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An NMR Study of Proton Exchange in Alcohols. I. Oxygen Effects in Methanol*[1]

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Molecular interactions between oxygen and organic molecules are investigated in detail. It was confirmed that the broadening of spectral lines due to oxygen is appreciable only with hydroxyl protons. This effect is attributed to the enhancement of the proton exchange of OH groups by oxygen. Detailed investigation was made with methanol-oxygen system. In relation with this, a new method is proposed which makes the measurement of heat of dissolution of oxygen in methanol possible.

It has long been known that the line widths of the electron spin resonance are much broadened by oxygen, but not by nitrogen, argon, and hydrogen.[1] This oxygen effect has tentatively been ascribed to a dipolar broadening of the line from adsorbed paramagnetic oxygen. The reversible interaction of carbon-free radicals with molecular oxygen has also received considerable attention.[2-6]

A similar broadening effect is assumed to exist in high-resolution NMR spectra. Chiarotti and Giulotto made an effort to obtain the T_1 of water which is completely free of oxygen.[7] Gaven, Stockmeyer, an Waugh referred the oxygen effect in the T_1's of methane and other diamagnetic gases.[8] They interpreted the oxygen effect in the same way as in ESR, in terms of local magnetic fields which alter the lifetimes of nuclear-spin states.

However, so far as we know, there is no evidence which shows that the observed line-width broadening with oxygen is mainly due to paramagnetic dipolar interactions. On the contrary, in our preliminary experiment, we encountered several cases where the paramagnetic dipolar broadening due to oxygen is relatively small. The broadening effect is, indeed, so small in several cases that it is only detectable in the wiggles, or in the hyperfine structure. Figure 1 shows the resonance lines of methine protons in degassed and in un-degassed

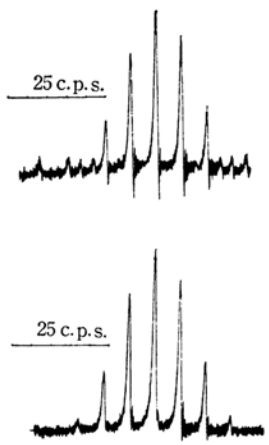

Fig. 1. NMR of methine protons in isopropyl chloride (at 100 Mc).
a) upper: degassed b) lower: undegassed

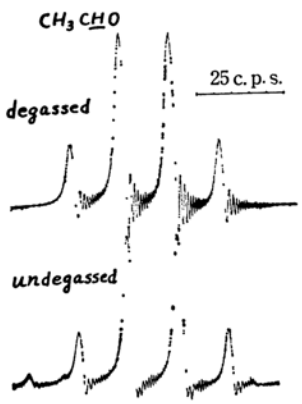

Fig. 2. NMR of active protons in acetaldehyde (at 100 Mc).

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1) R. C. Fehel, *Phys. Rev.*, **114**, 1219 (1959).
2) D. J. E. Ingram and J. G. Tapley, *Chem. & Ind.* **1955**, 568.
3) J. Uebersfeld and E. Erb, *J. Phys. Radium*, **16**, 340 (1955).
4) D. E. G. Austen and D. J. E. Ingram, *Chem. & Ind.* **1956**, 981.
5) J. E. Uebersfeld, *C. R. Acad. Sci., Paris*, **241**, 371 (1955).
6) L. S. Singer and W. T. Spry, *Bull. Am. Phys. Soc.*, **1956**, 214.
7) G. Chiarotti and L. Giulotto, *Phys. Rev.*, **93**, 1241 (1954).
8) V. J. Gaven, W. H. Stockmayer and J. S. Waugh, *J. Chem. Phys.*, **37**, 1188 (1962).

