HOKKAIDO UNIVERSITY

Title	ESR Desaturation Effect of Life Time of Free Radicals in Chemical Reaction
Author(s)	Sohma, Junkichi
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 11(4), 397-402
Issue Date	1963-03
Doc URL	https://hdl.handle.net/2115/37831
Type	departmental bulletin paper
File Information	11(4)_397-402.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

ESR Desaturation Effect of Life Time of Free Radicals in Chemical Reaction

Junkichi SOHMA

Contents

1. Introduction 397
2. Life Time Effect 398
3. Discussion 400
4. Conclusion 401
5. Acknowledgement 402

1. Introduction

Among various kinds of magnetic centers causing magnetic resonance, free radical is the only species whose life time is considered to be finite. However, if the free radicals have too short a life time, the decay proceeds so rapidly that sufficient concentration for ESR observation from the radicals is hard to obtain. This is the reason why most of ESR research works on free radicals have been done on either frozen radicals in solid matrix or on stable aromatic ion radicals. In these conditions the radicals survive long enough for giving a sufficient concentration for ESR. Normally the number of decaying radicals is negligibly small in such cases, it is quite reasonable to consider that no radical decays during a run of experiment. In other words, to a good approximation each radical is assumed to have an infinitely long life time. In so far as radicals in the above mentioned condition are concerned it is not surprising that so little attention has been paid to the effect of the life time of radicals on ESR spectrum, in spite of the fact that instability is one of the most significant properties of radicals.

Recently, the observations of ESR signals from active radicals, which are not in frozen but in reactive state, were done by Piette et al for photochemical reaction[1] as well as for biological one[2]. In such a reactive state, life time of radicals is no longer considered to be infinitely long and at the same time sufficient concentration of radicals for observing ESR are apparently obtained. In this case both creation and annihilation of the radicals occur simultaneously. And the rate of radical creation by stimulation is larger than the decay rate initialy, and this predominant creation rate gives sufficient concentration of radecals for ESR observation. As the concentration increases, the decay rate, which is the recombination rate of radicals, must be accelerated and a stationary

state may be obtained finally. In such a situation it is worthy to consider how the finite life time of radical affects the ESR signal.

2. Life Time Effect

The change of the concentration of radicals is expressed by the following equation

$$\frac{dN}{dt} = -k_t N^2 + U \qquad (1)$$

where N stands for the number of the radicals, k_t for the annihilation rate by recombination, U for the creation rate of the radicals through the stimulation. For stationary state, $\frac{dN}{dt} = 0$. In this stationary state, the intensity of the ESR signal does not change. The effect of life time will be discussed assuming this stationary state.

In order to consider how the finite life time of the radicals affects the ESR signal, there are two ways to treat this effect. The first one is the treatment from the stand point of the uncertain principle. This may of describing the effect was already discussed by Weissman[3] and Fraenkel[4]. From the stand point of the uncertainty, however, no more progress is expected in the discussion on the effect of the life time of radicals to ESR signal, because, without knowing the interrelation between the life time of radical and other time factors of ESR, such as spin-lattice relaxation time, no one can tell which time factor is predominant and important.

The other way to discuss the effect is to consider it as a kind of spin-lattice relaxation. This treatment is discussed below.

For this discussion, the life time is reasonably assumed to be independent of the magnetic state, because energy for radical recombination is far larger than that of the separation between the magnetic states. And also the life time is considered to be constant for a definite kind of radicals. Suppose molecules are in a static magnetic field and sitimulated by either light or other agents. By the stimulation free radicals are produced with the rate U from the stable molecules in the static field and are distributed with the weight of the Boltzmann factor between the magnetic energy states. This Boltzmann distribution is perturbed by the microwave radiation in the resonance condition, and the population at the higher magnetic energy state is increased and that at the lower one is decreased. From the assumption that the decay rate of the radical is independent of the magnetic energy, the number of the radicals decaying from the higher magnetic energy state which are partially saturated

is larger than that of the decaying radicals from the same magnetic state which are unsaturated. For the lower magnetic energy state the decay frequency of the radicals in the partially saturated condition is smaller than in unsaturation. On the other hand, new radicals are produced by the stimulation and the distribution of these newly born radicals is the Boltzmann distribution. In other words, the magnetically fresh radicals are supplied through both annihilation and creation of the radicals, that is, the decay of the unstable radicals to non-radicals serves to remove the saturation of the magnetic resonance.

This contribution of the decay of the radicals to the desaturation may be estimated quantitatively in a similar way to Singer's discussion on the flow rate effect to the relaxation[5]. The relaxation equation is expressed by

$$\frac{dn}{dt} = \frac{(n_0 - n)}{T_1} + k\,(n_0 - n) \qquad (2)$$

The first term is known as the ordinary spin-lattice relaxation, the second term represents the relaxation by the annihilation of the radicals. In Eq. (2), k is the decay rate of the radicals, 0 suffix means non saturation, n stands for the population difference between the upper and lower magnetic states. Now the apparent spin-lattice relaxation time T_1' is defined as $\frac{1}{T_1'} \equiv \frac{1}{T} + k$, and also it is well known that the ESR signal intensity is proportional to the saturation factor $(1+Z)^{-1}$. In the stationary state, in which the annihilation and creation of the radicals is balanced to hold a constant concentration, T_1 in Z of the saturation should be replaced with T_1' which involves both T_1 and the decay rate k. Thus, the signal intensity I_r, in this stationary state, is proportional to $\left(1 + \frac{Z}{1+kT_1}\right)^{-1}$, and we get

