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# PHOTOCHEMICAL BEHAVIOUR OF THE HEXACHLOROTECHNETATE(IV) ION

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## INTRODUCTION

The chemistry of technetium, one of the artificial elements, has been investigated by a number of researchers since its discovery. Interest in the chemistry of technetium seems to be focussed upon comparison of the chemical properties of the element with those of its homologues, manganese and rhenium, and with other transition metals. Considerable work[1] has been carried out on the synthesis of various types of coordination compound, on the measurement of absorption spectra and magnetic properties and on theoretical considerations.

However, the photochemical behaviour of technetium complexes has not been studied so far. The $Tc^{IV}$ ion forms complexes with halogen ions stable with respect to redox and substitution reactions in acidic solutions. If, however, the solution is exposed to light, the complex undergoes decomposition to give aquated species. The present paper summarizes our recent work[2,3] and some new observations on the photochemical behavior of $Tc^{IV}Cl_6{}^{2-}$.

## EXPERIMENTAL

$(NH_4)_2TcCl_6$ was prepared by refluxing $NH_4TcO_4$ with excess of concentrated hydrochloric acid. The solution was evaporated almost to dryness when another aliquot of concentrated hydrochloric acid was added and the solution kept in a dark and cold place; crystals of $(NH_4)_2TcCl_6$ were obtained.

Irradiation of the $TcCl_6{}^{2-}$ solution was performed in two ways. For qualitative work, the solution of $TcCl_6{}^{2-}$ was irradiated with 10 watt fluorescent lamps. For quantitative work, a 500 watt Xenon lamp equipped with a Hitachi grating monochrometer was used as an irradiation setup. The solution was intermittently shaken during the irradiation to ensure adequate mixing. Since the effect of dissolved oxygen was negligible, the solution was not deoxygenated before use. The intensity of the light was calibrated by means of a ferric oxalate actinometer[4].

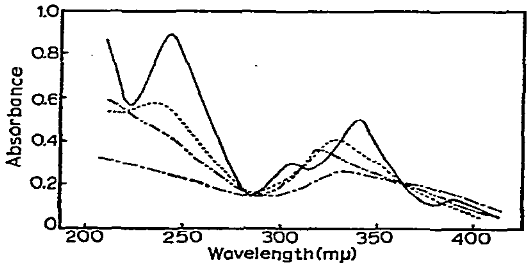
A Shimadzu automatic recording spectrophotometer SV-50A was used to measure absorption spectra. Complexes formed by the photolysis were separated by ion exchange. All the procedures were carried out in the dark to prevent further photolysis. Cationic species were removed by passing the solution through a cation exchange column (0.5 × 20 cm) filled with Dowex 50W, 100 200 mesh and subsequently eluted with perchloric acid solution. The effluent which did not contain cationic species was chromatographed on an anion exchange column (1 cm × 40 cm) filled with DEAE cellulose exchanger and eluted with perchloric acid.

It was possible to isolate various anionic chlorocomplexes not only from each other but also from free chloride ions in the sample solution. Chloride ion attached to technetium was titrated according to Clarke's method[5], after making the effluent alkaline (1*M* KOH) and boiling it for several minutes in order to librate the chloride ion. Technetium was analysed either by its radioactivity or by a spectrophotometric method[3,6].

The electrical charges of the complexes isolated were determined according to Connick and Cady[7]. The electrophoretic method was also investigated for this purpose.

## RESULTS AND DISCUSSION

When $(NH_4)_2TcCl_6$ is dissolved in hydrochloric acid at different concentrations and the solutions are irradiated with visible or uv light, the absorption spectra of the solutions begin to change. On prolonged photolysis an equilibrium is reached which depends on both the hydrochloric acid concentration and the intensity of the light (if the temperature is maintained constant). Some solution spectra after photolysis with visible light are shown in Fig. 1.



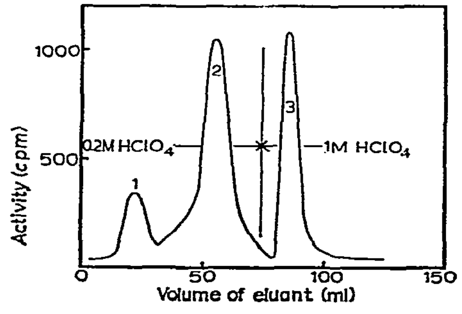


Fig. 1. Absorption spectra of $Tc^{IV}$ chlorocomplexes in hydrochloric acid after photolysis
——— in 12, 6, 3, and 1*N* HCl solutions kept in the dark for two weeks
– – – – – – in 6*N* HCl solution after irradiation for two weeks
· · — · · — in 3*N* HCl solution after irradiation for two weeks
· — · — · in 1*N* HCl solution after irradiation for two weeks
Temp: 25° C, Light Source: visible light from fluorecent lamps.

