

THE REDUCTION OF Cr(VI) BY DIFFERENT REDUCING AGENTS

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The reduction of Cr(VI) with different reducing agents was studied. In the case of reduction with hydrazine perchlorate, hydrogen peroxide, hydroxylamine hydrochloride, the spectra of solutions were the same as that of Cr(III) aquo-complex. With As(III), Sn(II) and Ti(III) as reductants a rather strong interaction between Cr(III) and the oxidized form of reductant was observed, which exhibits in the absorption spectra of solutions.

The reduction of Cr(VI) in the presence of different complex forming agents especially the ethylenediaminetetraacetic acid (EDTA) is thoroughly investigated by us [1]. Namely, the Cr(III) complexes are immediately formed under these circumstances, although the formation of these complexes from Cr(III) ion and from different complex forming molecules takes place very slowly. The most important requirement for the reducing agent is the indifference of it: no interaction between the reductant — or its oxidized form — and the Cr(III) ion must be observable. Results of our experiments performed by many reductant are shortly described.

Experimental

Materials: 0,04797 mol/l $\text{Na}_2\text{Cr}_2\text{O}_7$ solution. The Merck c. p. $\text{Na}_2\text{Cr}_2\text{O}_7$ was dissolved in twice distilled water.

Hydrazine perchlorate. From c. p. hydrazine sulphate prepared by barium-perchlorate. The pH of filtered solution was adjusted by sodiumhydroxide to 5.

Hydroxylamine hydrochloride. May & Baker c. p. compound.

Hydrogen peroxide. Merck c. p. quality.

Stannous chloride. Merck c. p. quality.

Stannous perchlorate. Stannous oxide was prepared by DITTE method [2] from Sn(II) chloride and then dissolved in c. p. perchloric acid.

Ti(III) chloride. 10 per cent solution. Spolek reagent.

As(III) perchlorate. Aqueous solution of sodium arsenite (Thomas Tyler c. p. quality) was acidified with perchloric acid.

Perchloric acid. Riedel c. p. quality.

The concentration of perchloric acid was 0,07 mol/l in these experiments. Increasing the concentration of perchloric acid the spectra remained unchanged. These reductants were termed by us as "indifferent" reducing agents.

Carrying out the reduction with arsenous perchlorate a green solution was obtained instead of the violet one. The spectrum of this solution is shown in Fig. 2. As it can be seen the position of maxima are shifted toward the longer wave lengths. At twentyfold increasing the concentration of perchloric acid the spectrum becomes identical with the spectra obtained by the "indifferent" reducing agents. Thus the interaction between Cr(III) and As(V) ceases by increasing the hydrogen ion concentration. These results

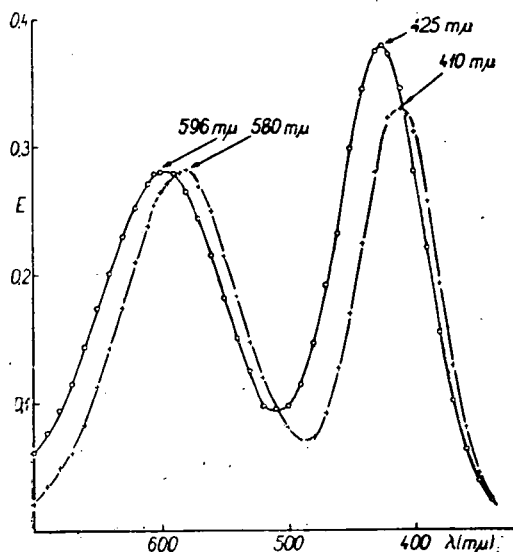


Fig. 2. Absorption spectra of solutions obtained by reduction with arsenous perchlorate at different acidity

○ ○ ○ ○ 0,07 mol/l perchloric acid
 + + + + 1,40 mol/l perchloric acid

are in accordance with SIMON and BAUMGÄRTEL's observations [3] according to which Cr(III) reacts with As(V) in weakly acidic solution and an emerald green $\text{Cr}(\text{HAsO}_4)$ complex ion is formed.

Reduction with stannous chloride solution results in a green solution the spectrum of which is greatly altered related to spectrum of Cr(III) aquocomplex.

This alteration is not the consequence of the presence of chloride ion, because this phenomenon does not occur in the case of reduction with hydroxylamine hydrochloride or with hydrogen peroxide in the presence of great amount of sodium chloride. (Fig. 3.)

