# Corresponding Member of the Academy of Sciences of the USSR V. M. VDOVENKO, E. K. LEGIN, O. B. STEBUNOV

and V. A. SHCHERBAKOV

1960

SovietRxiv

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR V. M. VDOVENKO, E. K. LEGIN, O. B. STEBUNOV
and V. A. SHCHERBAKOV

# RELAXATION OF PROTONS IN HYDROGEN PEROXIDE SOLUTIONS IRRADIATED WITH ULTRAVIOLET RADIATION

Recent studies of the relaxation time of protons in aqueous solutions subjected to ionizing radiation have shown that such solutions have relaxation times reduced in comparison with unirradiated ones. Thomas and Duffy ([1]) found in 20% tritiated water an almost threefold shortened time $T_1$ of the protons. Vdovenko and Shcherbakov ([2]) observed an analogous effect in various aqueous media irradiated by $\beta$- and $\gamma$-radiation sources introduced into them or located outside them. They concluded that paramagnetic particles arise in the solutions studied, appearing during their radiolysis and, as experiment showed, not disappearing when it ceases but existing for a fairly long time. Decabrune and Purmal ([3]), in the reaction of thermal decomposition of hydrogen peroxide, also noted a decrease in the relaxation time of protons, which the authors explained by the formation of a large number of free radicals $HO^{\cdot}$ and $HO_2^{\cdot}$, whose paramagnetism affects $T_1$ of the solution protons.

It is well known ([4]) that when $H_2O_2$ is irradiated with ultraviolet radiation, owing to the photochemical reactions taking place, decomposition of the peroxide occurs, having a chain character, in which a large number of free radicals are formed. In connection with the above-mentioned works, the study of proton relaxation in such a system is of undoubted interest. The first results of work in this direction are presented in this communication.

The method used did not differ from that described in ([2]). The gain of the apparatus was determined and monitored with special standard solutions of manganese sulfate. Measurements were carried out on the rectilinear portion of the calibration curve (from $0.1 \cdot 10^{-4}$ to $4.0 \cdot 10^{-4}$ $M$ $Mn^{+2}$). The initial reagent was $H_2O_2$ of chemically pure grade. Its concentration was carried out by distilling 30% peroxide at 15–20 mm Hg in a quartz apparatus with a dephlegmator. The concentration was determined permanganatometrically. The experiments were carried out in quartz ampoules. A PRK-2 lamp without filters served as the radiation source. The temperature of the experiments was room temperature.

As in the case of thermal decomposition, upon exposure of $H_2O_2$ to ultraviolet

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

radiation one should expect a decrease in $T_1$. Indeed, this was noted already in the very preliminary experiments. In Fig. 1 are presented curves characterizing the increase of the signal (the ratio of the signals from irradiated and unirradiated solutions) as a function of the time of irradiation of the peroxide for different concentrations of the latter. All the curves are of the same type and have the character of so-called saturation curves.

Fig. 2 represents the dependence of the quantity $\alpha$, corresponding to the "saturation" of the curves in Fig. 1, for solutions of different concentrations of $H_2O_2$. It shows that the effect is observed over a wide range of concentrations, and its intensity ($\alpha$) changes in a very different manner. Measure-

signal were measured both directly during irradiation and after some time, necessary for transferring the ampoule from the radiation source into the generator circuit (5–10 sec). Since the lifetimes of free radicals are very short, one should expect in this case, if the signal is wholly or partly due to the effect of the paramagnetism of free radicals, a sharp drop in the signal at the first moment after cessation of exposure. As Fig. 3a shows, this was not observed; i.e., the products causing the shortening of $T_1$ do not disappear immediately, but only after a considerable interval of time. If free radicals nevertheless were present in the irradiated peroxide, then the apparatus did not sense a change in the signal corresponding directly to an increase in the number of paramagnetic particles owing to the formation precisely of free radicals, in the full sense of the word.