Fig. 2. Separation of Complexes
Exchanger: DEAE, Column: 1 cm × 40 cm
1. $TcCl_4$, 2. $TcCl_5^-$, 3. $TcCl_6^{2-}$

TABLE 1

IDENTIFICATION OF COMPLEXES SEPARATED

| *Run No.* | *CG. Peak* | *Tc Conc.* | *Cl⁻ Conc.* | *Cl⁻/Tc* | *Charge* | *Complex* |
|---|---|---|---|---|---|---|
| 1 | 3 rd | $4.641 \times 10^{-3}$ *M* | $2.820 \times 10^{-2}$ *M* | 6.046 | −1.8 | $TcCl_6^{2-}$ |
| 2 | 3 rd | $4.641 \times 10^{-3}$ *M* | $2.806 \times 10^{-2}$ *M* | 6.077 | −1.8 | $TcCl_6^{2-}$ |
| 3 | 2 nd | $1.077 \times 10^{-3}$ *M* | $5.429 \times 10^{-3}$ *M* | 5.040 | −0.9 | $Tc(OH_2)Cl_5^{-}$ |
| 4 | 2 nd | $7.484 \times 10^{-4}$ *M* | $3.760 \times 10^{-3}$ *M* | 5.024 | −0.9 | $Tc(OH_2)Cl_5^{-}$ |

On the other hand, the spectra of solutions which have been kept in the dark do not show any changes irrespective of the concentration (above 1 *M*) of hydrochloric acid at 25 °C for two weeks.

An example of the separation of complexes formed in the photolysis is shown in Fig. 2. The solution irradiated was 3 *M* in hydrochloric acid. The first peak corresponds to the neutral species of the technetium complex, accompanied by free chloride ions.

The separation of chloride ion from the second and the third peaks was quantitative, indicating that the complexes were stable enough not to decompose during this procedure.

The chloride to technetium ratio in each of the complexes separated is shown in Table I together with the charge per species.

It is concluded that the species eluted in the second peak is pentachloro-

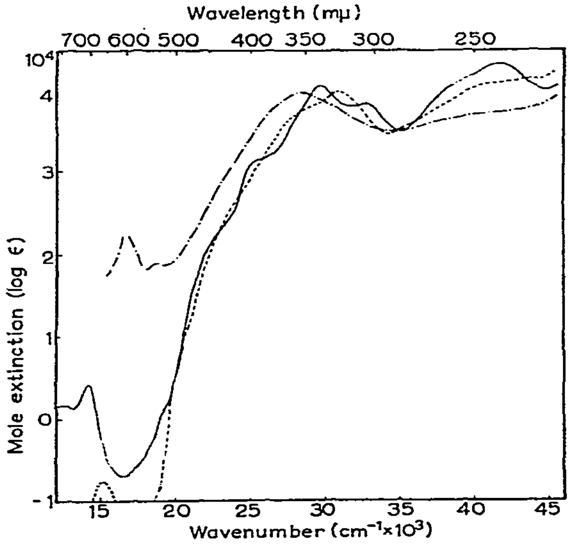


Fig. 3. Absorption spectra of Tc$^{IV}$ chlorocomplexes.
———— $TcCl_6^{2-}$
– – – – – $TcCl_5^{-}$
· —— · —— · $TcCl_4$

monoaquotechnetate(IV) ($Tc(OH_2)Cl_5{}^-$). The third peak contains the parent complex which can easily be identified from its absorption spectrum.

The absorption spectra of a series of complexes are shown in Fig. 3. The spectrum of $TcCl_6{}^{2-}$ agrees well with that presented by Jørgensen et al.[8]. The spectrum of $Tc(OH_2)Cl_5{}^-$ intersects that of $TcCl_6{}^{2-}$ at seven different wave lengths. On the other hand, fewer isosbestic points can be seen in Fig. 1. The difference in the number of crossing points in these Figures indicates that hydrolysis proceeds further on prolonged irradiation or perhaps some other chemical reaction occurs.

The spectrum of the neutral species was tentatively assigned as that of $TcCl_4$. However, as will be discussed later, the species may consist of more than one component.

The quantitative investigation of the photochemical reaction was carried out by irradiating the light at two different wave lengths, *i.e.*, 253 m$\mu$ ($\pi-\gamma3$), and 340 m$\mu$ ($\pi-\gamma5$). Some intermediates of a redox type might be involved in the reaction sequence. Since these wavelengths correspond to charge transfer bands.

