# *Nuclear Magnetic Resonance Study of Hydrogen Bond in Salicylaldehyde*

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It is well accepted that a strong intramolecular hydrogen bond is formed between the hydroxyl and aldehyde groups in a salicylaldehyde molecule. This evidence was obtained by various molecular spectroscopic methods[1] and dipole moment measurements,[2] and some characteristic structures for this hydrogen-bonded system were suggested on the basis of these measurements. Nuclear magnetic resonance (NMR) measurement is expected to give further informations concerning the

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[1] a) M. Tsuboi, This Bulletin, **25**, 60 (1952); b) H. Yamada, ibid., **32**, 1051 (1959); c) A. E. Martin, *Nature*, **166**, 474 (1950); d) P. D. Simova and B. Skorchev, *Izvest. Bulgar. Akad. Nauk., Otdel. Fiz.-Mat. i Tekh. Nauki Ser. Fiz.*, **4**, 47 (1954).

[2] a) H. Lumbroso and P. Rumpf, *Bull. soc. chim. France*, **1950**, 371; b) R. Mecke and A. Reuter, *Z. Naturforsch.*, **4a**, 368 (1949).

hydrogen bond in this molecule.

Compounds with intramolecular hydrogen bond so far well investigated by the NMR method are *o*-chlorophenol[3,4], *o*-bromophenol[5], and *o*-cresol[3,5]. The resonance field for the OH proton in these compounds was comparatively dependent on concentration in various solutions. This suggests that the intermolecular hydrogen bond in these compounds is easily disrupted by dilution of solutions. On the other hand, the intramolecular hydrogen bond in compounds such as *o*-nitrophenol or salicylaldehyde is so strong that it would scarcely form a intermolecular hydrogen bond. It is expected therefore that the OH lines of NMR for these compounds would not show remarkable concentration dependence[6].

In the present experiment, the measurement of the OH resonance shift in NMR spectrum of salicylaldehyde was carried out in solutions of several solvents with various concentrations. In addition to this, the concentration dependence of the resonance spectrum of the ring protons was also investigated.

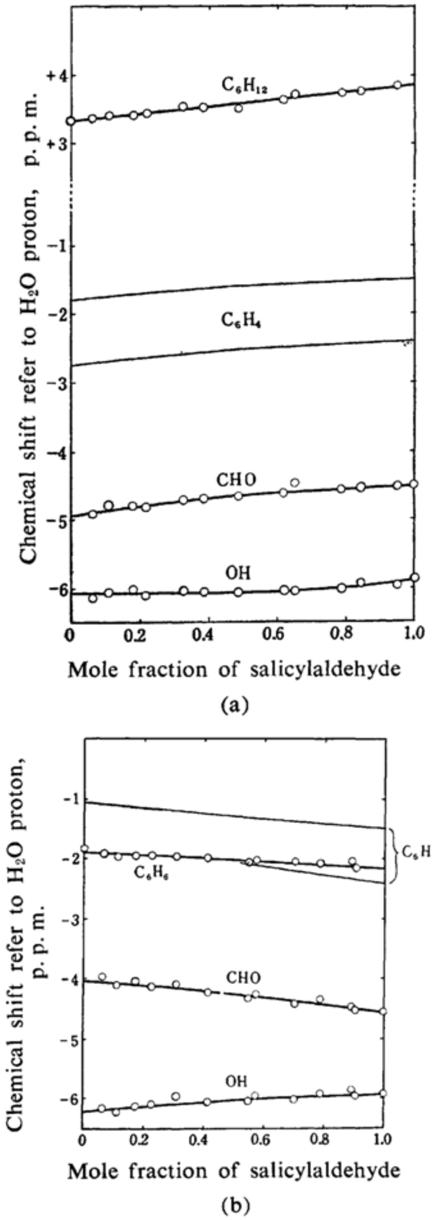
## Experimental

NMR measurements were made at 20°C with a Varian NMR spectrometer operating at 56.4 Mc./sec. Salicylaldehyde was a guaranteed grade reagent and used without further purification. Solvents chosen in this experiment were cyclohexane and carbon tetrachloride (inert solvents), and chloroform, methanol, benzene, acetone, ether and pyridine (proton donors and acceptors). These solvents were purified for eliminating extra lines in their NMR spectra.

