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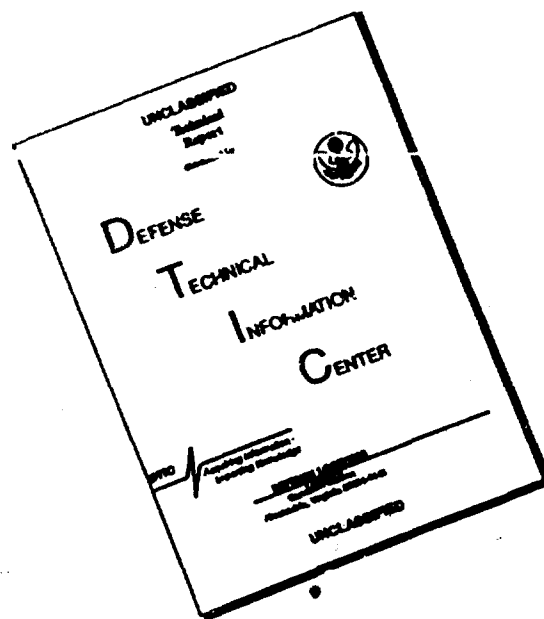document from DDC.

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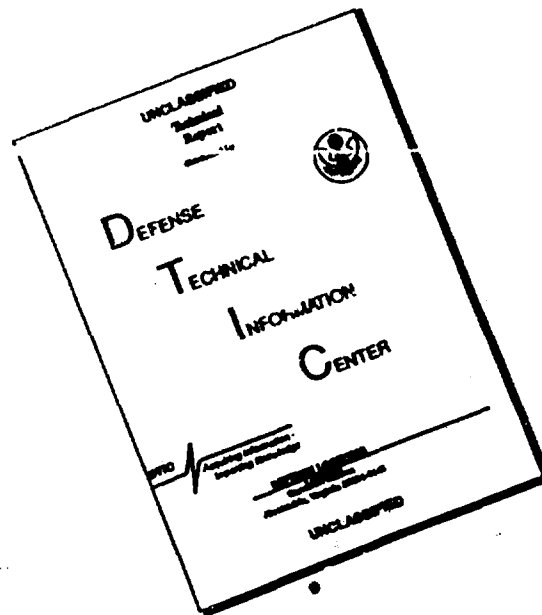DEPARTMENT OF THE ARMY
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INVESTIGATION OF THE CHEMOLUMINESCENCE OF THERMAL
DECOMPOSITION OF HYDROGEN PEROXIDE IN WATER

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Decomposition of hydrogen peroxide in water is accompanied by an ultraweak luminescence. As compared with the bright chemoluminescence of widely known reactions of oxidation by hydrogen peroxide of phtalic hydrazides, lucigenine, etc. (Sveshnikov, 1940), the intensity of detected luminescence is extremely low. The quantum yield equals approximately one photon per 10^{14}-10^{16} transformation acts of hydrogen peroxide. To analyze the spectral composition of such radiation is a rather complicated matter; therefore, the present article has not aimed to identify the excited particles which emit light. The kinetics of luminescence and its dependence on the reaction of hydrogen peroxide decomposition have been investigated; an attempt was made to determine the elemental reaction which is accompanied by a most intensive luminescence.

Decomposition of hydrogen peroxide in water is carried out in sealed ampules with a flat bottom made of "pyrex" glass after a preliminary freezing of the solution and removal of the air with a rough exhaust pump. The ampule was placed in a copper cylindrical block, heated with a spiral coil made of nichrome wire (diameter of ampule 30 millimeters, probe volume 40 milligrams). The luminescence was recorded with a FEU-19 M photomultiplier, subsequent amplification of the photocurrent with an electrometric EMU-3 amplifier and automatic recording on a EPP-09 potentiometer.

It is well known that hydrogen peroxide decomposition is accelerated by admixtures in water and in the peroxide proper,

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as well as by the surface of reaction container, and that it depends on the pH of the medium (Shamb et al., 1958). Therefore, in order to inactivate the surface, the ampules were heated with nitric acid for 3-4 hours, kept for 24 hours with distilled water and heated at 100°C with a hydrogen peroxide solution (0.1 M) for 8-10 hours. Pure 95-99% hydrogen peroxide was used; its dilution to 0.02-0.2 M makes it possible to consider its admixtures as negligible in comparison with the admixtures in water. The water was purified with ion-exchange resins and 3-4-fold distillation in a quartz apparatus with the use of reagents (H_2O_2, $KMnO_4$) for the removal of organic admixtures. Nevertheless, there still remains after such purification a certain amount of admixtures in the water, which were detected through the weak luminescence of water at 120-150°C and their weak absorption in the ultraviolet band, at a considerable thickness of the absorbing layer (10 centimeters), as well as per the pH of water which was always under 7 (4.75-5.5). According to literary data, the most probable admixtures in our employed methods of water purification might be ions of metals of general concentration of $10^{-5}-10^{-6}$ (Vasilevskaya et al., 1959).

