On the Reduction of Technetium(VII) by Hydrochloric Acid

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Abstract

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On the Reduction of Technetium(VII) by Hydrochloric Acid

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The pertechnetate ion, in contrast to its closest analogue, the perrhenate ion, possesses a number of interesting properties: inhibiting properties, the ability to oxidize ion-exchange resins, to be selectively reduced in HCl solutions to the tetravalent state, etc. The reduction of technetium ions in hydrochloric acid is a little-studied and very complex process ([1]). For example, the nature of the transitional forms of technetium, the influence of acid concentration, time, and temperature on the reduction process, etc., remain unclear. In connection with the foregoing, we carried out spectrophotometric studies of the behavior of technetium ions in HCl solutions which, in combination with the results of extraction experiments, made it possible to propose a possible mechanism for the reduction of TcO_4^- by hydrochloric acid.

Spectrophotometric studies of the behavior of technetium ions in HCl solutions of different concentrations showed that, up to concentrations of 7–7.5 M, practically no changes are observed in the absorption spectra of pertechnetate ions. However, a further increase in acid concentration up to 10 M causes a noticeable change in the spectrum, accompanied by an increase in the molar absorption coefficients and a shift of the characteristic peaks, especially in the shorter-wavelength region of the spectrum (Fig. 1).

Beginning with an HCl concentration of 10 M and above, the character of the spectrum and the values of the molar absorption coefficients remain practically constant, independent of the acid concentration. Detailed measurements of the spectra showed the presence of peaks at 230 and 293 mμ, the molar absorption coefficients of which are 10400 and 4700, respectively. These results agree with the data reported for 12 M HCl in the review cited above ([1]). In the authors' opinion, in 12 M HCl, TcO_4^- is reduced by chloride ions directly to the pentavalent state. However, our experiments on the extraction of the rhodanide complex of pentavalent technetium, as it seems to us, do not confirm this assumption. It is known ([1–3]) that Tc(V) is very stable in 3 M HCl solutions and rapidly forms with rhodanide ions a pink-colored complex compound, which is practically completely extracted by such organic solvents as butyl acetate and ethyl ether. However, the addition of rhodanide ions to a technetium solution diluted from 12 to 6–3 M gives only a yellow coloration, which with time acquires an increasingly intense pink color. This is explained by the gradual reduction by

rhodanide ions of technetium ions to Tc(V), which then forms a colored complex compound with CNS^- anions. With the simultaneous addition to a hydrochloric acid solution of technetium of rhodanide ions and some not very strong reducing agent, such as ascorbic acid, the coloration develops within several seconds and subsequently disappears (the reduction proceeds to the tetravalent state).

The results of experiments on the extraction of the rhodanide complex of Tc(V) as a function of the time elapsed from the moment of addition of CNS^- anions up to the moment of extraction, are presented below. From these data it follows that the most complete extraction of the rhodanide complex of technetium is achieved only 20 minutes after addition of CNS^- anions to the initial solution, i.e., after approximately the same time as that required for the reduction of Tc(VII) to Tc(V) by rhodanide ions [(2)]. The decrease in distribution coefficients with time can be explained by reduction of technetium to the tetravalent state.

Standing time of the Tc solution containing CNS^-, min	1	5	10	15	20	30	35	45	90
Distribution coefficient, D	0.18	0.86	2.6	3	10	3.5	4.4	3.7	0.72

The experiments we carried out on extraction with butyl acetate from 3 M HCl solutions containing rhodanide ions and tetravalent technetium showed practically complete absence of extraction ($D = 0.004$).

Thus, from the data obtained it follows that reduction of technetium in concentrated HCl does not proceed to the pentavalent state; to convert it into this state, the use of other reducing agents is required.

Fig. 1. Change in the absorption spectra of pertechnetate ions as a function of HCl concentration.
Tc concentration: $8.5 \cdot 10^{-5} M$

Fig. 3. Rate of reduction of technetium ions in concentrated HCl; a—at 23°, b —at the boiling temperature of the acid

Figure 1: Fig. 3. Rate of reduction of technetium ions in concentrated HCl; a —at 23°, b—at the boiling temperature of the acid

Fig. 2. Change in the absorption spectra of technetium ions as a function of the duration of exposure to 11 M HCl. Tc concentration: $8.5 \cdot 10^{-5} M$; $t = 23^{\circ}$

Further spectrophotometric study of the behavior of technetium ions in concentrated HCl solutions as a function of time showed that in such solutions technetium accumulates in the tetravalent state. In Fig. 2 are presented absorption spectra of technetium ions in 11 M hydrochloric acid measured at various times. With time the position of the maximum of the peak at 230 mμ gradually shifts to 240 mμ, with a sharp increase in the molar absorption coefficients, and in the longer-wavelength region of the spectrum there is observed the curve shape characteristic of the chloride complex of tetravalent technetium, with a peak at 338 mμ [(4)]. In Fig. 3 are shown curves for the increase in the content of tetravalent technetium in 11 M HCl as a function of time and temperature. The rate of reduction was studied by the increase in the concentration of Tc(IV) on the basis of the growth of the peak at 338 mμ, which, within the investigated concentrations of Tc(IV), obeys Beer' s law. As is seen from Fig. 3, complete reduction by concentrated HCl of technetium ions to the tetravalent state at room temperature takes place in almost 100 hours, whereas at the boiling temperature it is 100 times faster. It is interesting to note that attempts to extract technetium, subjected to exposure to concentrated HCl for different durations, in the form of a rhodanide complex were not successful, as before; apparently, the reduction

reduction to Tc(IV) occurs without the formation of an intermediate pentavalent state.

On the basis of the foregoing, it may be assumed that the reduction of pertechnetate ions in concentrated HCl solutions proceeds to

Fig. 3. Rate of reduction of technetium ions in concentrated HCl; a—at 23°, b —at the boiling temperature of the acid

the hexavalent state, in which technetium slowly at room temperature and more rapidly upon heating disproportionates according to the reaction

$$\mathrm{Tc(VI)} \rightarrow \mathrm{Tc(VII)} + \mathrm{Tc(IV)}.$$

It is possible that the observed long duration and nonlinearity of the reduction process with time are explained precisely by the occurrence of the proposed disproportionation reaction.

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Note: Figure translations are in progress. See original paper for figures.