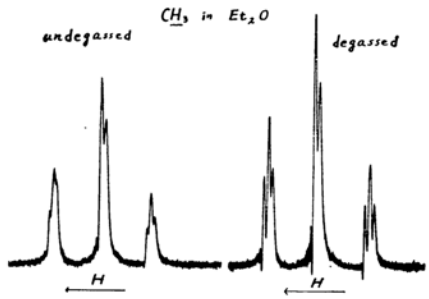

Fig. 3. NMR of methyl protons in ethyl ether at 40 Mc.
(By courtesy of Dr. Hayashi of the Japan Electron Optics Company.)

isopropyl chloride. The line width of the degassed sample is slightly narrower than that of the un-degassed sample, as may be deduced by the large amplitude of wiggles. A similar fact may be deduced from the resonance lines of the active protons of acetaldehyde (cf. Fig. 2). Figure 3 presents another case where the small difference in line-widths is observed in the change in line shapes of the hyperfine structure. The left-hand-side signal refers to the methyl proton signal at 40 Mc. in un-degassed ethyl ether, and the right-hand side signal, to that in the degassed sample. The line-widths of the degassed sample is smaller than that of the un-degassed one.

It should be noticed that all the compounds referred to above are those which do not contain exchangeable protons. According to the results of these measurements, we may conclude that the dipolar broadening effect of oxygen, present in the liquid in a concentration of a magnitude of contamination, is only about 0.1, or 0.2 cycles per second at room temperature.

This value is about two hundredths of the value calculated by the equation for paramagnetic dipolar broadening derived by Bloembergen[9] with the use of the value of the specific susceptibility of oxygen[10] as $+3449\times10^{-6}$ (293°K), and taking the oxygen content in water or in other liquids, which is in equilibrium with air, as 20 p. p. m. in weight. The latter value was determined by the use of an oxymeter of Magna Corp.[11] On the other hand, those compounds which contain hydroxyl groups give line-widths larger than those which can be ascribed to simple electron paramagnetic dipolar or contact interactions. Typical examples are obtained with methyl alcohol, ethyl alcohol, isopropyl alcohol, aquated acetaldehyde, and hemiacetal.

9) N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
10) "Handbook of Chemistry and Physics," Chemistry and Rubber Publishing Company, 44th Ed., P. 2731.
11) Oxymeter Model 1070, Magna Corporation, Santa Fe, New Mexico.

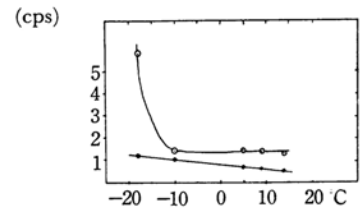

Fig. 4a. NMR in 40% aqueous solution of acetaldehyde.
-○- hydrated molecule
-●- non hydrated molecule

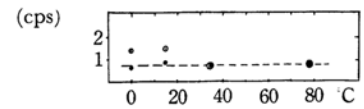

Fig. 4b. NMR in acetaldehyde dissolved in methyl alcohol.
⊙; CH_3 of hemiacetal, $CH_3(CH)(OH)(OCH_3)$
●; CH_3 of acetal, $CH_3(CH)(OCH_3)_2$
---- instrumental line width

Figure 4(a) shows the spectrum of a proton resonance in an aqueous solution of acetaldehyde. The aquated molecule is coexistent in the same capillary tube with a molecule of pure acetaldehyde. The spectral lines of the two molecular species are distinguished from each other by separate lines which refer to each species. The line-widths of the spectrum of the hydrated molecule are, as shown in the figure, larger than those of the pure acetaldehydre by about 0.5 cycles per second.

Figure 4(b) presents the line-widths of acetaldehyde in a methyl alcohol solution. The width of the methyl signal of hemiacetal, which contains a hydroxyl group, is larger than that of acetal, which does not contain a hydroxyl group. It should be noted that these differences refer to differences between molecular species which are coexistent in the same capillary.

Degassed ethyl alcohol reveals hyperfine structures for all the groups, OH, CH_2, and CH_3, as is shown in Fig. 5. However, in the spectra of the un-degassed sample, the second-order hyperfine structure of CH_2 proton signal, which is observable in the degassed sample, is missed. It must be noted

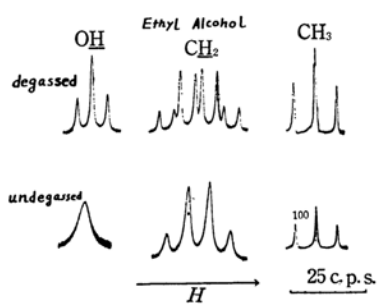

Fig. 5. Hfs. in degassed ethyl alcohol.

that the half-maximum line-widths of one component of the hyperfine lines of the methyl signal is only a few tenths cps. larger in the un-degassed sample than in the degassed sample. This implies that the paramagnetic dipolar or contact broadening effect of oxygen is very small, even in systems which contain hydroxyl protons. It is, therefore, apparent that the large broadening effect which is observed in alcohols and other related compounds is due to the effect of air and to the chemical exchange of hydroxyl protons.

