

ON THE STABILITY AND CATALYTIC ACTIVITY OF IRON(III)- TRIETHYLENETETRAMINE COMPLEX

By S. GÖRÖG and M. T. BECK

Institute of Inorganic and Analytical Chemistry, The University,
Szeged

The chemistry of iron(III)polyethylenepolyamine complexes is not well known. Therefore WANG's observation [1] that the iron(III)-triethylenetetramine /Fe(III)TETA/ complex is a very effective catalyst of the decomposition of hydrogen peroxide is of great interest.

According to WANG the four N atoms of TETA are not coplanar thus in the plane determined by Fe(III) and the two secondary N of TETA, two coordination places are free. These places are filled at the relatively high pH (pH 9-11) where the experiments were carried out by hydroxyl ions, which are displaced by OOH⁻ ion in the presence of H₂O₂. The O-O bond looses due to intramolecular rearrangement and this intermediate easily reacts with another OOH⁻ to yield oxygen and regenerate the catalyst.

The rate of process is determined by the first reaction and thus the rate of decomposition of hydrogen peroxide can be expressed by a bimolecular rate expression:

$$-\frac{d[H_2O_2]}{dt} = k [(TETA)Fe(OH)_2^+][H_2O_2]$$

WANG's most decisive evidence for the above mechanism is that the Fe(III) complexes of ethylenediamine and diethylenetriamine are much smaller effective catalysts than the Fe(III)TETA, the tetraethylenepentamine complex is practically inactive. This argument is reliable only if the stability of these complexes allows their existence in a real concentration at pH 9-11. In the case of ethylenediamine and diethylenetriamine complexes it is beyond doubt that these complexes cannot exist at such a high pH for the tetraethylenepentamine complex there are no data. It would be very important to study the action of tetraethylenepentamine on the catalytic effect of Fe(III)TETA. If WANG's supposition is right inhibition effect would have to be observed. In lack of tetraethylenepentamine these planned experiments are not performed.

We carried out kinetic experiments to learn more about this system. The reaction was followed by permanganometric determination of non-decomposed hydrogen peroxide.

It was stated that the rate of the reaction is strongly influenced by hydrolysis and to obtain well reproducible result one must work under strictly defined experimental conditions.

Experiments showed that during the catalytic decomposition of hydrogen peroxide the TETA is oxidized. This oxidation leads to the gradual decomposition of the complex and so the reaction becomes slower and slower. The oxidation of TETA during the decompos:

tion was quantitatively studied [2]. The oxidation of TETA takes place parallel to the decomposition of hydrogen peroxide: this process is also catalysed by the Fe(III)TETA complex. A consequence of the oxidation of TETA is the decrease of bimolecular velocity "constant" in time.

In the case of smaller concentration of TETA (10^{-3} mol/l) this oxidation involves an interesting phenomenon: the relative quantity of catalytically decomposed hydrogen peroxide firstly increases with increasing Fe(III) concentration, after reaching a maximum slowly decreases to a limit value. This maximum curve of conversion can be explained as follows: The rate of the oxidation of TETA increases more quickly than that of the decomposition of hydrogen peroxide with increasing the Fe(III) concentration. Over certain Fe(III) concentration the TETA which is necessary for the catalytic decomposition of hydrogen peroxide is oxidized in initial stage of reaction and during this time the extent of decomposition of hydrogen peroxide is small.

In the case of higher concentration of TETA ($5 \cdot 10^{-3}$ mol/l) the rate of reaction is not strictly proportional to the Fe(III) concentration. The rate constant calculated according to the bimolecular expression increases with increasing concentration of Fe(III). When the Fe(III) concentration is higher than 10^{-5} mol/l the catalytic effect of colloid Fe(OH)₃ has to be taken into consideration.

The rate of decomposition reaction depends on the pH. WANG's equation refers only to a given pH. On the basis of WANG's data we found that the rate constant of following equation is independent of pH:

$$-\frac{d[\text{H}_2\text{O}_2]}{dt} = k \frac{[\text{Fe(III)TETA}][\text{HO}_2^-]}{[\text{OH}^-]^{0.7}}$$

The effect of hydroxyl ions is a double one. On the one hand, the hydroxyl ions promote the formation of perhydroxyl ions, on the other, they compete with the perhydroxyl ions for the coordination places of catalyst molecule. This supports the view that the perhydroxyl ions are built into the complex, however, we don't know whether the perhydroxyl ion should occupy one or two coordination place(s).

We had to know the stability constant of the Fe(III)TETA complex in order to estimate the upper limit of concentration of the complex at given pH and TETA concentration. Since under our experimental conditions this value is not greater than about 10^{-6} mol/l stability constant cannot be determined by the usual methods. The catalytic properties of complex makes possible the determination of the stability constant on the basis of a new principle. The method is based on the inhibition effect of ethylenediaminetetraacetic acid (EDTA). Namely, the EDTA forms with the Fe(III) a very stable and catalytically inactive complex. From the extent of inhibition on the effect of EDTA the stability constant of Fe(III)TETA complex can be calculated, knowing the total concentrations, the stability constants of Fe(III)EDTA complex and the acidic dissociation constants of EDTA and TETA. Using SCHWARZENBACH's data for the stability of Fe(III)EDTA the stability constant of Fe(III)TETA was found to be $8,8 \cdot 10^{21}$. From the comparison of the inhibition effect of

EDTA and 1,2 diaminocyclohexanetetraacetic acid (CDTA) the stability constant of Fe(III)CDTA complex can be calculated, considering the different stability of mixed complexes formed with hydrogen peroxide [4], [5].

The enormous great catalytic activity of Fe(III)TETA complex makes possible the simple and accurate permanganometric determination of minute amount of Fe (0.03 - 1.2 μ g) [6].

References

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