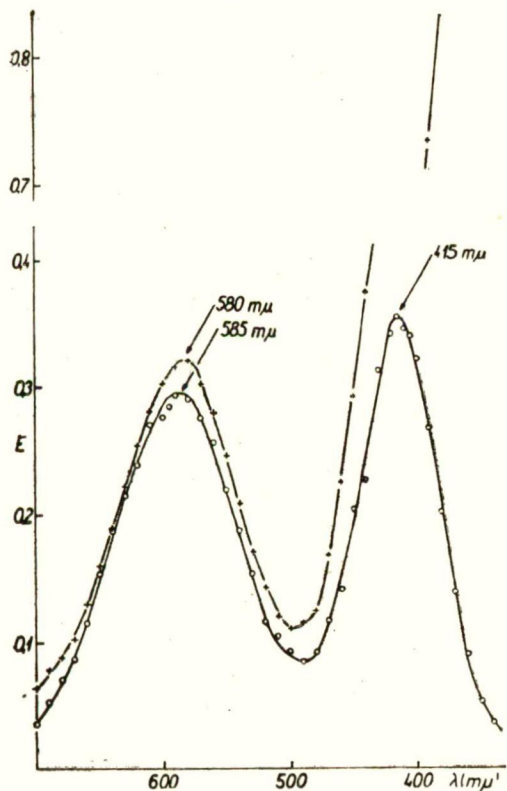


Fig. 3. Absorption spectra of solutions obtained by reduction with stannous chloride and with hydrogen peroxide in the presence of 0,5 g sodium chloride

++++ reduction with stannous chloride
 oooo reduction with hydrogen peroxide
 Acidity: 0,07 mol/l perchloric acid

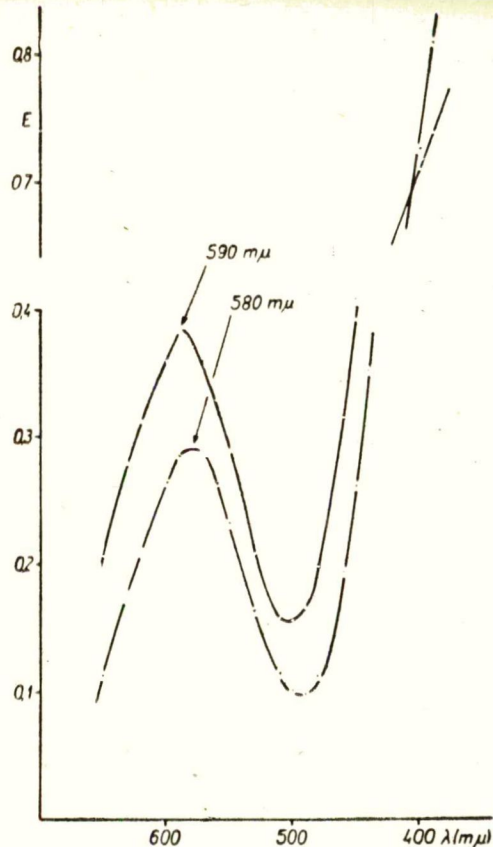


Fig. 4. Absorption spectra of solutions obtained by reduction with stannous perchlorate at different acidity

oooo 0,07 mol/l perchloric acid
 ++++ 1,40 mol/l perchloric acid

A similar phenomenon was observed in the case of reduction with stannous perchlorate. As it seems from the figures the "optical interaction" increases toward the shorter wave lengths. Increasing the acidity of the initial solution the absorbancy decreases at the longer and increases at the shorter wave lengths. This interaction does not occur on mixing the solutions of Cr(III) and Sn(II) or Sn(IV). Consequently, the interaction between Cr(III) and Sn(IV) is greater than in the case of Cr(III) and As(V).

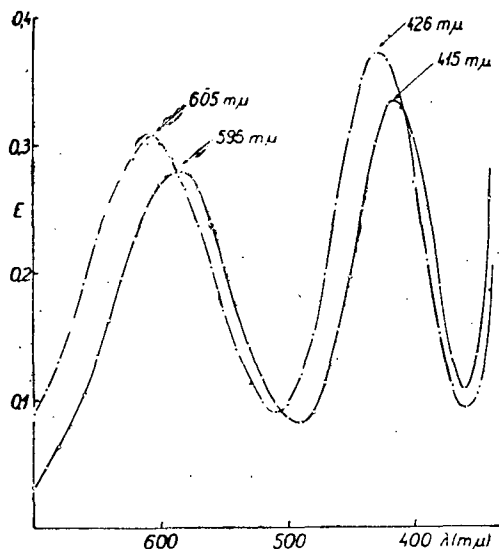


Fig. 5. Absorption spectra of solutions obtained by reduction with titanous chloride at different acidity

○○○○ 0,07 mol/l perchloric acid
++++ 1,40 mol/l perchloric acid

When the reduction was carried out with titanous chloride a green solution was obtained.

It is remarkable that the absorbancy of the solution increases with increasing acidity in the visible region.

On the basis of our experiments the most suitable reducing agents for the study of the reduction of Cr(VI) in the presence of complex forming agents are hydrazine perchlorate, hydroxylamine and hydrogen peroxide.

References

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- [2] Ditte: Pogg. Ann. **27**, 145 (1882).
- [3] Simon A., E. Baumgärtel: Z. anorg. Chem. **282**, 307 (1955).