Methyl alcohol is taken as the sample for detailed investigation because it is the simplest alcohol, and a strong oxygen effect is observed in it.

Experimental

Measurements were made at 60 Mc./sec. with a C-60 spectrometer of the Japan Electron Optics Laboratory, and at 100 Mc./sec. with an HA-100 spectrometer of Varian Associates. The sample temperature could be varied from $-100°$ to $+80°C$ with an accuracy of $\pm 1°C$. The line-width was measured in the lower temperature range as the half-maximum line width of one component of the spectra's hyperfine structure. In the higher temperature range, where the hyperfine structure is smeared out, the half-maximum line-widths of the whole envelope of the spectrum was measured. In the intermediate range, measurements were made in line with the nature of the spectrum, according to the method proposed by Alexander.[12]

About twenty samples were prepared and used in the present experiment. They differ according to the procedure used to purify them and according to the impurity concentration. For convenience, however, they may be classified into four groups: (a) the purest one, prepared from anhydrous methanol by a three-stage distillation over magnesium; (b) those prepared by twice distilling them over magnesium: (c) commercial methanol, of the purest guaranteed grade, used as the starting material for the other distillations, and (d) the one prepared by saturating the degassed sample, (a), with one atmosphere of oxygen. Sample (d) will be referred to as "the oxygen sample" in later discussions. As will be shown, these samples show remarkable differences in their chemical shifts and in the exchange rate of their OH protons. It was noticed during the experiment that the spectrum of each sample changed considerably with time. As this happened in sealed-glass tubes, we assumed it to be due to impurities coming from the walls of the glass tubes. Because of this sensitivity in the spectral features, all the results reported here have been obtained from freshly prepared samples.

Degassing was carefully done by repeated freezing and melting, either under a vacuum or under a nitrogen atmosphere. The latter procedure was most effective in removing oxygen.

The chemical shift was measured in two ways: one, by using tetramethyl silane as an internal reference, and the other, by locking the CH_3 signal without any addition of tetramethyl silane. By the former method, the CH_3 signal was found to be independent of the temperature and to be effectively constant, regardless of the presence of oxygen. Figure 6 shows the results of measurements where the methyl signal of tetramethyl silane is locked as the internal standard. It was noticed that tetramethyl silane affects the exchange rate of hydroxyl protons; therefore, precise measurements of the line shape and of the chemical shift of OH protons were made by the latter method. The chemical shift of OH protons in the purest methanol is taken to be -300 ± 1 c. p. s. at 100 Mc., or -3.00 ± 0.01 p. p. m. from CH_3. The fluctuation in this value of ± 1 c. p. s. is due to contamination by trace amounts of oxygen. Contamination by other impurities, such as water and alkali, produces much larger fluctuations. In practice, the chemical shift and the line shape measurements reveal the difficulty of obtaining pure methanol.

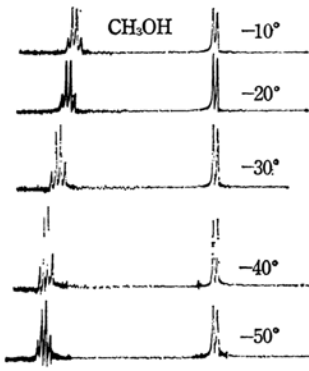

Fig. 6. Chemical shift of OH of MeOH as the function of temperature.