**Fig. 1**

Since the sensitivity of the setup, as determined by us for the $Mn^{+2}$ ion under these conditions, was $0.1 \cdot 10^{-4}$ $M$, the fraction of the concentration of free radicals is less than $1.2 \cdot 10^{-4}$ $M$, if their effective magnetic moment ($\mu_N$) under these conditions is taken to be $1.7\beta$ ($\beta$ is the Bohr magneton; the estimate was made by the method described in (5)).

Thus, the measured effect is caused not by the free radicals themselves as such, but by products genetically connected with them. Indeed, it turned out that if, before irradiation, a small amount of acrylonitrile is introduced into the peroxide solution, which polymerizes under the action of free radicals and thus leads to their disappearance, then no decrease in the relaxation time is observed.

**Fig. 2**

Experiments with the thermal decomposition of $H_2O_2$ (30%) showed that the

Fig. 3

Figure 3: Fig. 3

intensity of the decrease in the relaxation time in this case is greater than for the photochemical reaction under the action of ultraviolet radiation. It is significant that subsequent lowering of the temperature to the initial value did not restore the original signal magnitude. The character of the disappearance of the signal (Fig. 3b) apparently indicates a certain commonality of the observed effects.

Mechanical action on irradiated peroxide (stirring, for example, at different rates) over the entire range of concentrations studied led to a fall of the signal at a rate depending on the intensity of the action. At the same time, the release of bubbles of oxygen formed during photolysis was observed. Calculation of the amount of $O_2$ that could create the $T_1$ time observed in irradiated $H_2O_2$ indicates considerable supersaturation with oxygen of the solutions studied. For medium peroxide concentrations the supersaturation is 10–20 times relative to atmospheric air; for the case of thermal decomposition the supersaturation is higher (30–50 times).

These estimates were made for $\mu_N$ of $O_2$ in $H_2O_2$ equal to $1.2\beta$ (6) (as also for water), and for the solubility of oxygen in $H_2O_2$ solutions equal to its solubility in water. Bearing in mind the denser structure of peroxide solutions than that of water, these figures are probably underestimated by a factor of 1.5–2. It is interesting to note that in the region of high $H_2O_2$ concentrations (70–80%) the release of -

relatively large amounts of oxygen was not accompanied in its first moments by a noticeable decrease in the signal.

The totality of the experimental data presented can be explained by assuming that the observed effect is due to the action of dissolved $O_2$. The form of the curves in Fig. 1 may be due to the limit for supersaturation under these conditions. The beginning and end of the curve in Fig. 2 can be attributed to the gradual increase in the amount of oxygen evolved with the peroxide concentration and to the decrease in the degree of its supersaturation in the region of high concentrations. However, the signal-decay curves (Fig. 3) apparently indicate the presence of two processes proceeding at different rates. In the first moments after the cessation of irradiation, a sharp decrease in the signal is observed, which is then replaced by its slow decline, ending after 15–20 h. A different picture is observed in the case of thermal decomposition of the peroxide. The observed phenomenon probably cannot be explained solely by the process of oxygen evolution from the solution.

**Fig. 3.** Change in the signal magnitude with time after cessation of irradiation (a) and for thermal decomposition (b). The concentration of $H_2O_2$ is the same in both samples.

The authors are deeply grateful to Yu. V. Turikov for interesting discussion and advice.

Radium Institute named after V. G. Khlopin
Academy of Sciences of the USSR

Received
23 VI 1960

## REFERENCES

1. W. Thomas, J. Duffy, *Bull. Am. Phys. Soc.*, **2**, No. 4, 250 (1959).
2. V. M. Vdovenko, V. A. Shcherbakov, *DAN*, **127**, 127 (1959).
3. L. L. Dekabrun, A. P. Purmal, *DAN*, **116**, 983 (1957).
4. U. Shamb, Ch. Setterfield, R. Wentworth, *Hydrogen Peroxide*, IL, 1958.
5. V. M. Kozyrev, A. I. Rivkind, *ZhETF*, **27**, 69 (1954).
6. G. Chiarotti, L. Giulotto, *Phys. Rev.*, **93**, 1241 (1954).

*Note: Figure translations are in progress. See original paper for figures.*