The sweep rate was calibrated by taking the value of the chemical shift between the methyl group proton and the benzene ring proton in toluene as 4.90 p. p. m.[7] The value of chemical shift of each line was obtained referring to an external reference of water in a capillary, and the correction for bluk diamagnetic susceptibility was made. Solutions of twelve stages of concentrations between 0.05 and 0.95 mole fractions were prepared for each solvent.

## Results and Discussion

Fig. 1a shows the concentration dependence of the chemical shifts for protons of salicylaldehyde in cyclohexane solution. The lowest curve was assigned to the OH proton by reasoning which will be described later. The next lowest is for the CHO proton. The resonance lines for the ring protons are very complex as shown later. However the corresponding magnetic fields are expressed by two lines for simplicity in the figure, showing decrease with decreasing concentration. The displacement of the lines to a higher field at higher concentration is caused by the interaction among benzene molecules. The decrease of the resonance field for the OH group on dilution seems to correspond to a charge migration from the proton to the ring. Most of the chemical



(a)

(b)

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[3] C. M. Huggins, G. C. Pimentel and J. N. Shoolery, *J. Phys. Chem.*, **60**, 1311 (1956).

[4] I. Gränacher, *Helv. Phys. Acta*, **31**, 734 (1958); M. Martin and F. Hérail, *Compt. rend.*, **248**, 1994 (1954).

[5] R. L. Batdorf, Ph. D. thesis, Univ. of Minnesota, 1955.

[6] Puranik and Ramavataram observed the slight shift in the C=O vibrational frequency for salicylaldehyde in the presence of proton donor or acceptor group. This shift was attributed to the minute weakening of the intramolecular hydrogen bond. P. G. Puranik, *J. Chem. Phys.*, **23**, 761 (1955); K. Ramavataram, *Proc. Indian Acad. Sci.*, **45A**, 47 (1957).

[7] N. F. Chamberlain, *Anal. Chem.*, **31**, 56 (1959).

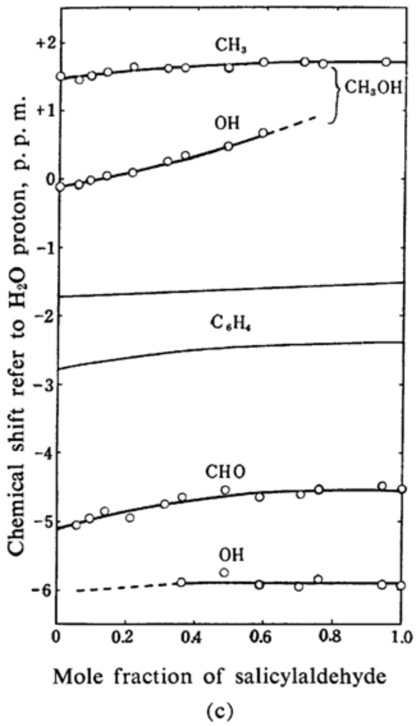


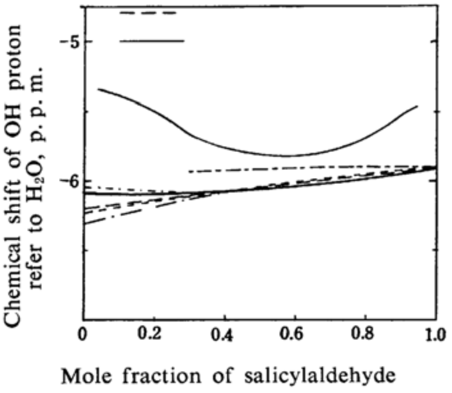
Fig. 1. Chemical shift diagrams of salicylaldehyde in several solutions; (a) cyclohexane solution, (b) benzene solution, and (c) methanol solution.

shift diagrams observed for the other solutions have much the same feature as that for cyclohexane solution except for benzene and pyridine solutions.