The chemical shift of OH protons is a linear function of the temperature, as has been reported already.[13] The chemical shift of OH protons in the purest methanol can be used as an accurate control of the temperature of an NMR sample.[14]

Results and Discussion

Line-widths.—The line shapes of the proton resonance in methanol are temperature-dependent; they can be divided into three types according to the temperature; one, a single line at a high temperature; two, a well-separated hyperfine structure at a low temperature; and three, a collapsing hyperfine structure at an intermediate temperature. Figures 7 and 8 present typical examples of the temperature dependence of the line shapes of OH protons. The relative position of each spectrum along the horizontal line is with reference to the chemical shift to the temperature at which the spectrum was measured. It may be seen in Fig. 7 that the hyperfine structure begins to appear between 10 and 20°C, and that the components of the quadruplet's structure are well separated at about $-20°C$.

12) S. Alexander, *J. Chem. Phys.*, **37**, 967, 974 (1962).

13) J. T. Arnold and M. E. Packard, ibid., **19**, 507 (1951).

14) This technique was also referred to independently by Prof. L. W. Reeves at the NMR Symposium held in Tokyo in 1965.

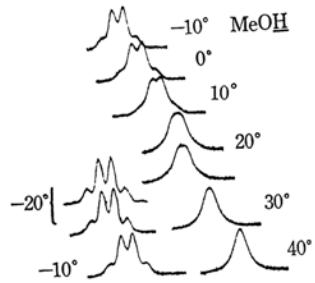

Fig. 7. Temperature dependence of the line shapes of OH protons in MeOH undegassed.

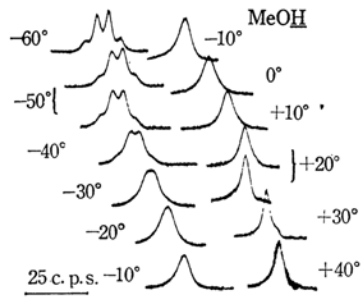

Fig. 8. Temperature dependence of the line shapes of OH protons in MeOH saturated with 1 atmospheric O_2.

However, in Fig. 8, in the oxygen sample the hyperfine structure begins to appear as low as at from -30 to -40°C, and a quadruplet is well separated at -60°C. This is surprising, because both samples have been prepared from the same purified methanol at the same time; they differ only in the concentration of oxygen. If we define T_{hfs} and T_{quad} as the temperature where the hyperfine structure begins to appear and that where the quadruplet structure begins to be well separated respectively, the observed differences in T_{hfs} and T_{quad} between the two samples must be attributed to the effect of oxygen. It may clearly be seen that the critical temperatures for the vacuum-degassed and the nitrogen-degassed samples are lowered by about 5°C in the un-degassed sample. This lowering may also be attributed to the effect of oxygen. It should especially be noted that the observed effect is not due to nitrogen. These results suggest that the lowering of the critical temperature, which is equivalent to the enhancement of the proton exchange between hydroxyl groups, is caused by oxygen.

In order to interpret this effect, we must investigate the interaction of oxygen with methanol. We will do by the method used to investigate the interactions between methanol and transition metal ions,[15] with necessary modifications being made in the course of interpretation. We assume a model which represents the system to be investigated. The system to be considered here consists of two nuclear environments, the coordination sphere of paramagnetic oxygen and the bulk solvent. The two environments are designated by the indices M and A. We will treat a special case where the number of protons in the A environment is much larger than that in the M environment; the ratio of M protons is written as pq, where p is the number of oxygen molecules per solvent molecule, and q, the solvation number of oxygen. Hence, $pq \ll 1$.

The magnetic resonance of A and M protons are characterized by the relaxation times, T_{1A}, T_{2A}, T_{1M}, and T_{2M} respectively. The difference in Larmor frequencies between the two environments is designated by $\Delta\omega$. Protons can be exchanged between the two environments at a rate characterized by the average residence time of a proton in the M environment, τ_M. In fact, we can not assume, in the lower temperature range, a diffusional motion of molecules which produces exchange between bonded and free molecules.

The NMR spectrum actually observed consists essentially of a single peak; i. e., A and M protons do not show separate peaks. We assume that this is not due to the low concentration of oxygen, but to the rapid motion of oxygen, which averages out the resonant sites of all protons in the medium. In such a case, the line-widths of the bonded molecule is related to the electron relaxation time, τ_s, and the hyperfine interaction constant, A. The behavior of the OH and CH_3 peaks is similar, and the same remarks apply to both. At low temperatures, the exchange of molecules between the bulk methanol and the coordination sphere is too slow to affect the spectrum. We assume that the peaks of the bulk methanol are characterized by equal longitudinal and transverse relaxation times, which change little with the temperature.