The kinetic curves of changes in luminescence intensity as related to time, at various temperature (74-150°C) and various pH (2.5-13), enabled us to obtain a number of data concerning the course of the chemoluminescence reaction. The obtained data were compared with the results of hydrogen peroxide decomposition, under the same conditions, obtained by the iodometric titration. In all series of tests, the linear dependence has been established of luminescence intensity on the hydrogen peroxide concentration in the 0.04-0.4 M interval. The rate constant of the luminous reaction was determined from

the dependence of $\lg \frac{I_o}{I_t}$ in relation to time, where I_o represents

the initial intensity and I_t -- the intensity at the t moment.

The reaction course on luminescence and on iodometric titration turned out to be the first in every case (pseudomolecular). The values of activation energy, calculated according to the initial luminescence intensity, coincide within the range of an experimental error with the values of activation energy of the gross-reaction of peroxide decomposition. Depending on the presence of admixtures, the activation energy had values of 6, 15, 16, 20 kg-calories/mole. The rate constants of the luminous reaction in some processes revealed a slight dependence on temperature.

The dependence was investigated of the luminescence intensity and the rate constant of the luminous reaction on the

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pH medium (Fig. 1). The luminescence intensity, as well as the rate constant of the luminous reaction reach their maximum value at pH 12, when 50% of peroxide becomes dissociated and the product $[HO_2^-] \cdot [H_2O_2]$ has a maximum value. Investigation of alkaline solutions was carried out within the thermal interval of 74-100°C; it was found that the velocity rate of the light reaction constant is very little dependent on the temperature.
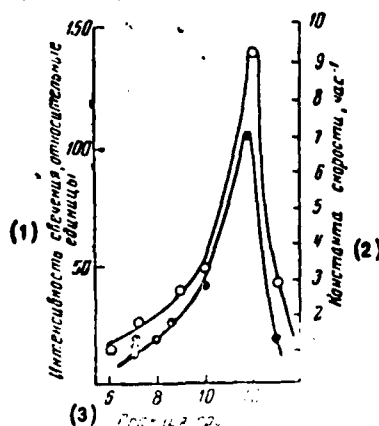

Fig. 1. Dependence of Luminescence Intensity and Rate Constant of the Chemoluminescence Reaction on the pH of the Medium.

1 -- Luminescence intensity, in relative units; 2 -- Rate constant, in hour^{-1}; 3 -- Reaction of the medium, in pH.

It was established that pure hydrogen peroxide of any given concentration, free of admixtures, in a container with non-catalyzing walls, behaves as an extremely stable compound: purification is the best method of its stabilization (Shamb et al., 1958). The energy of disruption of the HO--OH bond equals approximately 50 kg-cal/mole, that of HOO--H bond -- approximately 87 kg-cal/mole (Cf. "Energy of Disruption of Chemical Bonds," 1962) (Cf. Bibliography, International Literature). Therefore, H_2O_2 decomposition in water, even at high temperatures (150°C), at the expense of disruption of these bonds, is scarcely probable. However, it is also well known that extremely small concentrations of a large number of compounds catalyze the decomposition of hydrogen peroxide (Shamb et al., 1958).

Let us analyze the obtained results and the most probable reactions of its decomposition. In aqueous solutions, hydrogen peroxide is partially dissociated:

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$$H_2O_2 \rightleftharpoons H^+ + HO_2^-$$
$$C_{dis} = 2.4 \cdot 10^{-12} \text{ at } 25 \,^\circ C \text{ (Journer. 1912)}.$$
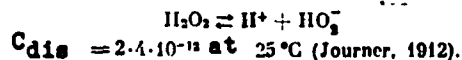
The configurations of hydrogen peroxide (bath) and perhydroxyl ion (incomplete bath), established spectroscopically according to the spectra of the combined diffusion of alkaline solutions (Simon, Feher, 1935), render as probable the hypothesis of the formation of a six-membered complex at the expense of hydrogen bonds. It leads to the decomposition mechanism suggested by Erdey (1953) and Inczedy and Erdey (1955):
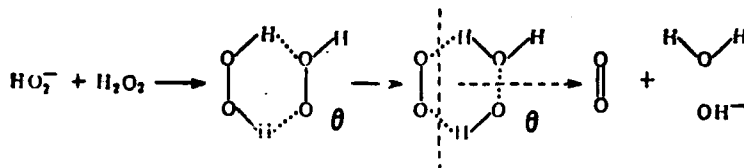
According to this equation, hydroxyl ions do not catalyze the dissociation, and only upon increase of their concentration they shift the equation of electrolytic dissociation in the direction of formation of a perhydrox 1 ion and affect the decomposition rate, which is proportional to $[HO_2^-] \cdot [H_2O_2]$. The decomposition rate reaches its maximum value at pH 12 and 50% ionization. This has been confirmed by the works of Erdey and Inczedy (1955), Duke, Trice (1961) et al.

