysis of Chloride. The chloride of the eluted species was analyzed by titration with mercuric ion, using diphenylcarbazone as an indicator.[12] Prior to the titration, the complexes had been hydrolyzed by making the solution alkaline with the addition of potassium hydroxide and had been boiled for five minutes in order to liberate the chloride ion.

Measurement of Charge per Species. The charge per species was measured according to the method of Connick and Cady.[9]

The technetium distribution was obtained by measuring the radioactivities of ^{99}Tc. Before these measurements, the solutions were neutralized with NH_4OH in order to avoid the vaporization of pertechnetate as Tc_2O_7 and were dried up in glass counting dishes.

Separation of the Species by Paper Electrophoresis. The species, spotted on paper strips (Toyo No. 53, 40×2 cm) which had been immersed in an electrolytic solution (0.1 M $NaClO_4$+0.1 M HCl), were separated by high voltage (500 V). The heat generated during electrophoresis was removed by cooling the strips through a glass vessel filled with ice water. Electrophoretic patterns were obtained by autoradiography.

Results and Discussion

When K_2TcCl_6 was dissolved in hydrochloric acid and the solutions were irradiated with visible or UV light, the absorption spectra of the solutions changed and reached equilibria depending on the hydrochloric acid concentrations and the intensity of light. The spectrum of the 12 M HCl solution, however, did not change upon photo-irradiation, and so it was identified as the original species.

The spectra of the solution equilibrated by photolysis are shown in Fig. 1, where the 12 M, 8 M, 6 M, and 3 M HCl solutions show two isosbestic points at 311 mμ and 362 mμ. The isosbestic points can be employed to determine the total amount of technetium(IV) in the solution.

From the hydrochloric acid solutions, two anionic, one neutral, and one cationic species of technetium chlorocomplex were isolated by the ion-exchange method.

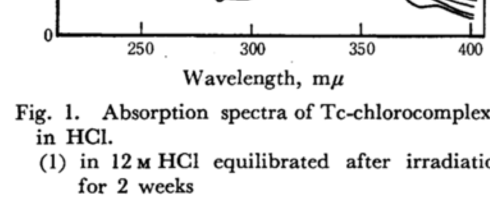

Fig. 1. Absorption spectra of Tc-chlorocomplexes in HCl.

(1) in 12 M HCl equilibrated after irradiation for 2 weeks
(2) in 6M HCl equilibrated after irradiation for 2 weeks
(3) in 3M HCl equilibrated after irradiation for 2 weeks
(4) in 1M HCl equilibrated after irradiation for 2 weeks

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Prior to the following experiments, the stability of the separated species in perchloric acid solution was examined. From the fact that the absorption spectra remain unchanged for several days, the separated species seems to be stable in the elutant, perchloric acid, if they are kept in the dark. The degradation of the complexes during the spectrophotometric procedure is too small to be detected.

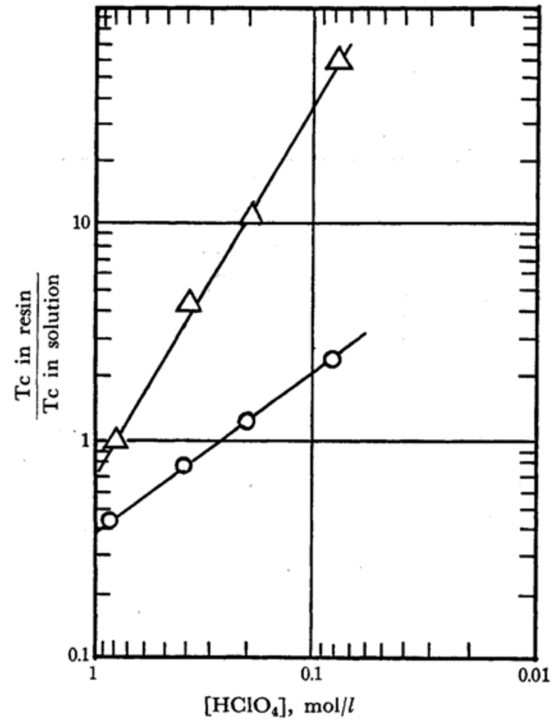

Fig. 2. Relative distribution ratios of anionic complexes between Dowex 1×8 and HClO$_4$.
○ anionic species (−1)
△ anionic species (−2)

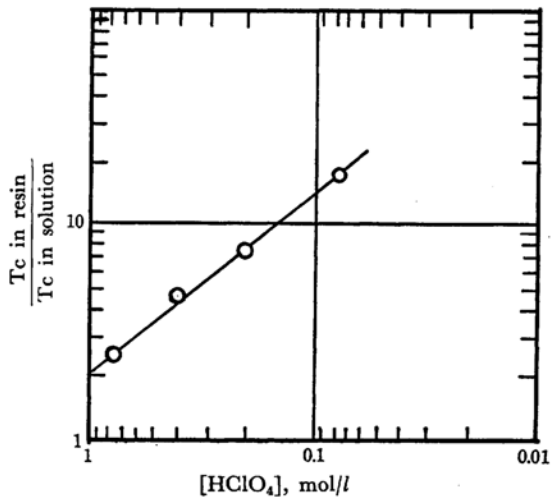

Fig. 3. Relative distribution ratios of cationic complex between Dowex 50×8 and HClO$_4$.