As the temperature is increased, exchange sets in and the line width increases. It reaches a maximum, and then decreases with an increase in the temperature. This movement is attributed to the exchange between OH protons, resulting in an averaging of the hyperfine lines. It must be noted that the temperature where the maximum width occurs is the same for both the OH and CH_3 signals, and that it depends upon the character of the sample, i. e., the concentration of impurities.

In the lower temperature range, we take the electron spin relaxation time, τ_s, for the correlation time of the interaction between the paramagnetic oxygen and methanol molecules. Kinetic parameters are calculated for molecular interactions in this range by the use of Eqs. 1 to 4. They were originally derived by Solomon and Connick[15] and used by Meiboom.[16]

15) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 308 (1962).

16) Z. Luz and S. Meiboom, ibid., **40**, 1058, 1066, 2686 (1964).

$$1/T_{2M}=pq/T_{2M} \quad (1)$$

$$\Delta\omega=pq\Delta\omega_M/[(\tau_M/T_{2M}+1)^2+\tau_M^2(\Delta\omega_M)^2] \quad (2)$$

$$\Delta\omega_M/\omega_I=\frac{s(s+1)}{3kT}\frac{g|\beta|}{\gamma_I}A \quad (3)$$

$$1/T_{2M}=\frac{4}{3}\frac{s(s+1)\gamma_I^2g^2\beta^2}{\gamma^6}\tau_s+\frac{2}{3}\frac{s(s+1)}{\hbar^2}A^2\tau_s^2 \quad (4)$$

In practice, we assume, regarding the relations between τ_s, τ_M, $\Delta\omega_M$, that $\tau_{2M}\gg\tau_M$ and that $\tau_M\Delta\omega_M\simeq 1$. We also assume that r, the distance between oxygen and a methanol molecule, is equal to 3 Å. In Eq. 1, $1/T_2$ is taken to be 0.2 c. p. s. or less, while $\Delta\omega$, in Eq. 2, is taken to be less than 1 c. p. s. The latter is the value for the sample which is saturated with one atmosphere of oxygen; the p value for this solution is found to be 1×10^{-4} from the solubility data. The values obtained are $1/T_{2M}\leqq 500$ c. p. s., $\Delta\omega_M\leqq 1\times10^4$ c. p. s., $A/h=2.3\times10^2$ c. p. s., and $\tau_s=1.5\times10^{-12}$ sec. These values may be compared with those obtained for the methanol-metal ion interactions.[16] It is noted that τ_s is shorter than the correlation time of methanol, which is expected to be about 3×10^{-11} sec., and about the same as that for transition metal ions in methanol. The hyperfine interaction constant is smaller than that of the methanol-metal ion system by a factor of two or three.

The apparent activation energy for the relaxation rate in this range, when calculated from the slope of the temperature dependence of the line widths, is found to be less than several tenths of kcal./mol. This value is about the same order of magnitude as that of the methanol-metal ion system, 0.9 kcal./mol.; it is significantly less than the activation energy for diffusion. This low value of the activation energy may be assumed to be related to the mechanism of relaxation, where the electronic interactions between oxygen and methanol are transmitted rapidly through the methanol medium.

In the higher temperature range, where the hyperfine structure begins to smear out, the activation energy for the change in line width is found, from spectra showing the hyperfine structure, to be about 3 kcal./mol. This coincides with the value generally adopted as the activation energy for the molecular diffusion of methanol; it suggests that the smearing of the hyperfine structure is due to the diffusional or rotational motion of methanol.

