

possible models: a) a model having the chlorine atoms in  $\epsilon$  position, the bromine atoms in  $\kappa$  positions (Fig. 1 a), and with all valency angles strictly tetrahedral, b) a corresponding idealized model of the second possible configuration (the chlorine atoms in  $\kappa$  positions, the bromine atoms in  $\epsilon$  positions, Fig. 1 b), c) a *distorted* model having the chlorine atoms in  $\epsilon$  position and the bromine atoms in  $\kappa$  position. It is easily recognized that the second line diagram cannot account for the maxima of the experimental curve and that the first is in fair agreement with the experimental result. It seems obvious, however, that some minor distortions of the valency angles will be necessary to bring the line diagram in full agreement with the experimental curve. First of all the C-Cl bond will have to be bent away from the chief axis of the carbon ring. We found that an angle of  $8^\circ$  between this bond and the directions of the chief axis leads to the best agreement with experiment. It is interesting to note that a distortion of the same kind and very nearly the same magnitude was observed in the corresponding tetrachloro-compound both in the crystal and in the vapour<sup>3</sup>. It is no doubt due to repulsive forces acting between the chlorine atoms and the nearest ( $\epsilon$  bonded) hydrogen atoms. In addition to this deviation from strictly tetrahedral valency angle a smaller distortion ( $3^\circ$ ) of the C-C-Br angle bringing the neighbouring bromine atoms a little further apart than in the idealized structure was introduced.

1. Hassel, O., and Lunde, K. To be published shortly.
2. Hassel, O., and Wang Lund, E. *Acta Chem. Scand.* In publication.
3. Hassel, O., and Wang Lund, E. *Acta Cryst.* 2 (1949) 309.

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## Hydrogen Peroxide Decomposition Catalyzed by Ferric Salt in Solutions acidified with Perchloric Acid

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In a previous work<sup>1</sup> the author has shown that the course of hydrogen peroxide decomposition catalyzed by ferric salt in solutions containing nitric acid deviates from the unimolecular scheme. Bray and Peterson<sup>2</sup> states in a paper published recently that this deviation should be ascribed to the presence of nitrate ions, as they have been able to reproduce the deviation in experiments made in solutions acidified with nitric acid, but not in solutions acidified with perchloric acid.

Abel<sup>3</sup> is likewise of the opinion that the deviation must be due to the influence of nitrate ions, although this author has not any experimental results on which to base this contention.

As the said deviation forms the actual experimental basis on which the author of the present work has established the mechanism proposed for the hydrogen peroxide decomposition catalyzed by ferric salt<sup>1,4,5</sup> the author considers it necessary once more to revert to this subject quite briefly by presenting the results of a single experiment with two repetitions. The experiment was made with hydrogen peroxide, ferric salt and acid in the same concentrations as those used for the purpose of the experiments of table 1 of the paper quoted above<sup>1</sup>, but this time the ferric nitrate and the nitric acid were replaced with ferric perchlorate and perchloric acid. The ferric perchlorate used was prepared by Robertson\* during his

\* C. A. Robertson, who has published several works dealing with this problem, *e. g.* *J. Am. Chem. Soc.* 45 (1923) 2493.

stay in 1933 at the Institute of Physical Chemistry of the University of Copenhagen, the hydrogen peroxide used was Merck's Perhydrol, which was redistilled in an apparatus of glass to avoid all traces of inhibitors, and the perchloric acid used was of Merck's quality "analytical reagent".

The experimental results have been calculated by means of the formula applied previously<sup>1</sup>.

The constants found were (average of 3 experiments):

$$A = (0.93 \pm 0.03) \cdot 10^{-3}$$

and

$$B = (1.66 \pm 0.02) \cdot 10^{-2}$$

An experiment made by Arne Nielsen, the Institute of Physical Chemistry of the University of Copenhagen, gave a similar result.

The corresponding experiment with a solution containing nitric acid provided the following results:  $A = 1.50 \cdot 10^{-3}$  and  $B = 1.78 \cdot 10^{-2}$ .

In proof of the applicability of the formula the two functions  $\log \frac{a}{x}$  and  $f(x) = \log \frac{a}{x} + A \left( \frac{1}{x} - \frac{1}{a} \right)$  have been plotted against  $t$  in Fig. 1 curve I and curve II respectively.

The figure shows quite clearly:

1. that the reaction cannot be considered to be a unimolecular reaction, if so, curve I should have been a straight line.

2. that the reaction, even when it has proceeded almost to completion, conforms with close approximation to the velocity expression used for calculation of the experiments<sup>1</sup>. Curve II is a straight line.

The difference between the magnitudes of the constants  $A$  and  $B$  as calculated from the experiment on decomposition in a solution containing nitric acid and as calculated from the experiment on decomposition in a solution containing perchloric

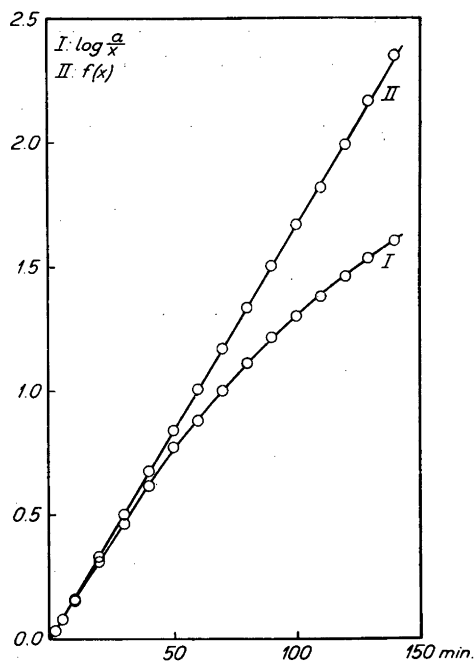


Fig. 1. The decomposition of hydrogen peroxide at 25°C in solution 0.004 M as to ferric perchlorate and 0.01 M as to perchloric acid. The initial concentration of hydrogen peroxide was 0.05 M. Curve I is a plot of  $\log \frac{a}{x}$  against time  $t$ . Curve II represents the function  $f(x) = B \cdot t = \log \frac{a}{x} + A \cdot \left( \frac{1}{x} - \frac{1}{a} \right)$  plotted against time  $t$ ;  $A = 0.95 \cdot 10^{-3}$ ;  $B = 1.67 \cdot 10^{-2}$ .

acid should no doubt be ascribed to a difference in the salt effect.

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1. Andersen, V. S. *Acta Chem. Scand.* **2** (1948) 2.
2. Bray, W. C., and Peterson, S. *J. Am. Chem. Soc.* **72** (1950) 1401.
3. Abel, E. *Monatsh.* **80** (1949) 776.
4. Andersen, V. S. *Acta Chem. Scand.* **4** (1950) 914.
5. Christiansen, J. A., and Andersen, V. S. *Acta Chem. Scand.* **4** (1950) 1538.

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