The changes in spectra (Fig. 4) correspond to the aquation reaction (1) at least in the early stage of the photolysis; clear isosbestic points are observed.

$$TcCl_6^{2-} + OH_2 \rightarrow Tc(OH_2)Cl_5^- + Cl^- \qquad (1)$$

The aquation reaction occurs at two wave lengths with different quantum yields*[1], $2.49 \times 10^{-1}$ at 253 m$\mu$ and $6.35 \times 10^{-2}$ at 340 m$\mu$ in a solution of 1.1 *M* $HClO_4$ which does not contain any free chloride ion.

It was observed that the quantum yields of the aquation reaction of $TcCl_6{}^{2-}$ depend on the concentration of the chloride ion in the solution. Quantum yields of the aquation by irradiation at 340 m$\mu$ are plotted as a function of the chloride ion concentration (varied by adding sodium chloride to the 1 *M* perchloric acid solution) are shown in Fig. 5. The solution of 6 *M* chloride ion was prepared by adding hydrochloric acid, because of the low solubility of sodium chloride in the solution.

The reaction mechanism involved may be very complicated. The first excitation step should be a type of charge transfer process. However, the principle reaction is aquation and evolution of chlorine in the solution is not appreciable. If, however, one postulates aquation and exchange of chloride ion from one excited species as competing reactions, it is possible to explain the effect of the chloride ion upon the quantum yield of aquation. A sequence of reactions is proposed.

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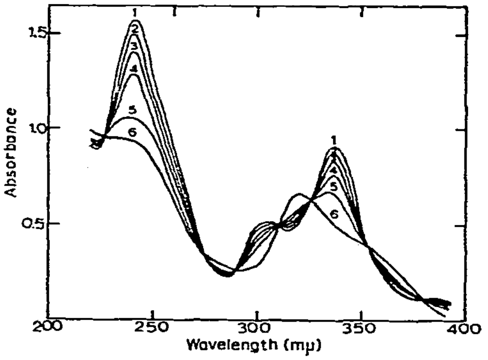
[1] Quantum yields were calculated as follows: Samples were irradiated with a known light intensity. The amount of light absorbed by $TcCl_6{}^{2-}$ was calculated by correcting the amount of the light transmitted through the sample with that absorbed by $Tc(OH_2)Cl_5{}^-$ produced during the photolysis. After the photolysis, the absorption at 340 m$\mu$ was measured. The molar extinction coefficients of $TcCl_6{}^{2-}$ and $Tc(OH_2)Cl_5{}^-$ at 340 m$\mu$ are 11040 and 6422 respectively. Thus the value of chemical change per photon absorbed was obtained.



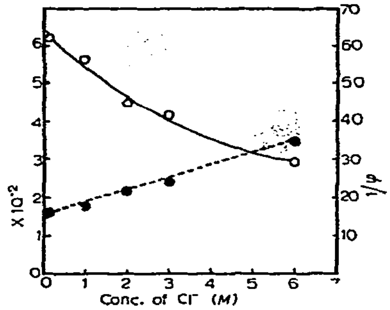


Fig. 4. Change of absorption spectra by photolysis at charge transfer bands. Composition: TcCl$_6^{2-}$ 7.882 × 10$^{-5}$$M$, HClO$_4$ 1.1$M$, Cl$^-$ 0$M$; Wave length: 340 m$\mu$, Flux: 2.86 × 10$^{-5}$ einst./$M$/min. 1: 0 min., 2. 5 min., 3. 15 min., 4: 30 min., 5: 50 min., 6: TcCl$_5^-$ (pure).

Fig. 5. Dependence of quantum yield on the concentration of chloride ion.
Flux: 2.86 × 10$^{-5}$ einst./M/min. Composition: 1.1$M$ HClO$_4$. Temp. 25° C.
○—○: $\varphi$; ●--●: $1/\varphi$.

Equation 2 is the excitation process caused by the absorption of photon. Equation 3 describes the deactivation or recombination process. Equation 4 and 5 correspond to the exchange and aquation reaction, respectively.

$$\mathrm{TcCl_6^{2-}} \rightarrow \mathrm{Tc^*Cl_6^{2-}} \tag{2}$$

$$\mathrm{Tc^*Cl_6^{2-}} + \mathrm{M} \xrightarrow{k_{st}} \mathrm{TcCl_6^{2-}} + \mathrm{M^*} \tag{3}$$

$$\mathrm{Tc^*Cl_6^{2-}} + \mathrm{Cl^-} \xrightarrow{k_{ex}} \mathrm{TcCl_6^{2-}} + \mathrm{Cl^{*-}} \tag{4}$$

$$\mathrm{Tc^*Cl_6^{2-}} + \mathrm{OH_2} \xrightarrow{k_{aq}} \mathrm{Tc(OH_2)Cl_5^-} + \mathrm{Cl^{*-}} \tag{5}$$

Here, (M) can be regarded as a water molecule.