Our investigations showed that the luminescence intensity and the luminous reaction rate also reach their maximum value at the maximum value of the product $[HO_2^-] \cdot [H_2O_2]$ and at pH 12; hence, the chemoluminescence reaction is also determined by the formation and decomposition of this complex. However, from the kinetic curves of luminescence and decomposition at pH 12, it can be seen that the luminescence intensity decreases much faster than the expenditure of peroxide, i.e., chemoluminescence does not fully reflect the gross-decomposition of hydrogen peroxide. Besides, in the pH 2.5-7 interval, the luminescence intensity shows almost no change. Apparently, also other elementary decomposition reactions are accompanied by luminescence, but the decomposition intensity is lower.

We also attempted to elicit the presence of the complex spectroscopically. In fact, in the area of 215-200 millimicrons one finds in alkaline solutions a maximum of absorption (Fig. 2). The optic density increases with the rise in pH -- hence, with the increase in concentration of the perhydroxyl ion. There is an inverse ratio between optic density and temperature: with the rise of temperature there is a decrease of optic density, and when the temperature decreases, the initial value of optic

density is restored within 8% accuracy. This dependence is
characteristic for hydrogen bonds. The dependence of optic
density on concentration is linear, but it does not pass through
zero. This fact can be explained by the formation of complexes
of hydrogen peroxide or perhydroxyl ion with admixtures in water.
When the assumed complex is very stable, its concentration at
once reaches its maximum value, which enters as an additive
value in the total optic density of the solution. In water
which was deionized and distilled in a quartz apparatus, the
maximums and intensity of absorption of the aqueous solutions of
hydrogen peroxide are shifted -- a fact probably connected with
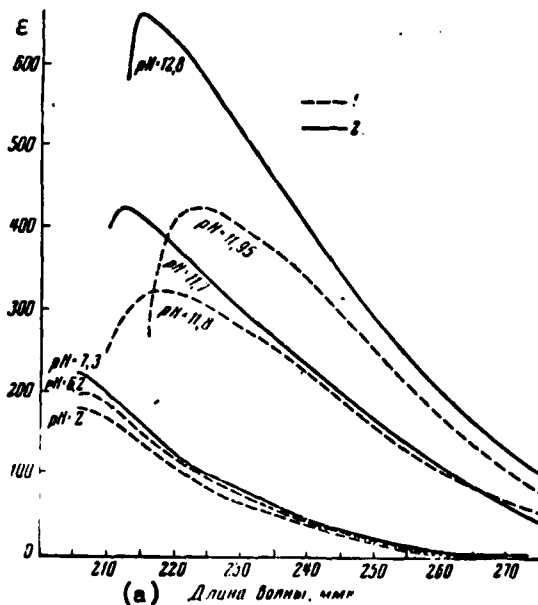the various nature of admixtures.

Fig. 2. Absorption Spectra of Alkaline Solutions of
Hydrogen Peroxide at Various pH of the Medium. 1 --
Deionized water; 2 -- Twice-distilled water; along
ordinates axis -- the intensity of absorption (M^{-1}
liter·cm^{-1}).

a -- Wavelength, in millimicrons.

On the basis of obtained experimental data, it can be
assumed that the decomposition of hydrogen peroxide takes place
as a result of complicated complex-formation between hydrogen
peroxide, perhydroxyl ion and admixtures, according to the
equation:

$$HO_2^- + H_2O_2 + M \rightarrow [HO_2^- \cdot H_2O_2 \cdot M] \rightarrow O_2 + H_2O + OH^- + M.$$
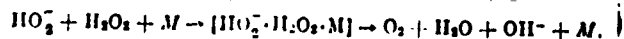
The peroxide decomposition, according to this equation, supplies the energy of excitation to a given particle, which subsequently emits light. The concentration of the complex depends on the degree of dissociation of hydrogen peroxide.

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