$$\frac{I_r - I}{I} = \frac{Z\left(1 - \frac{1}{1+kT_1}\right)}{\left(1 + \frac{Z}{1+kT_1}\right)} \qquad (3)$$

where I is the ESR intensity of the frozen state. To a good approximation in the case of $\frac{Z}{1+kT_1} \gg 1$,
we obtain

$$\frac{I_r - I}{I} \approx kT_1 \qquad (4)$$

3. Discussion

Temperature Dependence

As it has been shown in the former section, the recombination and creation of the radicals provide an additional path of the spin-lattice relaxation. Therefore, this process affects the line width of the ESR spectrum. The line width of ESR spectrum is influenced by various factors, such as spin-lattice relaxation time, dipole-dipole coupling. As shown in the above section, the life time is proved to be one of the factors affecting the ESR line width through its relaxation mechanism. The line width determined by ordinary spin-lattice relaxation time is known to cause width narrowing with rising temperature because spin-lattice relaxation increases with temperature. If the dipole-dipole coupling is the main source of the line broadening, the line width also narrows with the increasing temperature. On the other hand, if the life time of the radicals is the predominant factor for the line broadening, the line width increases with increasing temperature because the life time of the radicals become generally shorter as temperature is raised. This temperature dependence is the inverse of that of the line width due to other factors and the characteristics of the life time effect to the line width.

Using this characteristic temperature dependence of the line width we can discriminate the case, in which the line width of ESR signal is mainly determined by the life time effect of the radicals, from others. That is, by checking the temperature dependence of the line width one can say that the line width is mainly attributed to the life time relaxation process if the line width is observed to become broader with the rising temperature.

Estimation of Life Time and Relaxation Time

By measuring the ESR intensities I and I_0, it is possible to estimate the recombination rate of the radical by use of the Eq. (3) and the known spin-lattice relaxation time.

However, the Z in the Eq. (3), which is well known to be expressed as $\gamma H_1 T_1 T_2$, is not easily estimated with good accuracy. In order to estimate the k, therefore, it is not wise to use the Eq. (3). Instead of the Eq. (3), the Eq. (4) may be useful because this equation does not involve the factor Z.

In order to consider the validity of the condition, with which the approximation becomes reasonable, the orders of magnitude of the factors involved, such as Z, T_1 and k, must be examined. The factor Z is considered to have the order of magnitude of 10^0, because in the case of larger values of Z than 10, the saturation is so strong that the signal is hardly observed.

The spin-lattice relaxation time T_1 is known to vary in the order of magnitude from 10^{-8} sec. to several seconds. Okamura, Yoshida and Nakai measured the spin-lattice relaxation time in ESR by saturation method and reported that its order of magtitube is 10^{-6} sec. at room temperature[6]. Assuming that the condition $\frac{Z}{1+kT_1} \gg 1$ holds with the facts above stated, then kT_1 must at least be negligible to unity. This means that $k \ll \frac{1}{T_1}$, that is $k \ll 10^6$ $\sec^{-1}$. Since the recombination rate k is a reciprocal quantity of mean life time of a radical, the recombination rate $k \ll 10^6 \sec^{-1}$ is considered not to be an unreasonable value.

The condition $kT_1 \ll 1$ holds if the spin-lattice relaxation time has the order of magnitude of 10^{-6} sec and the recombination rate is smaller than $10^5 \sec^{-1}$. These values of both T_1 and k may not be said to be unreasonable, although sufficient information on these quantities is still not available at present. The approximated equation (4) may possibly be used for the experiments which are supposed to satisfy the condition $kT_1 \ll 1$. In this case it is possible through Eq. (4) to estimate the life time of the radicals with known T_1 by measuring the ESR intensity I_s for the stationary state and that I for the frozen state.

By a similar procedure T_1 may be obtained if k is known. Although the necessary condition for the validity of Eq. (4) is that $kT_1 \ll 1$ as discussed above, Eq. (4) shows that the ESR intensity I_s for the stationary state is equal with sufficient approximation to the intensity I for the frozen state in the case where kT_1 is too much smaller than unity. It is found from the above consideration that Eq. (4) has practical availability only for the favorable circumstances in which kT_1 is smaller than unity but not too smaller.

4. Conclusion

The effect of the finite life time of radicals to the ESR spectrum is discussed and it was found that finite life time of radicals provides an additional path of the spin-lattice relaxation, through which the absorbed energy dissipates. This additional relaxation acts as the desaturation effect when the line width is partially saturated. The line width due to this additional relaxation arising from the life time effect has the inverse of the ordinary temperature dependence, that is to say the line width increases with increasing temperature in this case. This additional relaxation is shown to be treated quantitatively and the results of the quantitative treatment of this effect give us a means to estimate the life time of the radical with known T_1 in favorable conditions.

Acknowledgments

The author would like to express his appreciation for the financial support of the Asahi Chemical Industry Foundation which enabled this research.

References

1) L. H. Piette and W. L. Landgraf: J. Chem. Phys. **32**, 1107 (1960).
2) I. Yamazaki, W. Mason and L. Piette: J. Biol. Chem. **235**, 2444 (1960).
3) R. I. Ward and S. I. Weissman: J. Am. Chem. Soc. **76**, 3612 (1954).
4) D. M. Gardner and G. K. Fraenkel: J. Am. Chem. Soc. **78**, 3279 (1956).
5) J. R. Singer: J. App. Phys. **31**, 125 (1960).
6) H. Yoshida, H. Nakai, S. Okamura: Ann. Meeting of Phys. Soc. Japan, 1962, April.