The distribution of the anionic and cationic species between ion-exchange resins and aqueous perchloric acid are shown in Figs. 2 and 3, these data can be used in calculation the values of the charge per ion.

The ratios of technetium to chloride for two anionic species are shown in Table 1, along with the charge per species. The ratios for the cationic and neutral species could not be determined by analysing technetium and chloride, because it was impossible to separate the two forms of technetium from chloride by either the ion-exchange or precipitation method without any destruction of the complexes in question. For the neutral species, however, it is reasonable to assume that the ratio of Tc to Cl is 1 : 4.

TABLE 1. IDENTIFICATION OF ISOLATED COMPLEXES

Fraction	Mole ratio Cl : Tc	Charge/ Species	Complex
Anionic (−2)	5.98 6.05	−1.7	$[TcCl_6]^{2-}$
Anionic (−1)	5.27 5.23	−0.73	$[TcCl_5(H_2O)]^-$
Neutral (0)	—	0	$[TcCl_4(H_2O)_2]$
Cationic (+1)	—	+0.81	$[TcCl_3(H_2O)_3]^+$

TABLE 2. SPECTRAL CHARACTERISTICS OF Tc-CHLOROCOMPLEXES

Complex	λ_{max}	ε_{max}
$[TcCl_6]^{2-}$	234 mμ	19200
$[TcCl_5(H_2O)]^-$	235 mμ	11100
$[TcCl_4(H_2O)_2]$	354 mμ	5500
$[TcCl_3(H_2O)_3]^+$	342 mμ	—

λ_{max}: Wavelength of absorption maximum.
ε_{max}: Molar extinction coefficient at the absorption maximum.

Isosbestic points	λ	ε
of $[TcCl_6]^{2-}$ and	311 mμ	6000
$[TcCl_5(H_2O)]^-$	362 mμ	3500

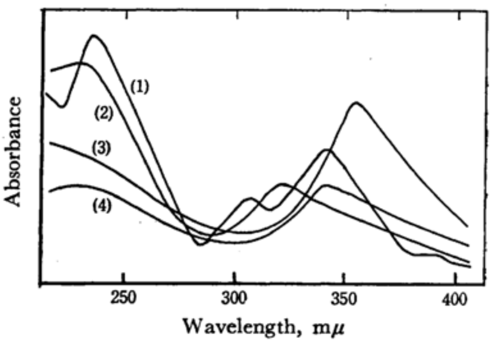

Fig. 4. Absorption spectra of Tc-chlorocomplexes separated by ion exchange.
(1) $[TcCl_6]^{2-}$ (3) $[TcCl_4(H_2O)_2]$
(2) $[TcCl_5(H_2O)]^-$ (4) $[TcCl_3(H_2O)_3]^+$

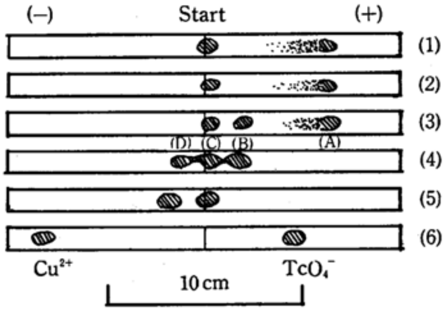

Fig. 5. Electrophoretic patterns of Tc-chlorocomplexes in HCl electrolytic solution.
0.05 M $NaClO_4$ 500 V 40 min
0.05 M $HClO_4$
Tc-chlorocomplexes
(1) in 12 M HCl (4) in 3 M HCl
(2) in 8 M HCl (5) in 1 M HCl
(3) in 6 M HCl (6) reference Cu^{2+}, TcO_4^-

The spectra of the four isolated technetium complex species are shown in Fig. 4, while their wave lengths of maximum absorption and extinction coefficients are tabulated in Table 2. From these results, it can be quantitatively explained that the change in the absorption spectra of $TcCl_6^{2-}$ solution upon irradiation is due to the aquation of the complex in question.

Figure 5 presents electrophoretic patterns which give evidence of the isolation of four different species.

