ACTA CHEMICA SCANDINAVICA 4 (1950) 1538–1540

A Revision of the Mechanism of the Ferric Salt Catalyzed Hydrogen Peroxide Decomposition

J. A. CHRISTIANSEN and V. STEN ANDERSEN

Institute of Physical Chemistry, University of Copenhagen, and The Royal Danish School of Pharmacy, Copenhagen, Denmark

By means of recently published kinetic experiments at different temperatures it is shown that the mechanism of the ferric salt catalyzed hydrogen peroxide decomposition must be represented by a sequence which contains an active form of hydrogen peroxide anion instead of oxygen atoms as formerly assumed.

One of us has in a previous paper [1] given a reaction scheme for the ferric salt catalyzed decomposition of hydrogen peroxide.

The investigations are later [2] extended to include the dependence of the velocity of reaction on the temperature for the interval between 10° and 35° C.

The result of these investigations was, that the sequence proposed:

$$\begin{array}{lll} Fe^{+++} + HO_2^- \rightleftharpoons FeOOH^{++} & 12 & \\ FeOOH^{++} \rightleftharpoons FeOH^{++} + O & 25 & II \\ O + HO_2^- \rightarrow O_2 + OH^- & 50 & \end{array}$$

led to an unexpectedly high value for the ratio between the velocity constants for the two processes 50 and 52. The ratio was found to be equal to about 10^9 for the temperature interval mentioned above. As it is practically independent of the temperature one would have expected a value of the order of magnitude 1.

To avoid the above result we have now been compelled to modify the sequence as follows:

$$\begin{array}{lll} Fe^{+++} + HO_2^- \rightleftharpoons FeOOH^{++} & 12 & \\ FeOOH^{++} \rightleftharpoons Fe^{+++} + \overset{*}{HO_2}{}^- & 25 & III \\ \overset{*}{HO_2}{}^- + H_2O_2 \rightarrow O_2 + H_2O + OH^- & 50 & \end{array}$$

$\overset{*}{HO_2}{}^-$ symbolizes an active HO_2^--ion, possibly HO^-: O.

Table 1. Figures used for calculation of the ratio between the velocity constants for the two processes 50 and 52 ind the sequence III. k_{50}/k_{52} in column (6) are calculated by means of (35) and k_{50}/k_{52} in column (7) are calculated by means of (36).

1	2	3	4	5	6	7
T	c_{Ferric}	$A \cdot 10^3$	c_{H^+}	$K_{\mathrm{Fe}} \cdot 10^3$	k_{50}/k_{52} exp. Eqn (35)	k_{50}/k_{52} calcd. Eqn (36)
283.15	0.004	1.50	0.0102	0.66	1.08	1.15
288.15	0.004	1.50	0.0103	0.98	1.06	1.07
293.15	0.004	1.50	0.0105	1.41	1.02	1.00
298.15	0.004	1.50	0.0106	2.00	0.97	0.91
298.15	0.002	0.80	0.0103	2.00	0.91	0.91
303.15	0.002	0.80	0.0104	2.82	0.86	0.85
308.15	0.002	0.80	0.0106	3.98	0.79	0.79

The modified sequence leads to the same value of k_{25} as originally calculated. But now we get for the calculation of the ratio k_{50}/k_{52}:

$$A = 0.4343 \frac{k_{52} \cdot c_{\mathrm{H}^+} \cdot c_{\mathrm{Ferric}}}{k_{50}\,(K_{\mathrm{Fe}} + c_{\mathrm{H}^+})} \tag{35}$$

which gives a value for k_{50}/k_{52} of the order of magnitude one.

The values necessary for the calculation of k_{50}/k_{52} are given in Table 1; the values for A are taken from the above cited paper [2], the values for K_{Fe} are calculated from equation (27) (*l. c.*); the hydrogen ion concentration, which in the cited paper was presumed equal to the concentration of nitric acid is corrected by means of the equation:

$$c_{\mathrm{H}}^{\,+} = c_{\mathrm{HNO_3}} + \alpha \cdot c_{\mathrm{Ferric}}$$

where α is the degree of hydrolysis of the ferric ion in the solutions in question. The values for k_{50}/k_{52} which are calculated from equation (35) are given in column (6) in the table.

The table shows that the ratio varies a little with the temperature. By means of the usual method of calculation it can be shown that:

$$k_{50}/k_{52} = 10^{-1,88} \cdot e^{\frac{2514}{RT}} \tag{36}$$

for the temperature interval in question.

The values for k_{50}/k_{52} which are given in Table 1 column (7) are calculated by means of (36).

The order of magnitude which has been found for the frequency factor in (36) is in good agreement with the fact that 52 is supposed to be a reaction between two oppositely charged ions and that 50 is supposed to be a reaction between an ion and an uncharged molecule.

REFERENCES

1. Andersen, V. S. *Acta Chem. Scand.* **2** (1948) 1.
2. Andersen, V. S. *Acta Chem. Scand.* **4** (1950) 914.

Received November 8, 1950.