Fig. 1b. shows the proton resonance in benzene solution. The field for the CHO group increases with decreasing concentration in contrast to the other observed solutions. This may be due to a hydrogen bond formation between the acidic proton in the CHO group and the $\pi$ electron system of a solvent benzene molecule; the proton is located in a region where the effect of the benzene ring is diamagnetic as in the case of chloroform in benzene solution8).

Fig. 1c. shows the chemical shift diagram for methanol solution. The OH proton resonance line of alcohol disappears in the concentrated region. The some is true for the OH proton of salicylaldehyde but in the dilute region. This implies the exchange of protons between OH group of alcohol and that of phenol. The broadening of these two lines over all the concentration range may also be an additional evidence for this exchange process. From the separation of the above two lines for both groups, the upper limit for the exchange rate was estimated as about 330 c. p. s. It is therefore probable that even a proton contributing to a strong intramolecular hydrogen bond formation is also able to exchange.

Fig. 2 shows the concentration dependence of the chemical shift of proton resonance lines for the OH group in various solutions. Batdorf5) measured the chemical shift of the OH proton in various phenol derivatives in saturated solutions of acetone. He showed that among the OH lines for various phenol derivatives the OH line for salicylic acid derivatives appeared at the lowest field region (around −6 p. p. m. referring to water proton). The OH proton lines for the other phenol derivatives appeared at considerably higher fields than that for salicylaldehyde. In general, the OH line for phenol derivatives forming merely intermolecular hydrogen bond appears in the range of about −2 to −4 p. p. m. from the water proton line. Comparing these values with those for salicylic acid derivatives with intramolecular hydrogen bond, it may be said that the strength of the intramolecular hydrogen bond in salicylic acid derivatives is ranked to be considerably high.



Mole fraction of salicylaldehyde

Fig. 2. OH proton resonance shift in salicylaldehyde of various solutions.

Solvent
——— Cyclohexane
—·—· Carbon tetrachloride
-·-·-· Chloroform
— - — Methanol
- - - - Benzene
——— Acetone
——— Pyridine

For various solutions observed, the concentration dependence of the OH lines are almost the same except pyridine solution which will be discussed later. This fact is somewhat surprising because it may suggest that the nature of the OH proton in salicylaldehyde is scarcely affected at all by the solvents with high hydrogen bond forming ability. The above fact also suggests that the intramolecular hydrogen

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8) L. W. Reeves and W. G. Schneider, *Can. J. Chem.*, 35, 251 (1957).

bond in salicylaldehyde is considerably strong and does not allow a hydrogen bond to form with the other molecular species.

The resonance field of the OH proton is observed to decrease slightly as the concentration of the solution decreases. In general dilution of a phenol with some moderate solvent, intermolecularly hydrogen-bonded polymerized molecules dissociate to dimer molecules showing a decrease of the OH proton resonance field. However dissociation of dimerized ones to monomers shows an increase of the field. Thus, for intermolecularly hydrogen-bonded compounds the variation of the OH proton resonance field generally has a minimum, where the most effectively and strongly hydrogen-bonded species is seemed to form. In contrast to phenol, the field for the OH proton line of salicylaldehyde decreases monotonously with dilution of solution showing no increase even on extreme dilution. This suggests that the bonding becomes stronger as the concentration decreases and the hydrogen bond remains even in the solution of extremely low concentration. Therefore, for salicylaldehyde, the free single molecule with the intramolecular hydrogen bond is considered to be the most effectively hydrogen-bonded species. This result also suggests that in concentrated solutions there exist dimerized or polymerized molecules[9] which dissociate to monomer molecules on dilution. The broadening of the OH lines observed in concentrated range in almost all the solutions may be attributed to a rather slow exchange process of OH protons among several kinds of polymerized species.