Four main spots, A, B, C, and D, appear in the figure. From their mobilities, it is probable that these spots correspond to the following species:

A-anionic species (-2)
B-anionic species (-1)
C-neutral species (0) and precipitated TcO_2
D-cationic species ($+1$)

The species could not, however, be assigned definitely because the interaction between the paper and each species is not always the same. The pertechnetate and cupric ions which were used as pilot ions gave clear spots and did not have any tailing.

The spots at the original points appeared in the electrophoretic patterns of the samples of 12 M, 8 M, and 6 M HCl solutions where no zero-charge species were detected by means of the ion-exchange method. The reason for this is not clear, but it is assumed that complexes partly hydrolyze during the electrophoresis as a result of the local heating at the original point. The electrophoresis, however, provides a qualitative figure of the species in the solutions.

In Fig. 6, the abundances of the species are plotted against the hydrochloric acid concentrations. It shows the distribution of complexes found in the solution by the ion-exchange method. It seems that TcO_4^- is formed in the dilute hydrochloric acid by the photochemical formation of the Tc(IV) complex and its subsequent disproportionation reactions. This figure, however, represents only the distribution of technetium complexes under the experimental conditions employed here, as will be discussed later.

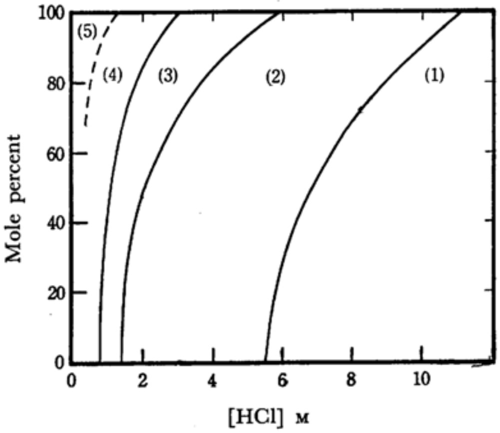

Fig. 6. Approximate compositions of Tc-chlorocomplexes at different concentration of HCl under the experimental conditions.
(1) $[TcCl_6]^{2-}$ (4) $[TcCl_3(H_2O)_3]^+$
(2) $[TcCl_5(H_2O)]^-$ (5) TcO_4^- and TcO_2
(3) $[TcCl_4(H_2O)_2]$

As has been mentioned previously, this experiment was performed in order to identify the species of technetium(IV) chlorocomplexes in hydrochloric acid solution.

The photochemical reaction was used to produce different chlorocomplexes in solution. By taking into account the experimental results of electrical charges and the Cl/Tc ratios of complexes, it may be concluded that the main reaction induced by the irradiation is not reduction but the step-by-step substitution of chloride with water molecules. Therefore, the four isolated species can be assigned to the group of chemical forms indicated in Table 1. Furthermore, it is confirmed that the backward reaction (1) proceeds almost quantitatively without any influence of photons; this supports the theory that the reaction taking place is not a redox type reaction but a substitution reaction.

However, the charge-transfer reaction in the primary step of the reaction sequence can not be excluded, for the technetate ion is detected in 0.1 M and 1 M HCl solutions in which the backward reaction can practically be ruled out.

It should be noted that the reaction system used here does not provide a thermodynamic equilibrium, but a transient one. The rates of the forward and backward reactions of the first step in Eq. (1) are expressed as follows:

$$R_f = K_f[TcCl_6^{2-}] \qquad (2)$$

$$K_f = K_{df} + f \cdot q \qquad (3)$$

$$R_b = K_b[\mathrm{TcCl_5}^-][\mathrm{Cl}^-] \tag{4}$$

where R_f: rate of forward reaction,
R_b: rate of backward reaction,
K_f: forward reaction constant,
K_{df}: forward reaction constant in the dark,
K_b: backward reaction constant,
f: flux of photon,
q: quantum yield

at the apparent equilibria:

$$R_f = R_b. \tag{5}$$

Therefore,

$$(K_{df} + f\cdot q)[\mathrm{TcCl_6}^{2-}] = K_b[\mathrm{TcCl_5(H_2O)}^-][\mathrm{Cl}^-] \tag{6}$$

$$\frac{[\mathrm{TcCl_5(H_2O)}^-]}{[\mathrm{TcCl_6}^{2-}]} = \left(\frac{K_{df}}{K_b} + \frac{f\cdot q}{K_b}\right)\Big/[\mathrm{Cl}^-] \tag{7}$$

From Eq. (7), it is clear that the $[\mathrm{TcCl_5(H_2O)}^-]/[\mathrm{TcCl_6}^{2-}]$ ratio in a given solution is proportional to the light flux irradiated and also inversely proportional to the concentration of chloride in the solution.

To elucidate the reaction mechanism and also to determine the thermodynamic constants, more quantitative experiments from the kinetic point of view are necessary.

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