The rate of formation of TcCl$_6$$^{2-}$ can be assumed to be a constant value ($A$) which is proportional to the flux of light absorbed. Experimental values are taken at an early stage of photolysis and corrections are made for the transmittance of the light from the solution under irradiation and the change of the concentration of the species in question during the irradiation. The next series of equations are obtained.

$$\frac{\mathrm{d(Tc^*Cl_6^{2-})}}{\mathrm{d}t} = A - (\mathrm{Tc^*Cl_6^{2-}})\,\{k_{st} + k_{aq} + k_{ex}(\mathrm{Cl^-})\} \tag{6}$$

At steady state,

$$(\mathrm{Tc^*Cl_6^{2-}}) = \frac{A}{k_{st} + k_{aq} + k_{ex}(\mathrm{Cl^-})} \tag{7}$$

$$\frac{\mathrm{d(Tc^*(OH_2)Cl_5^-}}{\mathrm{d}t} = k_{aq}(\mathrm{Tc^*Cl_6^{2-}}) \tag{8}$$

$$= \frac{A\,k_{aq}}{k_{st} + k_{aq} + k_{ex}(\mathrm{Cl^-})} \tag{9}$$

The quantum yield for aquation is expressed by equation (10) – (12).

$$\varphi = \frac{\mathrm{d}(\mathrm{Tc(OH_2)Cl_5^-})}{\mathrm{d}t} / A \tag{10}$$

$$= \frac{1}{\frac{k_{st}}{k_{aq}} + 1 + \frac{k_{ex}}{k_{aq}}(\mathrm{Cl^-})} \tag{11}$$

or

$$1/\varphi = \frac{k_{st}}{k_{aq}} + 1 + \frac{k_{ex}}{k_{aq}}(\mathrm{Cl^-}) \tag{12}$$

According to this argument, a plot of $1/\varphi$ *versus* ($\mathrm{Cl^-}$) should be linear with a slope of $k_{ex}/k_{aq}$ and intercept $\{(k_{st}/k_{aq})+1\}$. Despite the error associated with photochemical work which exceeds five percent, a fairly good fit is obtained, thus supporting the proposed mechanism. A value of 14.75 and 2.96 were obtained for $k_{st}/k_{aq}$ and $k_{ex}/k_{aq}$, respectively. It should be mentioned here that the excited state responsible for the substitution reaction may not be directly formed by the photon absorption. It is probable that an intermediate with enough excitation to break the Tc-Cl bond may be formed through the reverse charge transfer reaction. If the reverse reaction proceeds almost exclusively and instantaneously, the foregoing argument is still applicable. The reverse reaction of Equation 5 does proceed to give $\mathrm{TcCl_6^{2-}}$ from $\mathrm{Tc(OH_2)Cl_5^-}$ in a high concentration of chloride ions. However, the reaction in the dark can be neglected under these experimental conditions since the rate is small compared to the photo equation reaction.

It is very difficult to clarify what takes place subsequent to the aquation. $\mathrm{Tc(OH_2)Cl_5^-}$ can exist in the strongly acidic solution. If the pH of the solution becomes less than one, the yellow coloured $\mathrm{Tc(OH_2)Cl_5^-}$ decomposes into a brownish species, which may involve the dissociation of protons from the water molecule attached to technetium.

$$\mathrm{TcCl_5(OH_2)^-} \rightarrow \mathrm{TcCl_5(OH)^{2-}} + \mathrm{H^+} \tag{13}$$

Cationic and neutral species were detected in the hydrolytic products of $\mathrm{TcCl_5(OH_2)^-}$. Thus, the further dissociation of protons and chloride ions is involved. $\mathrm{TcCl_5(OH_2)^-}$ is still photochemically active in more than 1 *M* hydrochloric acid solutions to yield a green coloured species which was tentatively assigned as $\mathrm{TcCl_4(OH_2)_2}$. The green complex is also easily hydrolysed giving the brown coloured species which eventually precipitates $\mathrm{TcO_2}$. It was also observed that both $TcCl(OH_2)^-$ and $TcCl_4(OH_2)_2$ were susceptible to oxidation, $TcO_4^-$ being the product after some time.

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