An exceptional behavior of OH line was observed for pyridine solution. The curve in Fig. 2 shows apparently anomalous behavior. First, the resonance occurs at higher field than that for the other solutions. This may be ascribed to some change in its electronic configuration caused by interaction with a pyridine molecule. Secondly, the magnetic field decreases with decreasing concentration in concentrated range. This may arise from the same dissociation process as that the other solutions show and simultaneously from the formation of strong hydrogen bond between salicylaldehyde and pyridine. Thus the minimum resonance field appears at the equimolecular composition of the solution. The third is the increase of the curve in dilute range. This may be attributed to the formation of multiply hydrogen-bonded species with pyridine. This experimental result may suggest that the hydrogen bond between salicylaldehyde and pyridine is stronger than the intramolecular hydrogen bond in salicylaldehyde.

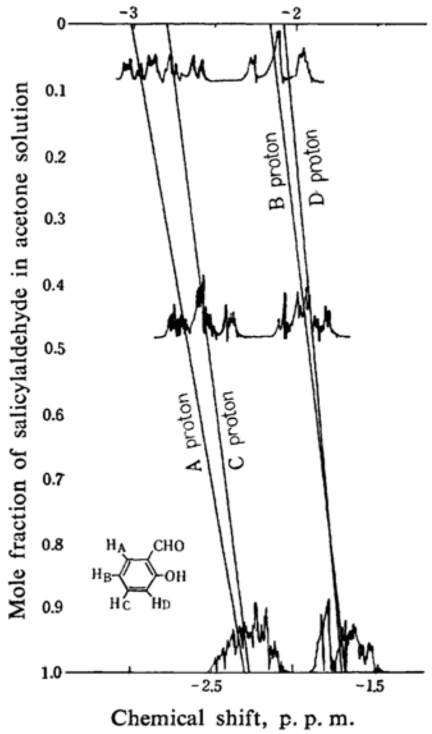

Fig. 3. Concentration dependent behavior of ring proton resonance lines of salicylaldehyde in acetone solution.

A remarkable solvent effect was also observed in the resonance spectra of ring protons, especially in the systems with proton donor or acceptor solvents. Although the spectrum of the ring protons could not be exactly analyzed, it was possible to assign the spectral lines to each proton by tracing the change in the spectral figure of the system on dilution. Fig. 3. shows an example of this solvent effect on the ring protons in acetone solution.

The whole spectrum of the ring protons displaces to lower field on dilution. This displacement is considered to arise from change in the interaction among benzene rings as mentioned previously. In a series of the spectra of solutions with different concentrations, the lines due to A proton (ortho to CHO group) and D proton (ortho to OH group) exhibit opposed dilution displacement to each other. The A proton lines displace to lower field while those of D to higher field on dilution relative to the displacement of the whole ring proton spectrum. Various effects may be attributed to these shift changes of dilution[10]. However, the essential feature to cause the

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[9] Simova and Skorchev also suggested the existence of dimerized molecules. See Ref. 1d.

[10] A. D. Buckingham, T. Schaefer and W. G. Schneider, *J. Chem. Phys.*, **32**, 1227 (1960).

spectral change, especially that for A and D protons, would probably be a charge migration in the molecule affected by the change in the hydrogen bonding situation of this molecule.

## Summary

The concentration dependent behavior of the proton resonance spectra of salicylaldehyde in several solution systems were measured. The behavior of the OH resonance line for the solution systems showed the evidence of the existence of considerably strong intramolecular hydrogen bond in the molecule. The behavior of the ring proton spectrum on dilution suggested the occurrence of the charge migration in the ring affected by the change in the hydrogen bonding situation.

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