L. L. DEKABRUN and A. P. PURMAL’

1957

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

L. L. DEKABRUN and A. P. PURMAL'

INDICATION OF RADICALS BY THE NUCLEAR-RESONANCE METHOD

(Presented by Academician V. N. Kondrat' ev, 29 III 1957)

The height of the nuclear-resonance absorption signal (when using the so-called rapid-passage technique) depends on the spin-lattice relaxation time T_1. A decrease in the value of T_1 causes an increase in the signal.

In 1946 it was shown (1) that the relaxation time is greatly reduced if paramagnetic ions Fe^{3+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, etc., are present in the system. Quantitatively this effect is described (2) by the following equation:

$$\frac{1}{T_1} = k\frac{\eta N \mu^2}{T},$$

where T_1 is the relaxation time, k is a constant whose magnitude depends on the magnetomechanical properties of the nuclei, N is the concentration of paramagnetic ions, μ is the effective magnetic moment of the ions, η is the viscosity of the liquid, and T is the temperature.

Small additions of paramagnetic ions make it possible to observe the resonance-absorption signal in samples with large values of T_1. Free radicals possess an unpaired electron and the corresponding magnetic moment. It was natural to suppose that the presence of radicals in the system would cause an effective reduction of the relaxation time and a corresponding increase in the resonance-absorption signal.

Preliminary study of the possibilities of applying the nuclear-resonance technique to the detection of free radicals was carried out on autodyne circuits being tested at the Institute of Chemical Physics of the Academy of Sciences of the USSR. A typical oscillogram of proton resonance absorption of water with an addition of $CuSO_4$, obtained on this apparatus, is shown in Fig. 1. Verification of our supposition concerning the influence of radicals on the magnitude of the spin-lattice relaxation time naturally had to begin with the simplest case—a solution of a stable radical. Pure benzene on our apparatus gives no proton-absorption signal. This is due to the fact that the relaxation time of benzene is measured in several seconds, whereas the apparatus used made it possible to detect an absorption signal from

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 1

samples having a relaxation time on the order of 1 sec and less. We expected that a 0.01 N benzene solution of the free radical diphenylpicrylhydrazyl would give a proton absorption signal. These expectations, however, were not fulfilled. The decrease in relaxation time was apparently insufficient. We then proceeded by artificially decreasing the relaxation time by increasing the viscosity of the system. Along this path we obtained the expected result. A solution of diffusion oil in benzene (30% by volume) gave a proton absorption signal at the noise level. The same solution, but containing diphenylpicrylhydrazyl, gave a quite distinct signal.

Fig. 2. Oscillograms of proton-resonance signals from decomposing hydrogen peroxide: **1**—at $T = 332°\mathrm{K}$, **2**—at $T = 368°\mathrm{K}$

It seemed to us that the effect could be observed on a large scale in the case of simpler radicals. Since simple radicals are not stable, it was natural to turn to a chemical reaction as a generator of such simple radicals. In choosing a reaction proceeding with the participation of radicals, we were guided by two criteria: a sufficiently high reaction rate at not-too-high temperatures and a high concentration of hydrogen nuclei in the system. As such an object we chose the reaction of thermal decomposition of H_2O_2. Neither water nor a 30-percent solution of H_2O_2 at room temperature gave a proton absorption signal. Upon raising the temperature, the appearance of a proton absorption signal from the decomposing H_2O_2 was observed. With a further increase in temperature and, correspondingly, in the rate of decomposition of H_2O_2, a further increase in the proton absorption signal was observed. Fig. 2 gives a reproduction of oscillograms obtained from decomposing H_2O_2 at two temperature values*.

Fig. 3. Oscillograms of proton-resonance signals from a solution of cupric sulfate ($n_{\mathrm{Cu}^{++}} = 6 \cdot 10^{18}\ \mathrm{cm}^{-3}$). **1**—at $T = 294°\mathrm{K}$, **2**—at $T = 368°\mathrm{K}$

From the formula given above it is seen that, as the temperature rises, the relaxation time will increase according to the law

Fig. 3

Figure 3: Fig. 3

$$T_1 \sim \frac{T}{e^{A/T}}$$

(the denominator takes into account the decrease of viscosity with temperature). The increase of the relaxation time with temperature causes a decrease in the height of the resonance-absorption signal. To estimate the scale of the change in the height of the proton absorption signal with temperature, Fig. 3 gives a reproduction of oscillograms (on the same scale as for H_2O_2) obtained from a $0.01\,M$ solution of CuSO** at two temperatures.

The anomalous temperature dependence of the height of the proton absorption signal in the case of decomposing H_2O_2 is quite natural, since an increase in temperature leads to a strong increase in the concentration of radicals.

* Since the process of decomposition of H_2O_2 is accompanied by the evolution of oxygen, which has paramagnetic properties, and there is the possibility that the "appearance" of the signal is due to oxygen dissolved in the water, we carried out special calibration experiments. The amplitudes containing water with oxygen dissolved under various pressures in the range from 4 to 50 atm were prepared. Comparing the heights of the proton-absorption signals obtained from H_2O_2 and from solutions of O_2 in water at the same temperatures, we found that the signal height from H_2O_2 at 95° corresponds to the amount of oxygen dissolved in water under a pressure greater than 50 atm. The question of the possibility of supersaturating water with oxygen was specially investigated by Seilor [3]. From the results of his work it follows that there can be no question of 50-fold supersaturations, even in the absence of stirring.

** The paramagnetic ion Cu^{2+} was chosen for comparison because its effective magnetic moment is closest in magnitude to the magnetic moment of radicals.

A very valuable observation, consistent with the results we have obtained, is the fact that the relaxation time is greatly reduced in certain solid samples subjected to high-energy radiation (4). The action of radiation leads to the formation of *F*-centers—holes in the crystal lattice occupied by a free electron. In its physical manifestations, an *F*-center is similar to a free radical. In particular, it gives an effective signal of electron-resonance absorption.

The decrease in relaxation time observed: a) upon adding the free radical diphenylpicrylhydrazyl to the system; b) in the decomposition reaction of H_2O_2, in the course of which $\dot{O}H$ and HO_2-radicals are generated; c) in samples containing *F*-centers—all this confirms the validity of our assumption that radicals effectively influence the relaxation time and can be detected by the method of nuclear magnetic resonance.

This method for indicating free radicals, while inferior in sensitivity and accuracy to the direct method of electron paramagnetic resonance, will apparently be able to supplement the latter and broaden the possibilities of its application (in particular, for example, in the study of radicals in media with high electrical conductivity).

In conclusion, we express our gratitude to V. V. Voevodskii for his constant interest in the work and for valuable discussions.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
18 III 1957

REFERENCES

1. F. Bloch, W. W. Hansen, M. Packard, *Phys. Rev.*, **70**, 474 (1946).
2. N. Bloembergen, E. M. Purcell, R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
3. C. A. Seylor, *Chem. News*, **67**, 87 (1893).
4. W. Heitler, E. Teller, *Proc. Roy. Soc.*, **155 A**, 629 (1936).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.