Oxygen Effect.—According to the results given previously, it is clear that the oxygen effect in methyl alcohol is far less than expected with regard to paramagnetic dipolar or contact broadening. However, the proton exchange between hydroxyl groups is strongly enhanced by oxygen. This effect may clearly be seen in Figs. 7 and 8; it will be expressed in terms of the exchange rate of hydroxyl protons, $1/\tau$, which is calculated using the data obtained from Figs. 7 and 8. The half-maximum line-width of one component of the spectra showing hyperfine structure is measured and designated as $1/T_2$. The measured line-width parameter, $1/T_2$, is related to the following equation, $1/T_2=1/T_{20}+1/\tau+1/T_1$, where $1/T_{20}$ is the linewidth of the spectrum for the state where there is no proton exchange, and where $1/T_1$ is the contribution of the spin-lattice relaxation of paramagnetic oxygen. The last term can not be neglected in principle; however, its contribution is assumed to be negligible in methyl alcohol which contains oxygen, since the line-width of the un-degassed sample is only by one- or two-tenths cycle per second larger than that of the degassed sample in the lower temperature range where there is no proton exchange. Similarly, the line-widths of methyl proton signals in un-degassed and in degassed ethyl alcohol differ from each other by only one or two cycles per second.

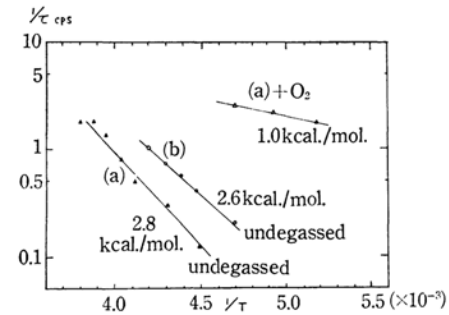

Fig. 9

The Arrhenius plots of the exchange rates obtained are shown in Fig. 9; the activation energy for the exchange, ΔE, is obtained as, for example, ca. 1.0 kcal./mol., and ca. 3 kcal./mol. for the with-oxygen and the un-degassed methyl alcohol respectively. The difference, ΔE, between these two samples may be ascribed to the energy evolved by the dissolution of oxygen in methyl alcohol. This can be done in view of the following considerations. As is clear from the results of Fig. 4 on ethyl alcohol, the molecular interaction between alcohol and oxygen is not homogeneous over a molecule of alcohol, and the oxygen relaxes more strongly at the site of a hydroxyl group than at that of a methyl group. This refers to the specific interaction between hydroxyl protons and oxygen, which results in the evolution of a heat of interaction as well as in an elongation of the OH distance. The latter situation is related to the enhancement of the proton exchange between the hydroxyl group and to the reduction of the apparent activation energy of the proton exchange, ΔE.

We may conclude that the results obtained here suggest a new method of measuring the heat of solution of oxygen in methyl alcohol, Q, which has not yet been made available in the literature. In practice, we could not find any significant difference

in ΔE between degassed and un-degassed methyl alcohol; all differences were within the limits of experimental error. We found $Q=3-1=2$ kcal./mole.

As may be seen in Figs. 7 and 8, the enhancement of the proton exchange between hydroxyl groups is clearly seen in the temperature range where the quadruplet structure begins to be unobservable; that is at -30 or -40°C for the with-oxygen sample, and at 10 or 20°C for the un-degassed sample. A lowering by about 5°C is observed between the degassed and the un-degassed samples. These results refer to the difference in frequency factors, ν_1 assuming a constant activation energy, ΔE. For example, we take:

ν(oxygen sample) $\exp(-3/233\,k)=\nu$(un-degassed) $\exp(-3/293\,k)$.

Hence,

ν(oxygen sample)/ν(un-degassed)$=4.5$

Similarly,

ν(un-degassed)/ν(degassed)$=1.4$

The catalytic effect of trace amounts of oxygen may be related to the short relaxation time of the electronic spin of oxygen; it suggests a very rapid transportation of the spin energies of oxygen. We will not here give a more detailed interpretation of this mechanism of transportation. However, we will note a case of molecular interaction between water and ammonia as an example of how a trace amount of impurity (water) dominates the orientation of the nuclear spins of ammonia.

Summary

1) The dipolar broadening effect of oxygen is small in NMR.

2) The proton exchange rate for hydroxyl groups is enhanced appreciably by the presence of oxygen. This may be attributed to an increase in the frequency factor of the exchange rate.

3) A new method has been proposed for the determination of the heat of the solution of oxygen; this method is based on the oxygen effect referred to in 2).